Investigations into plasmonic lithography concepts for high resolution nanoscale feature patterning

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**INVESTIGATIONS INTO PLASMONIC LITHOGRAPHY
CONCEPTS FOR HIGH RESOLUTION NANOSCALE
FEATURE PATTERNING**

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ENGINEERING

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Abstract

Plasmonic lithography, which is not restricted by free space diffraction limit, is one of the potential research thrust areas as it offers the possibility for high resolution nanopatterning. This thesis investigates novel concepts and relative configurations of plasmonic lithography to fabricate nanoscale periodic structures, which can find variety of potential applications.

Initially, the theoretical and experimental investigation of multiple beam conventional laser interference lithography (LIL) was carried out. It is shown that this technique is diffraction limited and hence cannot be useful for sub-wavelength feature fabrication. A near-field multiple beam interference lithography such as evanescent wave interference lithography (EWIL) beyond the conventional free space diffraction limit has been investigated for sub-wavelength feature patterning. Both theoretical and experimental investigation of the technique was carried out. However, this technique was unable to provide high aspect ratio features, due to the exponentially decaying evanescent fields. In this context, it was envisaged that surface plasmon interference lithography (SPIL) could be one of the straightforward solution to subdue this problem and to obtain high resolution good aspect ratio features.

Various configurations of plasmonic lithography are proposed and investigated. Multiple beam (two and four) surface plasmon (SP) interference generation based on prism coupling technique is theoretically analyzed and presented. The proposed concepts and methodologies were then numerically and experimentally illustrated by employing aluminum and silver metal at 364 nm illumination wavelength to realize high resolution and good aspect ratio 1D and 2D periodic nanoscale features on the recording medium. Further, a planar layer concept for surface plasmon interference lithography to fabricate periodic nanoscale structures was also proposed and illustrated. It is found that high electric field distribution compared to conventional prism based configuration is possible for this and hence facilitates improved exposure depth and good intensity contrast.

The effect of metal films such as Al and Ag on UV excited surface plasmon interference lithography is investigated using the proposed configuration. The

obtained periodic features show good exposure depth and high contrast when Al is used as the metal film. A comparative analysis between interferometric lithography techniques such as conventional laser interference, evanescent wave interference, and surface plasmon interference is experimentally carried out and illustrated. It is found that SPIL can provide high resolution periodic features with good aspect ratio as compared to the other two (LIL and EWIL) interference lithography techniques.

An investigation into nanoparticle (array) based system configuration to improve the feature resolution also carried out as a part of the research. One of the two concepts proposed and numerically demonstrated is one employing periodic metal (Ag and Al) nanoparticle array to fabricate sub-40 nm periodic nanostructures. Secondly, a novel plasmonic lithography technique beyond the diffraction limit based on the excitation of gap modes in a metal particle-surface system is also investigated and demonstrated by numerical simulation means. The theoretical simulation result shows that by employing Al nanosphere-Ag surface system, this configuration can provide strong enhanced field to give shorter wavelength of surface plasmons to fabricate sub-30 nm periodic structures. Also, 2D and 3D resist profile cross sections obtained using cellular automata model are presented.

Detailed investigation is carried out for extending the proposed concepts for potential applications as well as to subdue some of the limitations of plasmonic lithography. Thus focus the future work directions, which includes (i) investigation into compensation of LSP loss by optical gain medium for nanoparticle assisted plasmonic lithography, (ii) experimental investigation of nanoparticle assisted plasmonic lithography, (iii) experimental demonstration of metal nanograting based SPR sensors, and (iv) fabrication of 2D plasmonic crystals using patterned dot array features. The details of the initial studies of these future work directions are presented in the appendix section.

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List of Symbols

λ	wavelength
k_1	proportionality constant
ε	dielectric constant
ω	excitation frequency
θ	SP resonance angle
n	refractive index
t	Time
k	Wavevector
Δk	change in wavevector
E	electric field
B	magnetic field
c	velocity of light in free space
n_{eff}	effective refractive index
ν	Integer
a	grating period
g	grating constant
r	reflection coefficient
t_{pm}	transmission coefficient
Γ	damping constant
R	reflectivity
Δx	increment in x-direction
Δy	increment in y-direction
Δt	time step

V	intensity contrast
I	intensity
$I_{\max}$	maximum intensity
$I_{\min}$	minimum intensity
δ	skin depth
∞	evanescent wave amplitude
P	pitch of subwavelength grooves
A	amplitude
l	integer values
D	particle surface distance
α	polarizability, gain coefficient
C	absorption cross section
Q	scattering efficiency
τ	life time

List of Abbreviations

SP	Surface Plasmon
SPR	Surface plasmon resonance
LSP	Localized surface plasmon
SPP	Surface plasmon polaritons
LRSP	Long range surface plasmon
IC	Integrated circuit
CD	Critical dimension
TE	Transverse electric
SPIN	Surface plasmon interference nanolithography
ATR	Attenuated total reflection
TIR	Total internal reflection
EUV	Extreme Ultraviolet
LIL	Laser interference lithography
EW	Evanescent wave
EWL	Evanescent wave lithography
EWIL	Evanescent wave interference lithography
ENFOL	Evanescent near-field optical lithography
ITRS	International Technology Roadmap for Semiconductors
UV	Ultraviolet
DUV	Deep Ultraviolet
EM	Electromagnetic
NA	Numerical aperture
AFM	Atomic force microscope
PXL	Proximity X-ray lithography

EBL	Electron beam lithography
SPL	Scanning probe lithography
NIL	Nanoimprint lithography
STM	Scanning tunneling microscope
TPP	Two photon photopolymerization
FIB	Focused ion beam lithography
DPN	Dip pen nanolithography
LON	Local oxidation nanolithography
SIL	Solid immersion lens
NSOM	Near-field scanning optical microscope
DFB	Distributed feedback
FDTD	Finite difference time domain method
PML	Perfectly matched layer
2D	Two dimensional
3D	Three dimensional
CA	Cellular automata
SERS	Surface enhanced Raman scattering
LED	Light emitting diodes
OLED	Organic light emitting diodes
PC	Plasmonic crystal

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Chapter 1

Introduction

This chapter gives a general introduction to the thesis. The chapter begins by giving a background to the research project undertaken. The requirement for next generation photolithography techniques and how it can be met by surface plasmon resonance phenomena has been discussed. Then the motivation, objective and scope of the project are discussed in the subsequent sections. Based on the current-state-of-the-art literature, the proposed and identified research problems are illustrated and detailed with the help of a research road map.

1.1 Background

Photolithography has played a vital role in almost every aspects of modern technology for the past 50 years [1]. It has initiated transistor revolution in electronics and optical component developments in photonics. Advances in this field have allowed scientists to improve the resolution of the conventional photolithographic techniques, which is restricted by the diffraction limit [2]. However, recently developed high resolution lithography techniques beyond the diffraction limit have significant design and layout issues, which makes their implementation challenging. New research suggests that we may be able to develop new cost effective photolithographic technique beyond the diffraction limit. The key in achieving this goal lies in the use of near field photolithography technique such as surface plasmon interference lithography or plasmonic lithography. In recent years, surface plasmon resonance phenomenon has got considerable attention in almost every field of science and technology. Surface plasmons (SPs) are collective electron oscillations propagating at the interface between a metal and a dielectric [3]. The excitation of surface plasmon wave by light is called surface plasmon resonance (SPR). An important feature of surface plasmon resonance is that in order to excite surface plasmons the incoming beam has to match its momentum to that of the plasmons. It can be possible by passing the incident p-polarized light through a bulk dielectric layer to increase the wavevector component and hence to achieve the resonance at the given wavelength. The resonance condition

depends on various parameters, such as incident illumination wavelength, incident angle, metal film thickness, and dielectric constant of metal and surrounding medium. The wavevector of surface plasmon wave becomes significantly larger than that of the incident light wavevector when the real part of the dielectric constant of metal approaches negative of the dielectric constant of surrounding dielectric medium. At this condition, the wavelength of the excited SPs should be shorter compared to the wavelength of illumination light. The two well known methods proposed to excite surface plasmons on a thin metal film are prism coupling and grating coupling methods [3]. Since then, surface plasmon resonance has become important, leading to many subsequent developments in fabrication, theory and applications.

Surface plasmon resonances in metallic films are of interest for a variety of applications due to the large enhancement of the evanescent field at the metal/dielectric interface. Researchers recently observed the extraordinary transmission through perforated metal films and showing that surface plasmons on the metal film can greatly enhance the electric field distribution and redistribute the electromagnetic field in the nanometer scale dimension [4-6]. Hence surface plasmons enabled near field photolithography (Plasmonic lithography) technique has achieved much progress in the last decade, because it provides us a novel method of nanofabrication beyond the diffraction limit [7-18].

Different configurations have been proposed for plasmonic lithography to fabricate high resolution features (sub-100 nm). The surface plasmon interference nanoscale lithography based on Kretschmann-Raether attenuated total reflection (ATR) geometry has been proposed [7-9]. Moreover, a near field interference pattern can be formed by using metallic mask configuration that can generate surface plasmon for periodic structure fabrication [10-16]. In all the above mentioned works, surface plasmon interference can make a certain interference pattern on the photoresist layer when the incident p-polarized light passes through a prism or thin metallic mask. However, most of these reported techniques demands the fabrication of fine period mask grating and found to be not cost effective. The search has thus recently focused on metal nanoparticles due to its localization and enhancement of electromagnetic wave at plasmon resonance condition. It is worth mentioning the recent reported works on direct patterning employing micro or nanospheres as mask [17, 18]. In this context,

the work mentioned in this thesis mainly focuses on the fabrication of sub-100 nm resolution periodic features using novel plasmonic lithography techniques.

1.2 Motivation and Problem Identification

The improvement of integrated circuit performance in microelectronics is possible by the increase of transistor integration density suggested by Moore's law. That means, from one generation to next the spatial resolutions of critical features on integrated circuits have been steadily decreasing. Hence the smallest achievable pattern size has to regularly decrease in photolithography stage. With the advent of nanotechnology, cost effective development of nanoscale features have tremendous significance in microelectronics, biosensing and other applications for higher performances. Many nanofabrication techniques have been developed for this purpose. However, it is difficult to achieve critical dimensions at sub wavelength scale using traditional optical lithography techniques, due to the optical diffraction limit. For next generation lithography, maintaining the Moore's law is a critical challenge. To overcome this problem and to reduce the critical dimension, several solutions were introduced. The minimum critical dimension (half-pitch resolution) achievable by photolithography (Optical projection lithography) is given by $CD_{half-pitch} = k_1 \lambda / NA$, where λ is the incident source wavelength, NA is the numerical aperture of projection optics of the system and k_1 is a constant value as a indication of the effectiveness of the wavefront engineering techniques [2]. To reduce the half-pitch resolution, critical dimension equation demands either to decrease the wavelength of illumination light source or to increase the numerical aperture of the projection system. Also, lithography critical resolution can be further improved by reducing the value of k_1 . In recent years, research works have focused a great deal of attention to enable low k_1 value and hence to improve the performance of patterning techniques.

Techniques such as extreme ultraviolet lithography (EUV) and X-ray lithography have been proposed for nanofabrication to overcome the conventional diffraction limit associated with projection lithography systems [19, 20]. Here the illumination wavelength is decreasing down to the extreme UV range to get smaller features. The critical challenges facing to improve the resolution are (i) lack of availability of

suitable ultra-short wavelength lasers, and (ii) the unavailability of suitable optics and materials such as photoresist for the use at suitable wavelengths. Another technique is immersion lithography in which numerical aperture of the imaging system is increased by inserting high index fluids (prism or liquid) between the last optical component and wafer surface [21]. But this technique is either limited by air absorption or availability of high index fluids. Approaches such as electron-beam lithography can also be used to overcome the diffraction limit, but these are serial process and cannot be used for high throughput [22]. Nanoimprint lithography is another option to improve the resolution beyond the diffraction limit [23]. Nanometer scale features are possible by stamping a template on a thin polymer film and it can also generate sub-50 nm features by laser combination with AFM, NSOM and transparent particles. The main disadvantages of this technique are: the leveling of the imprint template and the substrate during the printing process, which determine the uniformity of the imprint results and process speed is quite slow, which limits their applications in industry. Laser interference lithography (LIL) can be used to fabricate high speed and large-area periodic nanostructures [24]. This is a cost effective and maskless optical lithography technique to realize large-area periodic patterning at subwavelength scale resolution. The basic principle is the interference of coherent light beams from a laser source to form a horizontal standing wave pattern in the far field, which can be recorded on a photosensitive medium. However, shorter wavelength laser sources are needed to fabricate sub-100 nm periodic features, which is quite expensive.

In recent years, near- field optical lithography has received considerable attention for its ability to produce high density sub-wavelength features. The underlying principle behind the high resolution capability of near-field optical lithography techniques lies in capturing high spatial frequency optical signals beyond the diffraction limit of the projection optics. These high spatial frequency optical signals are usually in the evanescence regime. Several near-field optical lithographic techniques have been developed by collecting the evanescent waves at the near field. One of the emerging areas of research is scanning probe lithography in which Scanning Tunneling Microscope (STM) or Atomic Force Microscope (AFM) can be used to pattern nanometer scale features [25]. The introduction of laser beam in to a gap between an AFM or STM tip and substrate surface with tip scanning over the surface. But this technique has stringent limitations with respect to certain materials and effectiveness

applies only for certain ambient conditions. Evanescent wave lithography (EWL) is the one of the near field interference lithography technique to achieve nanoscale feature at low cost [26]. It can create a shorter wavelength intensity pattern in the near field of diffraction grating or prism when two resonantly enhanced, evanescently decaying wave superimposed. However, because of the exponential decay of evanescent waves through the subwavelength structures, the optical intensity in the recording medium is strongly attenuated. It provides good resolution, but is limited by low contrast and shorter exposure depth. This problem could be solved by strongly amplifying the transmitted optical field at the near-field. The surface plasmon resonance effect offers a unique solution to solve this problem and stimulates extensive research interests due to its extraordinary transmission through perforated metal films.

Surface plasmon polaritons (SPP) are electromagnetic waves that propagate along the interface between metal and dielectric. The basic principle of the technique is that the SPP generated at the metal/dielectric interface can greatly enhance the weakly coupled evanescent field. It can provide high resolution, high density, and strong transmission optical lithography, which can be used to fabricate periodic structures for potential applications such as biosensors, photonic and plasmonic crystals, metamaterials and high density patterned magnetic storage [27-31]. Plasmonic lithography is an emerging area of near field photolithography techniques in which nanoresolution features can be fabricated beyond the diffraction limit at low cost. Many research groups have already demonstrated that sub-100 nm resolution nanostructures can be fabricated using plasmonic lithography techniques. Fig.1.1 represents the ITRS (International Technology Roadmap for Semiconductors) road map, which illustrates the demands for fabricating sub-30 nm structures beyond 2010 [32]. The recent thrust in this challenging area focuses on exploring novel concepts and configurations to meet the sub-30 nm nodes forecasted for 2010 and beyond. Detailed discussions about above mentioned lithography techniques are given in the literature review chapter.

The near field photolithographic techniques provide a promising platform for the fabrication of future miniaturized integrated circuits. In the current research work various configuration for near field surface plasmon enabled nanoscale lithography have been investigated and the results are discussed. In this context, the main objectives and scopes of the thesis are outlined in the following sections.

Fig. 1.1 ITRS Lithography Exposure Tool Potential Solutions [32].

1.3 Objectives

The main aim of this thesis focuses on investigating near field lithography approaches such as plasmonic lithography for obtaining high resolution periodic features with good aspect ratio at the nanoscale dimensions.

The main objectives of the undertaken research can thus be grouped as:

- Investigation into development of novel plasmonic concepts such as multiple beam SP interference for patterning of periodic nanoscale features.
- Comparative study (theoretical and experimental) between the proposed Surface Plasmon Interference Lithography, Evanescent Wave Interference Lithography and Laser Interference Lithography.
- Theoretical and numerical investigation of SP interference lithography to fabricate periodic nanostructures, which includes gap mode assisted patterning and periodic nanoparticle array based patterning.

- Experimental investigation of localized surface plasmon enhancement by gain assisted media, which can be applied in plasmonic lithography to minimize the optical absorption loss and hence to further improve the aspect ratio of the features.

1.4 Project Scope

Plasmonic lithography techniques have a great potential to achieve cost effective patterning of high resolution nanoscale features. The numerical and theoretical demonstration of prism based plasmonic configuration has been reported. However, the experimental demonstration of this configuration has not yet been carried out. The main technical challenges could be: (i) to make the perfect optical contact at the metal/photoresist interface by using refractive index liquid, (ii) to control the thickness of matching fluid at the metal/photoresist interface. Also, the damping of light intensity caused by the metal absorption loss affects the exposure depth and intensity contrast of patterns written by plasmonic lithography. To meet these challenges, the scopes of the undertaken research are identified as:

- Numerical simulation of plasmonic lithography based on Kretschmann and proposed planar layer configurations for sub-100 nm structure fabrication.
- Theoretical analysis of multiple beam (two and four) surface plasmon interference generation using a three layer configuration.
- Investigation into visible and near UV laser sources to fabricate sub-100 nm structures beyond the diffraction limit using proposed configurations.
- A comparative analysis between conventional laser interference lithography, evanescent wave interference lithography and surface plasmon interference lithography to fabricate periodic subwavelength features.
- Investigation into influence of metal films and metal film thickness on plasmonic lithography configurations.
- Theoretical and numerical analysis of metal nanoparticle assisted plasmonic lithography concept.
- Investigation into the excitation of gap modes in metal particle-surface system for plasmonic lithography in order to fabricate pillars with good aspect ratio.

- Investigation into periodic nanoparticle array based plasmonic lithography concept for high resolution nanopatterning.
- The numerical and experimental analysis of the effect of different configuration on the plasmon behavior and enhancement of surface plasmon in the presence of gain media to get good aspect ratio features.
- Investigation in to the use of fabricated one-dimensional periodic nanostructures using two beam surface plasmon interference lithography for the applications of SPR sensors, biosensors, single nanowire laser, etc.
- Investigation into the use of patterned two-dimensional periodic nanostructures using multiple beam (four) SP interference lithography for the fabrication of plasmonic crystals, and metal nanogratings and hence for the applications of thin film solar cell and biosensors.

The above mentioned investigation approaches are conceived so as to achieve the main targeted objectives outlined earlier. These are also presented as a research roadmap in the following section to illustrate the research plan of this undertaken project.

Research road map

The research road map of the undertaken research is given below, which describes the proposed concepts, methodology and research plan, for obtaining the targeted nanoscale features.

Fig. 1.2 Research road map.

1.5 Thesis Organisation

Chapter 1 begins with general introduction about surface plasmon resonance concepts, their properties and applications in near field photolithography. It also highlights the requirement for developing next generation photolithography concepts and discusses how it can be met by using surface plasmons. This was followed by the motivation, objective and scope of the project, which are discussed in the subsequent sections. Based on the current-state -of- the-art literature, the proposed research problems are identified and illustrated with the help of a research road map.

A comprehensive literature survey on optical lithographic techniques and surface plasmon resonance phenomena has been carried out and reported in chapter 2. It begins with a brief introduction of optical projection lithography and followed by, detailed discussion about resolution enhancement techniques. The requirements for next generation lithography techniques such as near field lithography techniques are highlighted and described in the following section. A brief history of surface plasmon concept and its various applications are given in the consecutive section. Different plasmonic lithography configurations so far reported in literature are presented. At the end of the section, a detailed theoretical background of surface plasmon concept is given. Finally, an outcome of the literature review is given detailing the significance of the undertaken review.

Chapter 3 investigates multiple beam optical interference lithography techniques. Initially, both theoretical and experimental analyses of conventional laser interference lithography are presented. A detailed discussion about near-field interference lithography such as evanescent wave interference lithography is presented in the subsequent section. A comparative analysis between laser interference lithography and evanescent wave interference lithography is carried out and presented. Also, the influences of polarization on both techniques are investigated.

Chapter 4 investigates the different configurations of plasmonic lithography based on surface plasmon interference generated by thin metal films. Initially, the well known metal mask grating based configuration is analyzed numerically. A detailed theoretical

analysis of multiple (two and four) beam surface plasmon interference based on prism coupling technique is presented. Then the configuration is numerically and experimentally analyzed by employing silver and aluminum thin films as metal medium. A planar layer configuration has been proposed for plasmonic lithography and investigated numerically and experimentally. Simulated resist profiles, using cellular automata model, obtained through the proposed configuration are presented and analyzed.

Chapter 5 investigates localized surface plasmons associated with metal nanoparticle assisted periodic nanopatterning. A plasmonic lithography concept based on periodic metal nanoparticle array has been proposed and numerically illustrated. The basic concept behind this technique is the electromagnetic energy transfer (local field) via periodic array of metal nanoparticles. A high resolution plasmonic lithography concept based on gap mode excitation is proposed and demonstrated. It is shown that such a metal nanoparticle-surface system can be used for the generation and excitation of gap modes.

Chapter 6 concludes the thesis contents with a summary of the work done in this thesis and discusses the future research directions. The major research contributions made during this period are also highlighted.

Chapter 2

Literature Review

A literature review on various optical lithography techniques are described in this chapter. Chapter starts with the introduction section where the basics of conventional optical projection lithography followed by various high resolution lithography techniques are discussed. The principle of near field optics and various near field lithography techniques are presented in the second section. A review on the surface plasmons concept and its applications followed by various reported plasmonic lithography techniques are discussed in the subsequent sections.

2.1 Introduction

Optical lithography (Photolithography), a technology driving the evolution of semiconductor industry, has played a significant role in the dramatic size reduction of semiconductor devices and circuits over the last three decades. Since the beginning of integrated circuits (IC), optical lithography has enabled semiconductor devices to progressively shrink their size. Current feature size of semiconductor devices are 45 nm and it will have 32 nm features in 2013, as indicated by international technology roadmap of semiconductor (ITRS) shown in Fig.1.1. Integrated circuit complexity is commonly measured by counting the number of transistors in the IC. The well known Moore's law states that on an average, the number of transistors in an integrated circuit has double every eighteen months [33]. The CPU transistor count against date of introduction according to Moore's law is shown in Fig.2.1 [34]. The main challenge of optical lithography is to keep pace with the projected transistor chart postulated by Moore's law. To achieve this goal, optical lithography has gone through technological innovations such as using deep ultraviolet lasers sources, optical system with high numerical apertures and near diffraction limited techniques. Detailed discussions on these techniques are given in the following sections.

Fig. 2.1 Transistor counts with date of introduction [34].

2.2 Optical projection lithography

To improve the resolution requirement in optical lithography, exposure systems have played a significant role in the past. Contact and proximity printers/aligners based photolithography systems were dominated the industry in the early years (1970-1980) [35]. In contact aligner systems, the mask is in direct physical contact with photoresist and when the light passes through the mask, will expose the patterns in the selective areas of the photoresist where the light is transmitted. But the main problem with this technique is the physical contact between mask and photoresist, which makes the mask contaminated. This technique is typically used to pattern 10 μm to 5 μm dimension features. In this context, a small gap is kept between mask and photoresist so as to avoid physical contact and hence the formation of contamination generally observed in the case of proximity printers/aligners. But this gap should keep under control to avoid the degradation in resolution, when the gap size increases. Proximity aligners typically provide 5 μm to 3 μm dimension features.

Fig. 2.2 Resolution scaling with process generation [37].

Projection systems were introduced in photolithography in the year 1980-1990 [35]. In this case, the image of the mask is projected by an optical system (lens) on to the photoresist coated wafer. Here the contamination issue due to physical contact is not a concern, by keeping the mask and wafer at an extremely large distance. This system has been used for patterning of 3 μm and 0.7 μm critical dimension features. ‘Steppers’ or step and repeat system started to be used in the late 1980s as an exposure tool to obtain the better resolution at a manageable lens cost. The main advantages of this system are (i) by reducing the mask image with this same magnification factor, the optical system became a reduction projection system and (ii) compared to the image on the recording medium, this allows the mask to become magnified with a factor of 4 or 5. This technique is typically used to get feature size down to 250 nm. The next advanced optical exposure tool in photolithography is based on scanners (step and scan systems) [36]. In this case, by only projecting one slit of the mask on to the wafer, further reduction in the complexity of the optics is possible. Here a continuous scanning motion is used to transfer the whole photomask patterns in to wafer. This technique also allows better control to print smaller dimensional features because of the improvement in optics. This system is used for 45 nm technology node for manufacturing of today’s integrated circuits and is expected to use further in the next stage critical layer lithography system of 32 nm technology node. In Fig. 2.2, the line width scaling with process generation is represented [37].

Fig. 2.3 Variation of K_1 value with year [40].

The laws of electromagnetic wave propagation determine the performance of optical projection lithography system. There are two key parameters such as resolution and depth of focus, which determine the lithography performance. These two parameters depend on the illumination wavelength (λ) and numerical aperture (NA) of the projection optics. The expressions of resolution and depth of focus are given by, resolution ($k_1\lambda/NA$) and depth of focus ($k_2\lambda/NA^2$), where k_1 and k_2 are coefficient of proportionality. For advanced devices $k_1=0.4$ and $k_2=0.7$ [39]. Therefore resolution improvement in optical projection lithography is possible by decreasing the illumination wavelength of laser source and by increasing the NA of projection optical system. Resolution also depends on the value of k_1 , which was originally introduced to represent the quality of the resist features. The value of k_1 is commonly considered when to represent the resolution enhancement technique in phase shift mask, off-axis illumination, optical proximity correction (OPC), etc. The variation of k_1 value with year of system introduction is shown in Fig. 2.3 [40]. In short, optical projection lithography is diffraction limited by wavelength of incident light and NA of the imaging system.

2.3 Resolution enhancement techniques

2.3.1 EUV and X-ray lithography

The ultimate limit in optical lithography is not yet achieved, and many optical lithography techniques are still under progress to fabricate high resolution structures beyond the diffraction limit of optical projection lithography. Among them, shorter wavelength lithographic techniques such as Extreme Ultra-Violet (EUV) lithography and X-ray lithography have proved to be a valuable technique for the production of subwavelength structures. Currently, the industry is leading the transition to 193 nm, 157 nm (DUV lithography) and EUV lithography to achieve 32 nm technology node [2]. 157 nm lithography or 193 nm lithography with alternating phase shift masks has been used for the patterning of 65 nm generation integrated circuits. The solutions of several material science challenges are required when move down to shorter wavelength. The challenges are (i) the development of etch-resistant and transparent photoresist, (ii) transmission and durability improvement of lens materials and coatings.

Extreme Ultra-Violet lithography is developed for the fabrication of integrated circuits with critical dimension at 45 nm [41-42]. In the past years, there has been an excellent progress on EUV lithography. EUV lithography uses 13.5 nm EUV laser wavelengths and it is often referred to as next generation lithography technology. However this technique presents unique technical challenges. EUV lithography is a vacuum based technology that uses reflective optics and reticles, because all matter including air absorbs EUV radiation. EUV optical systems are complex and totally different from other lithography systems. Optical surfaces are added in the refractive optical design of conventional optical projection lithography to provide degrees of freedom for further improving the performance. In contrast to conventional case, EUV system demands to minimize the number of surface involved. The reason is that the every added extra surface between the EUV system and wafer cuts number of photons transmitted by about 30%. This will lead to a per-surface decrease in optical efficiency. This issue limit the formation of high reflectivity multilayer coating for use at 13.5 nm and currently alternating layers of molybdenum and silicon are using

for this purpose. In contrast to conventional optical lithography, the value of k_1 in EUV lithography starts with near one.

Another candidate for next generation lithography for the semiconductor industry is the X-ray lithography [43-45]. X-ray lithography uses shorter wavelength sources (below 1 nm), that can be used to fabricate smaller dimension features beyond the diffraction limit of conventional optical lithography. In X-ray lithography, synchrotron radiation source is used as the broadband X-ray source and elementary collimating mirrors or diffractive lenses are used in the place of the reflective lenses used in the conventional case. For the fabrication of large area sub-100 nm feature, Proximity X-ray lithography (PXL) is an attractive approach [46]. However there are several technical problems which have to overcome before use in industry. The problems are (i) the lack of low cost, compact and reliable bright X-ray photon source; (ii) the small gaps (10 μm -30 μm) are required for the fine feature fabrication, which is difficult to control and maintain, (iii) X-ray mask distortion and difficulty of writing 1x mask. X-ray mask is typically fabricated using electron beam lithography, which consists of an X-ray absorbing layer of gold or compounds of tungsten on an X-ray transparent membrane (silicon carbide or diamond). The main issue in X-ray lithography is the distortion with X-ray mask. Several approaches have been proposed to overcome this problem. To fabricate deep and three dimensional high resolution features, Deep X-ray lithography (0.1 nm) with modified procedures such as LIGA process can be used [47].

2.3.2 Immersion lithography

As mentioned in the previous section, the improvement in lithography resolution is also achievable by increasing the numerical aperture of the exposure system lens, at the same time the exposure wavelengths have been reduced. The numerical aperture of the imaging lens is given by $NA = n \sin \theta$, where n is the refractive index of surrounding lens medium and θ is the maximum accepting angle of the lens [40]. Fig. 2.4 represents the variation of NA with year of system introduction [40]. If air is the medium between lens and wafer in the exposure system, the physical limit of NA is 1. The achieved practical limit of NA is 0.93 for ArF (193 nm) exposure system. From a lens design aspect, further increase in NA above 0.93 is practically impossible

if air is the medium between lens and wafer. However, an improvement in NA is possible by substituting a higher refractive index fluid for air.

Fig. 2.4 NA variation with year of system introduction [40].

Immersion lithography is the primary path for extending DUV (193 nm and 157 nm) lithography into future [49-50]. In immersion lithography, a fluid (water or other liquids) with refractive index greater than 1 is placed in the gap between the lens and the wafer. The practical limit of NA at 1.3 is achieved for a 193 nm exposure system with water as immersion fluid, thereby increasing resolution considerably. It should be noted that for 157 nm exposure system water is not a suitable fluid. Further improvement in resolution is possible by using 157 nm exposure systems with suitable transparent high refractive index fluids. It is already reported that this technique has the potential to extend ArF (193 nm) exposure system to 45 nm critical dimension and F₂ (157 nm) exposure system to 30 nm critical dimension. However, there are several technical challenges, which are to be resolved for water based immersion lithography for the mass production of integrated circuits. The engineering challenges include, (i) it is very difficult to maintain the thin layer of water between the moving wafer and the lens, (ii) imaging problem is possible with turbulence and bubbles in the fluid, (iii) wafer can cool and distort due to evaporation of water, and (iv) leaching of photoresist materials and degradation of lens surface is possible when water comes in to contact between the both lens and photoresist coated wafer. In next generation lithography,

immersion lithography may prove to be an essential tool for extending optical lithography through the end of the decade, by solving all the technical issues.

2.3.3 Non-optical lithography (E-beam, FIB, Nanoimprint)

The non-optical lithography approaches such as electron beam lithography (EBL), focused ion beam milling (FIB) and nanoimprint lithography (NIL) are being considered for the future nanopatterning applications and these approaches also promise to lower the cost of lithography substantially. These non-optical lithography approaches promise the development of wide range of nanostructures, and nanodevices for semiconductor industry.

Electron beam lithography provides better resolution and greater accuracy than optical lithography, has been used for many years in the research field to fabricate advanced semiconductor devices [51-53]. EBL technique is based on the definition of nanometer scale features by shooting a concentrated beam of electrons onto the photoresist coated wafer surface. Then the energy of deposited electron beam can chemically or physically modify the sensitive photoresist material. Nanometer scale beam width of focused electron beam provides the high nanoscale resolution of the technique. Also this technique is a serial process in which electron beam must be scanned across the surface to be patterned. The main two components behind the EBL are (i) Electron gun: a key element in E-beam lithography which can be used to shoot a beam of electrons in a specific direction. Zirconium oxide coated tungsten needle and lanthanum hexaboride crystal are the two commonly used electron guns in EBL. (ii) Electron optical column: this component consists of system of lenses and its job is to focus the electrons into a concentrated beam in a desired direction. In the recent years, EBL techniques are successfully used for the fabrication of periodic structures for the applications of photonic crystals, negative index materials, etc.

E-beam lithography has several disadvantages: (i) This is a low throughput and high fabrication cost technique due to serial pattern writing method used. That means, only small areas of the entire wafer can normally get patterned within reasonable time and at reasonable costs. (ii) The resolution of EBL is not limited to only the size of the focused beam due to electron backscattering. (iii) Proximity effect due to the hitting of focused electron beam to the surface produces secondary electrons that can generate

critical variations. (iv) Electrons are charged particle; therefore EBL should be performed inside the vacuum. In future, advanced E-beam components such as variable shaped electron gun and the use of arrays of optical columns can be used to improve the throughput significantly [53].

Another non-optical high resolution lithography technique for producing electronic devices with submicron dimensions is the focused ion-beam (FIB) lithography [54-56]. This technique can also be utilized for maskless ion implantation and maskless ion etching. FIB lithography is a new potential technique which can overcome some of the above mentioned limitations of E-beam lithography. In FIB, the resist exposure sensitivity is two or more orders of magnitude higher than that of EBL and low backscattering from the substrate, and negligible ion scattering in the resist compared EBL. The practical applications of FIB technology in semiconductor industry is started after the development of liquid metal ion sources. Unlike E-beam lithography, FIB lithography still need to accumulate more knowledge through energetic research work to overcome several technical challenges.

An alternate promising next generation non-optical lithography candidate is the nanoimprint lithography (NIL), which offers the fabrication of large area, high quality semiconductor devices at low processing cost and time [57-60]. In 1995, first nanoimprint lithography system was introduced. NIL is a very simple process compared to optical lithography. NIL uses a stamp process to transfer pattern by mechanical deformation of the resist. Thus the resolution of the printed feature is only limited by the features etched on to the stamp, but not the wavelength of light source as in the case of optical lithography. That means NIL can be used to print smaller features than the today's advanced optical lithography system and it also offers parallel processing with high throughput. There are two forms of NIL such as conventional nanoimprint lithography based on hot embossing and UV-based nanoimprint lithography. Thermal cycles and high pressures during the hot embossing procedure are required in conventional NIL. However, UV-based NIL does not require any thermal cycles and it can also perform under low pressures. Hence UV-based NIL is the best NIL technique, which uses less sophisticated mechanics and allows for more flexibility in material choice. At the same time, NIL depends on other lithography techniques such as E-beam lithography or optical interference lithography to fabricate fine structure nanoimprint stamp or template. Also, to meet the

requirement of extremely stringent manufacturing standard for leading-edge semiconductor fabrication, NIL still need to be developed significantly, especially in the area of overlay alignment accuracy and low defect density.

2.3.4 Two-photon photopolymerization

For three-dimensional (3D) nanopatterning, two-photon photopolymerization (TPP) technique has been used extensively in the past few years [61, 62]. In TPP, a nonlinear process such as two-photon absorption or multi-photon absorption that only occurs at the focal point of a tightly focused laser beam is used for the polymerization of materials. Hence 3D control over the location of polymerization is possible. Initially, this technique was focused on the fabrication of complex polymeric structures with diffraction resolution. Recently, TPP techniques have been studied for the fabrication of 3D metallic structure especially for the realization of 3D metamaterials [63].

2.4 Interference lithography

Optical lithography offers simple technique such as interference lithography to improve its resolution. Interference lithography is a popular and powerful technique for the fabrication of wide variety of samples for nanotechnology. It is also a cost effective and maskless optical lithography technique to realize large-area (up to $\sim\text{cm}^2$) periodic patterning at subwavelength scale resolution. In laser interference lithography (LIL), the interference of two or more coherent light from a laser source to form a horizontal standing wave pattern in the far field, which can be recorded either in a photoresist or directly in the material of interest [64-68]. The interference pattern period that recorded in the photoresist layer on the substrate is given by $\Lambda=\lambda/2\sin\theta$, where λ is the incident laser wavelength and θ is the interfering angle with respect to the normal. Laser interference lithography is further classified in to two, name by wavefront splitting and amplitude splitting. Amplitude splitting interference lithography techniques are widely using for the patterning of periodic structures [69-76]. The single exposure two beam interference lithography creates one-dimensional grating lines. However, second exposure with sample rotation of 90° and 60° is required to pattern hole/dot arrays with square and hexagonal symmetry, respectively.

But in these cases, the obtained holes/dots have elliptical shapes. Shank *et al.* previously reported an optical interference lithography technique for producing one dimensional periodic grating line in glass substrate [70]. The authors fabricated 110.8 nm periodic grating lines, by employing the interference of two 325 nm laser beams. Also, multiple beams single exposure interference lithography can be used to pattern structures with square and hexagonal symmetry. The multiple beam interference lithography enables fabrication of nanoscale periodic features with two or more dimensions that can find potential applications in photonic crystals, field emitter arrays, and nanodot array based biosensors, etc. Hence there is tremendous significance in multiple beam interference (relative phases of beams must be controlled) as a fabrication technique for realizing advanced devices. In multiple beam interference lithography, the need of multiple exposures is not required and it also eliminates the associated rotation of sample in between the exposures. Recently, our research group reported a conventional multiple (four) beam interference lithography technique to pattern two-dimensional periodic circular features with an average diameter of 123 nm [73]. Three beam set up with independently adjustable beams are also proposed for hexagonal symmetry patterning [75].

Compared to amplitude splitting techniques, wavefront splitting techniques are simple and easy to control. Very popular and simple set up for wavefront splitting techniques are based on biprism configuration and Lloyd's mirror configuration [65, 76]. These techniques combined with fast alignment and easily adjustable pattern size allows the mass production of nanoscale structures. Two and three beam single exposure Lloyd's mirror interference lithography configuration for patterning one-dimensional grating lines and two-dimensional hexagonal lattice patterns are proposed by de Boor *et al* [76]. Biprism based wavefront splitting technique is also a simple and efficient laser interference lithography tool for fabricating periodic structures. Here, the interference pattern period and hence the resolution could be further reduced by using large angle biprism and also by employing high refractive index material for biprism. Also, single exposure triprism based LIL could be used for the fabrication of hexagonal lattice periodic features [77]. Recently, a low cost interference lithography based on Lloyd's mirror interferometer for patterning 300 nm periodic features using 405 nm diode laser is reported [78].

However, the conventional laser interference lithography was unable to pattern high resolution structures using visible and near-UV wavelength illumination sources, due to optical diffraction limits. In short, to fabricate periodic structures with sub-100 nm critical resolution there are critical challenges to be faced. In this context comes near field lithography techniques or use of shorter wavelength light sources.

2.5 Near-field lithography concept

2.5.1 Near-field optics

Optical interactions on a subwavelength scale are termed as near-field optics, which mainly deals with the study of non-propagating inhomogeneous (evanescent) fields and their interaction with matter [79]. In most of the cases, optical near-fields are localized either to the surface of materials with free radiation or to the source region of optical radiation. And these fields are mainly explored for their energy to length scales smaller than the Abbe's diffraction limit of $\lambda/2$, where λ is wavelength of light. This localization has been explored for various applications including ultrasensitive detection, high resolution optical imaging and microscopy, and spectroscopy [80-82].

The near-field region in space is generally characterized by the region in which the evanescent waves cannot be neglected. In free space, mathematically evanescent wave is a solution of the Helmholtz equation. However, on physical ground, evanescent wave cannot exist in free-space. The total internal reflections at the interface of dielectric materials generate the evanescent wave, which represent the most elementary case of near field. In the near-field optics, longitudinal fields also enter into the light-matter interaction because evanescent waves are not purely transverse ($\nabla \cdot E$ is not zero everywhere). A validation for this concept is experimentally investigated by Paul Drude and Walther Nernst in 1891 [79]. The authors performed an experiment for the excitation of fluorescence by a standing evanescent wave and found that maxima of the field coincide with the maxima of the fluorescence yield, i.e. with the light-matter interaction strength.

In near field optics, nonradiative interactions play a key role. Therefore optical near fields have great importance in Forster energy transfer, Van der Waals attraction and

Sommerfeld's theory of dipole radiation over lossy ground. The fundamental aspects of near field optics still facing great theoretical challenges. Hence, in-depth research in the field of near field optics is still required for the advancement of fields such as nanooptics, nano-plasmonics and single molecule spectroscopy. Further, we can say that near-field optics has originated to overcome the diffraction limit of optical Imaging [83]. Hence various near-field optical imaging and lithography techniques are developed beyond the diffraction limit. Fabrication of nanometer scale structures (sub-100 nm) is referred as nanolithography and this field of research is very active in academia and industry. Recently, many optical near field photolithographic techniques have been developed as a promising parallel route to the fabrication of nanoscale features. These include (i) scanning probe lithography in which the probe of a near field scanning optical microscope can be used for nanopatterning, (ii) contact imaging through a binary phase shift mask or a transmission mask, (iii) embedded-amplitude mask and light coupling mask based evanescent near field lithography, (iv) evanescent wave interferometric lithography and (v) surface plasmon interference lithography (plasmonic lithography).

2.5.2 Near- field lithography techniques

2. 5.2.1 Scanning probe lithography

Over the past decade scanning tunneling microscope (STM) and the atomic force microscope (AFM) have been played a significant role in the imaging field with atomic resolution. This technique also successfully applied in many areas of research including, (i) gaining new knowledge of molecular organization and surface structure in the fields of physics, chemistry and biology, and (ii) for high density storage of digital data. Recently, researchers have applied this technique in nanolithography area to fabricate nanostructures for various applications.

Scanning probe lithography (SPL) is an emerging area of lithography techniques in which a microscopic or nanoscopic stylus is moved mechanically across a surface to form a pattern [84-88]. This technique uses STM or AFM to pattern nanoscale features on the surface. The factors which affect the applicability of SPL techniques are resolution, alignment accuracy, reliability, and throughput. The types of SPL method can be divided into two groups such as constructive and destructive. In

constructive method, the patterning is done by directly transferring chemical species to the surface, which is called dip pen nanolithography (DPN) [89]. Here AFM tip is used to transfer molecules to the surface via a solvent meniscus. In DPN, the tip of AFM cantilever act as a pen, that is coated with a chemical compound or mixture acting as an ink and then it brought in contact with a substrate (paper). Different types of scanning probe microscope tips such pyramidal tips, hollow tips, and even tips on thermally actuated cantilevers have been used as a pen for depositions. This technique was first reported in 1995 and it also allows a flexible manner direct deposition of nanoscale materials onto the substrate [90]. But in the case of destructive methods such as local oxidation nanolithography (LON), the patterning is realized by deforming the substrate surface via physically, chemically and electronically by providing energy to the substrate [91]. The energy could be in the form of mechanical, thermal, photonic, ionic, electronic, and X-rays. The basic principle of local oxidation nanolithography is the spatial confinement on an oxidation reaction under the AFM sharp tip. In 1990, first experiment on local oxidation of a surface by means of a scanning probe technique was reported [92]. In that work, the authors applied a bias voltage between the tip of a scanning tunneling microscope and the surface, to locally modify hydrogen terminated silicon surface into silicon dioxide. Later in 1993, the local oxidation experiments with an AFM are performed [93]. There after this technique has been applied to large variety of materials. Current form of local oxidation nanolithography is consisting of AFM operated in contact or non-contact mode and some additional circuits, which apply the voltage pulses between the AFM tip and the surface. Currently, researchers are widely using this technique to pattern graphene films.

However, scanning probe techniques are still facing some limitations, which are (i) it is sometimes difficult to determine the detailed shape of scanning tip, which affect the resulting data, (ii) due to the scanning process, this techniques are generally slower in acquiring images, (iii) issues such as specimen drift, feedback loop oscillation, and mechanical vibrations also affect the resulting data, and (iv) the patterned area is generally smaller and it is not useful for examining buried solid-solid or liquid-liquid interfaces.

2.5.2.2 Contact imaging through a phase shift mask

Another reported near field resolution enhancement technique is the contact imaging through a binary phase shift mask or a transmission mask [94-96]. The basic principle is that the interference generated by the phase difference of phase shift mask improves the image resolution of near field lithography. The phase shift mask can further divided into three: (i) conventional phase shift mask, (ii) alternating phase shift mask, and (iii) attenuated phase shift mask. A conventional phase shift mask is a transparent photomask in which same thickness everywhere. And some parts of photomask are covered with opaque elements (non-transmitting materials) to create patterns on the substrate when light illuminated. However, different transmitting regions (thinner or thicker) are made in alternating phase shift mask, which induces a phase-shift in the light travelling those regions of the mask [96]. At a suitable photomask thickness, the interference of the light coming from unmodified region of mask with the phase shifted light has the ability to improve the contrast on some parts of the substrate, which has the effect of increasing the resolution of the patterns on the substrate. But the entire incident light being scattered at a phase shift of 180° (ideal case) and also amount of scattering is not negligible even for smaller phase shifts.

In the case of attenuated phase shift mask, lithographers use a different approach in which certain opaque elements of the mask are modified to semi-transparent elements (small amount of light to be transmitted) [97]. That weak transmitted light does not create any patterns on the substrate. But it could interfere with the light coming from the transparent parts of the mask to further improve the contrast and hence ultimately increase the resolution of the patterns on the substrate. Attenuated phase shift masks are widely used in the industry compared to alternating phase shift masks, because of their simple construction and operation. But the usage of alternating phase shift mask is reduced, because they are very difficult to manufacture.

2.5.2.3 Evanescent wave lithography

The demand for improvement in optical resolution is one of the continuing challenges faced by lithography, data storage and optical imaging community. In the past decade, much progress has been achieved by the introduction of near field techniques including evanescent wave fields for resolution enhancement. Evanescent field can be

generated in a variety of ways, including total internal reflection (TIR) in an incident medium of high refractive index and through the use of sub-wavelength features. Initially, the solid immersion lens (SIL) technique has attracted much attention, which provided high transmission or reflection efficiency and fast imaging possibility [98]. In this case, high refractive solid immersion lens is combined with conventional far-field optical system. The lens is placed at a distance less than the wavelength away from the substrate. Here the critical dimension of the image is inversely proportional to refractive index of the SIL.

For resolution enhancement purpose, there are two possible methods to apply the solid immersion technique to optical lithography. The first method is by employing hemispherical solid immersion lens [99-101]. A hemispherical SIL focus a beam when an incident light from the range of low angle to high angle hits on the top hemispherical surface. There are two parts of the incident energy on the bottom planar surface of hemispherical SIL. One part of the incident energy propagates out of the SIL, which is a homogeneous cone of energy formed from the portion of the beam focused at low incident angle. Second part of incident energy is around the homogeneous cone of energy, which is an annular ring of evanescent waves (EWs) arises from the total internal reflection of the portion of the beam at high incident angles. The contribution of both waves, one that propagates out of the SIL and other that propagates on the bottom surface of the SIL, which generate the resultant high resolution spot at the imaging plane. Furthermore, the sharpest features of the focused spot define the EWs [101, 102]. However, complex optical system such as micro lens array should be required for the realization of parallel SIL writing system [103].

Second possible method of solid immersion technique is by exploiting the interference of the EWs. The important significant is the interaction of the evanescent field with propagating modes of radiation and evanescent field cannot be measured directly similar to the case with frustration of total internal reflection. Therefore indirect methods are needed. A sub-wavelength aperture with small displacement relative to each other can generate evanescent fields and couple the inhomogeneous field back to propagating modes [104, 105]. The use of evanescent fields in enhancing transmission through aperture on a screen has been demonstrated by researchers [106]. The authors have suggested that an array of sub-wavelength features can be generated the direct

interference of the evanescent modes and enhancement is due to the propagating modes traveling through an aperture. Also a sub-wavelength groove has been referred to as evanescent wave assist features [107]. The evanescent wave enhancement in sub-wavelength grooves is expressed as [108],

$$A(\lambda) = \left(1 + 2 \sum_{j=1}^N \frac{\alpha d}{jP} \cos \left(\frac{2\pi}{\lambda} n_{eff} jP + \frac{\pi}{2} \right) \right)^2 \quad (2.1)$$

Where λ the wavelength of light, α is the evanescent wave amplitude relative to the incident light amplitude, n_{eff} is the effective index of refraction and P is the pitch of the sub-wavelength grooves.

The basic principle of evanescent wave interference lithography is that a shorter wavelength intensity pattern can be created in the near field of sub-wavelength grooves or prism when two resonantly enhanced, evanescently decaying wave superimposed. In EWIL, the recording medium (photoresist) should be kept in close proximity to either the high refractive index medium or the sub-wavelength mask to capture the exponentially decaying evanescent fields. That means the amplitude of evanescent waves decay exponentially with a distance away from the medium or mask/photoresist interface. Evanescent wave interference was first proposed and demonstrated for holography recording by Stetson [109]. Recent literatures have proposed and studied this technique for lithography application using UV and DUV laser sources, thereby realizing even smaller features (high resolution) [110-112]. Blaikie *et al.*, has proposed an evanescent near-field optical lithography (ENFOL), which combines the aspects of ENFOL with interferometric lithography [102]. The authors used a diffraction grating to generate evanescent waves to obtain a high intensity, high contrast, frequency doubled pattern in a photoresist layer. The patterning of two dimensional features, employing four beams evanescent wave interference has been reported by Chua. *et al.* [111]. The EWIL using modified Lloyd's mirror set-up is experimentally demonstrated recently [112]. These techniques provide good resolution, but are still limited by low contrast and short exposure depth, because of the weakly decaying evanescent field.

2.5.2.4 Plasmonic lithography

The above mentioned issues with evanescent wave lithography can be overcome to some extent by using the concept of surface plasmon resonance. The plasmonic lithography technique involves the excitation of SP waves on a metallic mask or prism configuration that is generally put in contact with the photoresist layer in order to expose the plasmon near field. The presence of such SPs on the metal surface can greatly enhance the light transmission and gives a novel method of near field photolithography beyond the diffraction limit. Basically, surface plasmons enhance the weak evanescent field at the dielectric/metal interface of plasmonic lithography configuration. This field enhancement is due to the coupling between SPP and evanescent wave, and the effect of this enhancement can increase the exposure depth and intensity contrast of the plasmonic lithography as compared to evanescent wave lithography. Plasmonic lithography provides high resolution, high density, and strong transmission optical lithography, which can be used for the fabrication of periodic nanostructures.

2.5.2.4.1 Surface plasmons: An introduction

Surface plasmons are collective charge density oscillations occur at the interface between conductors and dielectrics. They can be divided into two: a freely propagating electron density waves along a metal surface called Surface Plasmon Polaritons (SPP) and localized electron oscillations on metal nanoparticles called Localized Surface Plasmons (LSP) [113]. Researchers found that a wide range of practical applications are possible with surface plasmons, because of their unique properties including biodetection at the single molecule level, optical imaging below the diffraction limit at high resolution, guiding and manipulation of light at the nanoscale, enhanced response of p-n junctions, negative index metamaterials, and enhanced optical transmission through subwavelength apertures. The most important applications of LSP are Surface enhanced Raman Scattering (SERS) and observation of Raman scattering from a single molecule. Furthermore, the concept of SPPs is widely used in optoelectronic and photonic devices, including splitters, couplers, quantum cascade lasers, waveguides, add/drop filters, and sensors.

The first scientific studies in which surface plasmon phenomenon were observed at the beginning of the twentieth century. An unexplained feature in optical reflection measurements on metallic gratings was observed by Prof. Robert W. Wood in the year 1902 and in the same year Maxwell Garnett reported the bright colors observed in metal doped glasses [113]. Maxwell Garnett used Drude theory of metals to explain the concept. The theory of light scattering by spherical particles was developed by Gustav Mie in 1908 for further understanding [113]. The collective oscillation of free electron in a metal is theoretically described by David Pines after fifty years, in 1956 [113]. The concept of polaritons for the coupled oscillation of bound electrons and light inside the transparent media is introduced by Robert Fano in that same year [113]. The first theoretical description of surface plasmons was reported by Rufus Ritchie in 1957 [113]. He carried out a study on electron energy losses in thin films, which showed that plasmon modes can exist near the surface of metals. The great achievement in the study of surface plasmons is made by Andreas Otto as well as Erich Kretschmann and Heinz Raether in 1968 [3]. They have developed a method for the optical excitation of surface plasmons on metal films, making experiments on surface plasmons easily accessible to many researchers. And in the same year Ritchie and co-workers reported the anomalous behavior of metal gratings in terms of surface plasmon resonance excited on the gratings [114].

The optical properties of metal nanoparticles in terms of surface plasmons were first time described by Uwe Kreibig and Peter Zacharias in 1970 [113]. They compared the electronic and optical response of gold and silver nanoparticles. In 1974, Stephen Cunningham and his co-workers suggested that the coupling between the oscillating electrons and the electromagnetic field is possible and they have introduced the term surface plasmon polaritons [115]. The strong Raman scattering from pyridine molecules in the vicinity of roughened silver surfaces is observed by Martin Fleischmann and colleagues in the same year as the another major achievement in the area of nanooptics [116]. However, at that time it was not totally understand the Raman scattering, the electromagnetic fields near the rough silver surface due to the presence of surface plasmons enhance the exchange of energy between photons and molecular vibrations. Later, this observation led to the development of well established field of SERS, which enables the rapid molecular assays for detection of chemical and biological species. In 1991, the first commercial surface plasmon

resonance (SPR) based sensor is developed and this added a major boost to this field to grow.

The metal nanostructures have got much attention most recently, because of their ability to guide and manipulate light at the nanoscale. In 1997, Junichi Takahara and co-workers reported that optical beams (nanometer scale dimension) can guide through a metallic nanowire [117]. One year later, the extraordinary optical transmission through subwavelength metal aperture is reported by Thomas Ebbesen and co-workers [4]. Recently, in 2001 John Pendry suggested that a thin film may act as a perfect lens. The development of powerful electromagnetic simulation codes, nanofabrication techniques, and physical analysis techniques also boosted the growth of this field. And these developments are useful to the researchers and engineers with necessary tools for designing, fabricating, and analyzing the optical properties of metal nanostructures. The present stage of surface plasmon based research controlling the crucial technological areas such as optical lithography, optical data storage, and high density electronics manufacturing, etc. The unique properties of surface plasmons may be useful to overcome the current technological challenges.

The collective oscillation of conduction electrons in the noble metal nanoparticles with incident electromagnetic radiation gives a strong absorption band in the visible region of electromagnetic spectrum. Among them, silver and gold nanoparticles have been studied much more extensively because of their unique optical properties. The silver and gold nanoparticles exhibit tunable optical properties over wide spectral range as shown in Fig.2.5 and their SPR band lie in the visible range of electromagnetic spectrum [118].

The factors effecting the SPR bandwidth and peak maximum are the shape and size of nanoparticle as well as the relative permittivity of the medium in which they are dispersed [119]. It is found that the SPR band of metal nanoparticles can only be slightly varied by changing their size (1 to 100 nm), but by simply varying the shape of the nanoparticles the SPR band can be tuned from visible to near-infrared range. SPR also depends on phenomena such as Rayleigh scattering from nanoparticles, aggregation of nanoparticles, charge transfer interactions, change in local refractive index, etc.

Fig. 2.5 Tuning of SPR of metal nanoparticles by varying their size and shape and by forming composite structures [118].

In the case of a periodic nanoholes array in a metal film, light transmission achieved is much larger than that predicted by the classical diffraction theory. This enhanced transmission suggesting that even the photons impinging between nanoholes can be transmitted and this could be larger than normally expected through number of nanoholes. The evanescent wave can be produced by diffraction of the incident light and the surface plasmons enhance the field associated with the evanescent waves, thereby resulting in the enhancement of the transmitted light intensity.

An important application of surface plasmon resonance phenomenon is in sensors, especially in biosensors [120]. Extensive research work on SPR biosensors made them suitable for high speed and high sensitive biomolecular detection. As an advantage, SPR biosensors eliminate time-consuming labeling process and reduce molecular binding disturbance compared to fluorescence based optical biosensors. Also, additional advantages in lab on chip application are possible due to the label-free detection capability of SPR sensors. The multi-channel SPR biosensor configurations including scanned SPR imaging configuration and sequential spectral encoding configuration were proposed. Recently, advanced lithography techniques made it possible to fabricate metal nanogratings on optical waveguides and optical fibers to be made suitable for SPR biosensors. The primary advantage of metal nanograting based SPR sensors are, to effect miniaturization and to make the size of the chips even smaller for commercial applications including antigen-antibody, protein, and

chemicals detection. Thus metal nanograting based SPR biosensors have received an increasing attention recently, which are extremely useful in miniaturization with recent improvements in interference lithography technique of maskless manufacture of gratings.

Recent development of plasmonic metamaterials brings new field of research area in plasmonics. Metamaterials are artificially engineered materials, which have a negative index of refraction (both permittivity and permeability are simultaneously negative) [121]. In the recent years, metamaterials have got great deal of attention due to its new prospects of manipulating light in the new direction. Furthermore, it can find variety of applications such as the development of novel devices including optical antennas with superior properties and a perfect lens (super lens and hyper lens), optical cloaking (special coating that can make an object invisible), super resolution imaging (imaging objects with resolution much smaller than the wavelength of light), and ultra compact optical circuits. However, the fabricated metamaterials do not really enter into the real meat-regime (unit cell size is orders of magnitude less than the wavelength of light) due to the limitations of current nanolithography techniques. At the same time, the choice of metals for plasmonic metamaterials is also crucial in the optical regime because the overall losses are dominated by losses in the metal components. Since metamaterials required periodic or quasi-periodic patterns, hence large area metamaterials fabrication is possible by employing high resolution interference lithography techniques. Currently, researchers are using electron-beam lithography, focused ion beam milling, nanoimprint lithography, and laser interference lithography for this purpose. Recently, the magnetic metamaterials working at 5 μm and 1.2 μm wavelengths were fabricated using interference lithography [122]. However, we need to develop high resolution nanolithography techniques to fabricate metamaterials that working in the visible and near UV wavelength range.

As mentioned above, the damping of light intensity caused by the metal absorption loss affects the most of the existing and potential future applications of nano-plasmonics. A straightforward solution to overcome this problem is by using an optical gain medium such as organic dye in the dielectric medium surrounding the metallic nanostructures. It is reported that the LSP resonance in metallic nanoparticle can exhibit a singularity when the interfacing dielectric medium has a critical value of

optical gain [123]. An evidence for enhancement of surface plasmon oscillation is performed by Lawandy, where he conducted a Rayleigh scattering experiment in which an increase of Rayleigh scattering intensity within the plasmon band shows the SP enhancement [123]. The SP enhancement also leads to low threshold random laser action, enhancement of SERS, and light localization effects. In 1989, Sudarkin *et al.* reported that a population inversion created in a dielectric medium adjacent to a metallic film can increase the propagation length of surface plasmon polaritons [124]. Recently, Nezhad *et al.* have been reported a theoretical work on gain assisted propagation of SPPs in planar metal waveguides [125]. Also, the enhancement of SPP at the interface between metal and dielectric with gain medium is reported. The first experimental observation of SPP amplification by optical gain medium has been reported by Seidel *et al* [126]. The authors observed the change of reflectance using Kretschmann geometry, which is an indication of the SPP propagation length. Recently, to substantially compensate the SPP propagating loss, an optical gain of 420 cm^{-1} has been achieved by Noginov *et al* [127]. The same group has experimentally observed the stimulated emission of SPPs at optical frequency, which proves the full compensation of SPP loss by gain. This observation opens the new path to many practical applications of metamaterials and nano-plasmonics at optical frequency.

Now researchers are moving their attention towards photovoltaic's (solar cell) and light extraction (light emitting diodes) applications of surface plasmons. Photovoltaic devices, a promising technology, provide a valuable mean to convert photon energy into electrical energy. Recently, thin film solar cells have found great interest in solar cell market because of the small film thickness. Therefore the structuring of thin film solar cell is very important to improve the absorbance via localization of light. At present, plasmonics concepts are widely used in thin film solar cells to achieve enhanced light localization and hence to improve the absorption. The light can be concentrated and folded into a thin semiconductor layer, by proper engineering of metallic nanostructures that support the surface plasmons. To allow the complete light absorption and photocarrier current collection, the absorbing layer in thin film solar cell should be optically thick. Recently, three plasmonic concepts are reported to reduce the physical thickness of absorbing layer while keeping their optical thickness constant. The freely propagating plane waves from sun can be coupled and trapped into the absorbing layer, by using nanoparticles as a subwavelength scattering element

[128]. Another technique is that by exciting localized surface plasmons in a nanoparticle. Here, the resonant plasmon excitation enhances the strong local field around the nanoparticle to increase the absorption in surrounding semiconductor medium [129]. Light localization using surface plasmon polaritons is the third reported concept. Light can efficiently be trapped and guided in the absorbing layer when SPPs get excited at the metal/semiconductor interface [130]. In all the above mentioned works, the efficiency improvements in single junction planar thin film solar cells are discussed. Many other plasmonic solar cell designs including multilayer structures also recently proposed for increased light confinement.

In the recent years, the role of surface plasmons have been extensively studied for light extraction applications such as the enhancement of light intensity in organic light emitting diodes (OLED) and light emitting diodes (LED) [131, 132]. The basic principle is that to increase the spontaneous recombination rate of the emitters by energy transfer between the surface plasmons and light emitters. Many authors have reported enhanced light emission from LEDs and OLEDs via surface plasmons. It has been reported that the efficient enhancement of semiconductor light source is possible with SPs in a thin metal layers [131]. Recent studies are performed on various OLED designs in which organic emitters such as dye-doped organic films and conjugated polymer films are placed in close proximity to metal surface [132]. In these works, the enhancement of spontaneous emission intensity has been observed by coupling its emission to SPs generated by metallic surface. More recently, photoluminescence intensity enhancement of dye-doped polymer films are investigated via exciton-field coupling of plasmonic crystals with dye [133]. Plasmonic crystals (PC) have attracted significant interest in the scientific community since the discovery of extraordinary optical transmission through sub-wavelength hole arrays. Plasmonic crystals are periodic arrays of nanopillars or nanowells embossed in a substrate film [134]. The plasmonic crystals can be easily fabricated by using soft lithographic techniques such as nanoimprint lithography, and interference lithography. An advantage of plasmonic crystals over periodic metal corrugation is that the plasmon resonance can be tailored by changing the shape of the unit cell, tuning the lattice periodicity, and varying the crystal symmetry.

The other important applications of surface plasmons are in plasmonic waveguides for nanofocusing and nanoguiding of electromagnetic light. The recent development of

plasmonic waveguides, made it possible to combining the compactness of an electronic circuit with the bandwidth of photonic components. In 1997, Takahara *et al.* first introduced the concept of diffraction limited nanoguiding of SPP modes in nanohole or cylindrical metal nanowire configuration [135]. In the same year, Nerkararyan *et al.* demonstrated the possibility of SPP modes assisted nanofocusing using a wedge like metallic structure [136]. These two papers laid the development of new research area in plasmonics such as plasmonic waveguides with subwavelength localization. The metallic nanostructures including metal films, cylindrical nanorods, nanoholes in a metallic medium, chain of metal nanoparticles, metal nanostrips on a dielectric substrate, sharp metal wedges, and nanogaps between metallic media have been recently proposed for guiding of SPP modes [137]. In plasmon nanofocusing, the plasmonic waveguides concentrate or focus the light energy into nanoscale regions (few nanometers). The tapered metallic nanostructures including sharp metal wedges, tapered metal rods, and tapered nanogap between two metallic media have been typically used as the guiding medium for plasmon nanofocusing [138].

2.5.2.4.2 Different plasmonic lithography configurations

The surface plasmon assisted nanoscale lithography, which is based on the local field enhancement, has been demonstrated both numerically and experimentally in recent years. Two main plasmonic lithography configurations such as metal mask configuration and Kretschmann configuration are recently proposed, which are respectively based on grating coupling and prism coupling techniques of SP excitation. Most of the theoretical and experimental work so far done is based on periodic metal mask configuration [139-153]. In this configuration, a periodic metal mask is brought into intimate optical contact with a thin photoresist film coated on a silica wafer. Light is incident normally from the top of the mask, and light tunnels through the mask via surface plasmon polaritons and reradiates in to the photoresist. A one-dimensional (1D) periodic lines and two-dimensional (2D) square array of holes can be treated as grating coupler. The incident light can excite surface plasmons on the metal mask by selecting suitable periodicity of lines or hole array and a suitable refractive index of medium surrounding metal layer. And these excited SPs reach to the other side of the metal layer by resonant coupling of periodic lines or hole array. Moreover, the SPs on the exit plane scattered on the lines or hole array will be converted back into light when the refractive index of dielectric medium at the both

sides of the metal layer match. Schematic of the metal mask configuration is shown in Fig. 2.6 and 1D (grating lines), and 2D (dot array) periodic features fabricated using this configuration is shown in Fig. 2.7 and Fig. 2.8 respectively [139, 141].

Fig. 2.6 Plasmonic lithography configuration based on metallic mask [139].

The plasmonic mask based configuration at UV wavelength has a great interest in plasmonic lithography to pattern subwavelength (nanoscale) features using conventional near UV light sources, because of the principle of extraordinary optical transmission of the SP waves through the subwavelength aperture. W. Srituravanich *et al.* have been first successfully patterned 90 nm dot array patterns on a 170 nm period using plasmonic lithography concept [139]. The authors have excited surface plasmons on a aluminum substrate perforated with two-dimensional hole array using 365 nm illumination wavelength. Later same group has been demonstrated subwavelength nanolithography using surface plasmon modes on a 2D hole array silver mask and obtained resolution about 60 nm using I- line (365nm) source, which is far beyond the resolution limit of conventional lithography using the same source [140]. Also, a surface plasmon interference lithography (SPIL) technique based plasmonic mask configuration has been reported to fabricate sub-100 nm grating lines using visible wavelength source [143]. Seo *et al.*, proposed proximity nanolithography based on plasmonic lens, another form of plasmonic mask [144]. They used a plasmonic lens, which consist of equally spaced ring apertures in a metal film to pattern 90-300 nm spots using 405 nm laser. The basic principle is that the cylindrical surface plasmons are excited in the plasmonic lens when a collimated laser beam illuminated. The two dimensional manipulation of surface plasmons utilizing sharp edge coupling mechanism have been investigated by Liu. *et al.* [145]. Moreover,

several theoretical and numerical simulation works on plasmonic lithography based on metal mask configurations have been reported [146-153]. However, most of these reported techniques require the fabrication of a fine-period mask grating or hole array and are found to be not cost effective.

Fig. 2.7 Periodic grating lines patterned using metal mask configuration [141].

Fig. 2.8 Periodic dot array patterned using metal mask configuration [139].

Another promising plasmonic lithography configuration is the Kretschmann configuration. In Kretschmann configuration, metal coated high index prism is kept in direct optical contact with a recording medium such as photoresist as shown in Fig. 2.9 (a) [7]. Kretschmann geometry has been widely used for many applications of plasmonics especially for SPR sensors. This is a maskless surface plasmon interference nanolithography configuration, which is based on the principle of prism coupling. The prism coupling technique is considered as one of the best SPP couplers because by using a high refractive index prism in Kretschmann–Raether geometry, it can achieve momentum matching condition in a very efficient way. It can also provide a large area patterning for plasmonic lithography. Recently, plasmonic lithography based on Kretschmann configuration has been theoretically and

numerically demonstrated [7-9, 154]. In these work, the authors carried out the finite-difference-time-domain (FDTD) numerical simulation to find out the intensity distribution on the photoresist, for both metal coated and uncoated cases. It is found that metal coated case (SPIL) gives much enhanced field distribution compared to uncoated case (EWL) as shown in Fig. 2.9(b) [7]. The authors have also showed that large area interference features can be patterned using this configuration by employing silver metal and visible wavelength sources.

Fig. 2.9 (a) Plasmonic lithography using Kretschmann configuration, (b) simulated interference patterns on the recording medium [7].

Later, Xiong et al. has been numerically proposed Kretschmann configuration at shorter wavelength (193 nm) to realize 32 nm node periodic nanostructures by using tungsten metal instead of silver [9]. It shows that prism based plasmonic lithography configuration has a potential to use at different wavelength to realize high resolution periodic features. The only technical challenge is to find a proper metal at shorter wavelengths.

Recently, several other plasmonic lithography configurations have been investigated and proposed, which all are the modification of above mentioned two configurations. A surface plasmon polariton interference lithography based on end-fire coupling method is proposed by Guo *et al* [155]. The FDTD simulation results of proposed configuration show that at 365 nm illumination wavelength, the interference of two face to face SPPs can be used to fabricate 80 nm periodic patterns. A polarization sensitive printing of surface plasmon interference for lithography application is

demonstrated by Lerondel *et al* [156]. For this purpose the authors used a specially designed metallic mask in which silver nanograting coated with a photosensitive azobenzene dye polymer and patterns are printed on the polymer layer. Recently, dielectric diffraction grating based surface plasmon interference lithography configuration for 1D and 2D periodic feature fabrication is proposed by Doskolovich *et al.* [157, 158]. In this configuration, in order to excite SPPs by various diffraction orders of grating, the metal film is coated on the dielectric substrate at a distance ‘D’ from the diffraction grating. The simulation results show that high contrast and high electric field energy density interference patterns with the period 3.5 times smaller than the illumination wavelength can be obtained. The numerical simulation result of nanolithography technique with surface plasmon interference to modulate localized exposure energy has been reported [159]. The authors have employed a metallic mask configuration having a well-regulated grating structure with a tapered metallic tip in order to excite the SPPs. They have shown that high local field enhancement around the tip is possible due to the energy accumulation at the tip via propagation of SPPs waves toward the tip along the taper surface. The numerical demonstration of this configuration shows that it can be used to produce sub- 20 nm line width patterns.

Recently, the nanofabrication techniques have achieved much attention towards metamaterials. Sub-diffraction limited surface plasmon interference lithography with metamaterials have been reported [160]. The SP interference is theoretically achieved by placing an anisotropic metamaterial layer under the conventional plasmonic mask. The authors obtained 40 nm 1D periodic features at 442 nm exposure wavelength. A programmable plasmonic lithography with nanoparticle arrays has been proposed [15]. This is also a mask based plasmonic lithography in which plasmon particle array mask allows the generation of large number of different subwavelength exposure patterns using a single mask. More recently, flying plasmonic lens based high speed nanolithography has been demonstrated by Xiang Zhang group [161]. The authors experimentally reported a new low cost, high throughput approach to maskless nanolithography for patterning of 80 nm line width features, which uses an array of plasmonic lenses that flies above the surface to be patterned. The search has thus recently focused on noble metal nanoparticles because of their localization and enhancement of electromagnetic waves at plasmon resonance. In this context, it is worth mentioning the recent reported studies on direct patterning employing

microspheres or nanospheres as masks. A nanoscale optical lithography based on dielectric microsphere is proposed by Heltzel *et al*, which utilizes the evanescent near-field surrounding the dielectric microspheres to directly pattern on various substrates [162]. Recently, the same group has reported surface plasmons assisted direct patterning technique [163]. The authors performed this by illuminating 532 nm wavelength laser beam on gold nanospheres, at their resonant frequency. However, researchers are still active in this area of research to develop a cost effective plasmonic lithography system for the patterning of high throughput, good aspect ratio, and high resolution nanoscale features for various potential applications.

2.6 Surface plasmons- Theoretical background

2.6.1 Surface plasmons

The surface plasmon wave or surface plasmon polaritons (SPPs) is associated with an electromagnetic wave. The speed of such wave is slower than the speed of light in the medium adjacent to the metal substrate, so that electromagnetic field is evanescent. Let z be the direction of propagation and the evanescent field is given by the expression [3],

$$E = E_0 \exp[i(k_x x \pm k_z z - \omega t)] \quad (2.2)$$

where wavevector k_z is imaginary, which is responsible for the exponential decay of the E field. The surface plasmon wavevector k_x lies parallel to the x direction and continues through the interface.

2.6.2 Surface plasmon dispersion relation

The SPP dispersion relation is derived to investigate the correlation between the wavevector of light and the wavevector of SPP. Figure 2.10 shows a planar interface between two medium with refractive index n_1 and n_2 ($n_1 > n_2$). Consider a p-polarized electromagnetic radiation with wavevector k_1 is propagating from medium1 to medium 2.

Fig. 2.10 Planar interface with two medium and exponential decay of evanescent field is illustrated.

The electric field radiation, which is in the plane of incidence (the plane containing both E and k_1), is described by two components E_z and E_x in the (XZ) plane. And the tangential component of magnetic field is described by H_y . The solutions of electromagnetic wave equation at the interface are expressed as [3],

$$z < 0 \quad E_1 = (E_{x_1}, E_{z_1}) e^{i(k_{x_1}x - \omega t)} e^{ik_{z_1}z} \quad (2.3)$$

$$H_1 = H_{y_1} e^{i(k_{x_1}x - \omega t)} e^{ik_{z_1}z} \quad (2.4)$$

$$z > 0 \quad E_2 = (E_{x_2}, E_{z_2}) e^{i(k_{x_2}x - \omega t)} e^{ik_{z_2}z} \quad (2.5)$$

$$H_2 = H_{y_2} e^{i(k_{x_2}x - \omega t)} e^{ik_{z_2}z} \quad (2.6)$$

where the wavevectors k_{xi} are given as $k_{xi} = k_{xi}^0 n_i$, and similar with k_{zi} , where k_{xi}^0 is the free space wavevector and n_i is the refractive index of the medium.

The Helmholtz equation is given by,

$$\nabla^2 E + \varepsilon k^2 E = 0 \quad (2.7)$$

By inserting the Eqns. (2.3) and (2.5) in (2.7), the resulting equation is the connection between the x- and z-component of the wavevector and the magnitude of the wavevector in a medium characterized by ε ,

$$k_x^2 + k_z^2 = k^2 \varepsilon \quad (2.8)$$

According to boundary condition, the tangential components of the fields, E_x and H_y across the interface between the two media should be continuous. Therefore,

$$E_{1x} = E_{2x} \quad (2.9)$$

$$E_{x_1} e^{i(k_{x_1}x - \omega t)} = E_{x_2} e^{i(k_{x_2}x - \omega t)} \quad (2.10)$$

Also the tangential components of the wavevector on each side of the interface should equal to fulfill the condition for all x values. That is, $k_{x_1} = k_{x_2} = k_x$. This gives the conditions,

$$E_{x_1} = E_{x_2} \quad (2.11)$$

$$H_{y_1} = H_{y_2} \quad (2.12)$$

We can also solve the following conditions,

$$E_{z_1} = -E_{x_1} \frac{k_x}{k_{z_1}} \quad (2.13)$$

$$E_{z_2} = -E_{x_2} \frac{k_x}{k_{z_2}} \quad (2.14)$$

$$H_{y_1} = \frac{\omega E_{x_1} \varepsilon_1 \varepsilon_0}{k_{z_1}} \quad (2.15)$$

$$H_{y_2} = \frac{\omega E_{x_2} \varepsilon_2 \varepsilon_1}{k_{z_2}} \quad (2.16)$$

Where ω is the excitation frequency, ε_0 is free space dielectric constant, ε_1 and ε_2 are the, dielectric constant of medium 1 and 2, respectively. Using Eqn. (2.11) and (2.12), the normal components of the wavevectors in both media is obtained as,

$$\frac{\varepsilon_1}{k_{z_1}} = \frac{\varepsilon_2}{k_{z_2}} \quad (2.17)$$

The wavevectors k_{z_1} and k_{z_2} can be expressed through Eqn. (2.8) as,

$$k_z = (\varepsilon k^2 - k_x^2)^{1/2} \quad (2.18)$$

It is required that k_z is purely imaginary for the fields in eqn. (2.2) to (2.5) to be surface waves or evanescent wave, which decay exponentially in to both media. It is satisfied when $k_x^2 > \varepsilon k^2$ and gives,

$$k_z = \pm i(k_x^2 - \varepsilon k^2)^{1/2} \quad (2.19)$$

It is clear from the condition $k_x^2 > \epsilon_1 k^2$ that the wavevector k_x is greater than the maximum wavevector k . Now the value of k_{z_1} and k_{z_2} obtained from Eqn. (2.18) is substitute in to Eqn. (2.16) and obtained as [3],

$$k_x = k \left(\frac{\epsilon_1 \epsilon_2}{\epsilon_1 + \epsilon_2} \right)^{\frac{1}{2}} = \frac{\omega}{c} \left(\frac{\epsilon_1 \epsilon_2}{\epsilon_1 + \epsilon_2} \right)^{\frac{1}{2}} \quad (2.20)$$

This equation represents the surface plasmon dispersion relation.

Fig. 2.11 Plot of the SPP dispersion relation (solid line) and the dispersion relation of electromagnetic radiation in vacuum (dashed line). The dotted line indicates the “cut off” frequency, ω_{cut} , of the SPP dispersion relation [164].

2.6.3 Spatial extension and propagation length of SP field

The field amplitude of the SPs decreases exponentially as $\exp(-|k_z||z|)$, normal to the surface and skin depth or spatial extension (the depth at which the field falls to $1/e$) is expressed as [3],

$$z = \frac{1}{|k_{zi}|} \quad (2.21)$$

Where k_{zi} is the z- component of wavevector in the material of interest and given by,

$$k_{zi} = (\epsilon_i \frac{\omega}{c} - k_x^2)^{1/2} \quad (2.22)$$

Where k_x is given by the Eqn. (2.20). Substitute Eqn. (2.20) into (2.22), the z-component of the wavevector in metal yields,

$$k_{zm} = \frac{2\pi}{\lambda} \left[\frac{\epsilon_m^2}{\epsilon_a + \epsilon_m} \right]^{1/2} \quad (2.23)$$

Where the real part of dielectric constant of metal is ϵ_m , ϵ_a is the dielectric constant of air and λ is the free space illumination wavelength. Therefore SP skin depth in metal is given by,

$$z_m = \frac{1}{|k_{zm}|} = \frac{\lambda}{2\pi} \left[\frac{\epsilon_a + \epsilon_m}{\epsilon_m^2} \right]^{1/2} \quad (2.24)$$

Similarly SP skin depth in air becomes,

$$z_a = \frac{1}{|k_{za}|} = \frac{\lambda}{2\pi} \left[\frac{\epsilon_a + \epsilon_m}{\epsilon_a^2} \right]^{1/2} \quad (2.25)$$

For example, at $\lambda = 650$ nm, the dielectric constant of gold and silver are -12.9 and -19 respectively. The calculated SP skin depth for gold, $z_m = 25.5$ nm and $z_a = 329.4$ nm and for silver, $z_m = 21.3$ nm and $z_a = 405.1$ nm [3].

The surface plasmons will gradually attenuate because of losses due to absorption in the metal and attenuation depends on the permittivity of the metal at the SP wavelength. As the SPs propagate along the metal surface the intensity decreases as $\exp(-2k_{xi}x)$, with k_{xi} is given by Eqn. (2.20). The length travelled after which the intensity has decreased to $1/e$ is given by (SP propagation length) [166],

$$\delta_{SPP} = \frac{1}{2k_{xi}} = \frac{\lambda}{2\pi} \left(\frac{\epsilon_{mr} + \epsilon_p}{\epsilon_{mr}\epsilon_p} \right)^{3/2} \frac{\epsilon_{mr}^2}{\epsilon_{mi}} \quad (2.26)$$

Where ϵ_{mr} and ϵ_{mi} is real and imaginary part of dielectric constant of metal and ϵ_p is the dielectric constant of prism. The propagation length increases when incident light wavelength increases.

2.6.4 Excitation of surface plasmons by light

Since the dispersion relation lies right from the light line ($k_x > \omega/c$), it is difficult to excite SPs by using light. To transform the incident photons into SPs, the wavevector of the photon energy has to increase by a value Δk_x . There are two methods to satisfy this condition.

Grating coupling

When a light of wavevector ($k = \omega/c$) incident on a grating at an angle θ and its component in the surface can have wave vectors given as, $(\omega/c)\sin\theta \pm \nu g$ where ν is an integer, and $g = 2\pi/a$, where a is the grating constant. Now the dispersion relation is written as [3],

$$k_x = (\omega/c)\sin\theta \pm \nu g = k_{SP}$$

or
$$k_x = (\omega/c)\sin\theta \pm \Delta k_x = k_{SP} \quad (2.27)$$

The reverse can take place, which is when SPs propagating along a grating or a rough surface can reduce their wavevector k_x by Δk_x . In both cases resonance can be observed as a minimum of the reflected light.

Prism coupling

Another method to satisfy the momentum matching is, by guiding the electromagnetic light through a prism placed above the metal surface. Kretschmann-Raether geometry as in Fig.2.12, in which metal film coated on to prism, can be used for this purpose. The total internal reflection is achieved when the incident angle is greater than the critical and hence $k_x^2 > \epsilon k^2$. At the same time an evanescent wave is propagating along the interface with its field amplitude decreasing exponentially into the metal film and the transmitted wave is represented as [3],

$$E_t(x, z, t) = e^{ik_z z} e^{i(\omega t - k_{ix} x)} \quad (2.28)$$

Where $k_{ix} = k_i \sin\theta_i$ and k_z is given by the eqn.(2.19). From the Eqn. (2.28), it is obtained that when the angle of the incoming wave is varied, k_{ix} changes and the phase of the evanescent wave changes.

Fig. 2.12 Schematic of Kretschmann-Raether geometry, in which projection of incoming light through a dielectric medium on the metal film yields, $k_x = \omega/c\sqrt{\epsilon_p} \sin \theta$.

The SP can be excited by choosing the proper k_{ix} to satisfy the SP dispersion relation at a given resonance frequency. At the resonant angle of incidence, the momentum of incident radiation is equal to the momentum of SP. In Kretschmann-Raether geometry, when light is travelling inside the dielectric medium its momentum is different from that of light travelling in air. The momentum of light inside the prism is $\hbar\sqrt{\epsilon_p} \omega/c$ and in air is $\hbar \omega/c$, where $\hbar = h/2\pi$. Therefore k_x is different when light impinges the metal through prism than if it impinges the metal through air. Now the dispersion relation through Eqn. (2.8) is expressed as

$$k_x^2 = k^2 \epsilon - k^2 \epsilon \cos^2 \theta \quad (2.29)$$

where $k_z^2 = k^2 \epsilon \cos^2 \theta$.

$$k_x^2 = k^2 \epsilon \sin^2 \theta$$

$$k_x = \omega/c\sqrt{\epsilon} \sin \theta \quad (2.30)$$

where θ is the SP resonance angle (the angle at which SPP is excited).

2.6.5 Field enhancement due to SP

When p-polarized light incident at the prism/metal interface, the reflectivity R of two interface system can be calculated by using Fresnel's reflection theory as [3],

$$R = \left| \frac{E_r}{E_{in}} \right|^2 = \left| \frac{r_{pm} + r_{ma} \exp(2ik_{zm}d)}{1 + r_{pm}r_{ma} \exp(2ik_{zm}d)} \right|^2 \quad (2.31)$$

Where r_{pm} and r_{ma} is the reflection coefficient at prism/metal and metal/air interface respectively. And given by,

$$r_{pm} = \frac{\frac{k_{zp}}{\varepsilon_p} - \frac{k_{zm}}{\varepsilon_m}}{\frac{k_{zp}}{\varepsilon_p} + \frac{k_{zm}}{\varepsilon_m}} \quad \text{and} \quad r_{ma} = \frac{\frac{k_{zm}}{\varepsilon_m} - \frac{k_{za}}{\varepsilon_a}}{\frac{k_{zm}}{\varepsilon_m} + \frac{k_{za}}{\varepsilon_a}} \quad (2.32)$$

The intensity of electric field reaches its maximum in the surface, when the reflectivity R has its lowest value. The value of the field enhancement is obtained by taking the ratio of magnetic field intensity at metal/air interface (H_{ma}) to the incoming magnetic field intensity at the prism/metal interface (H_{pm}) and is given by,

$$\left| \frac{H_{ma}}{H_{pm}} \right|^2 = \frac{t_{pm} t_{ma} \exp(ik_{zm} d_m)}{1 + r_{pm} r_{ma} \exp(2ik_{zm} d_m)} \quad (2.33)$$

where t_{pm} and t_{ma} respectively represents the Fresnel's transmission coefficient at prism/metal and metal/air interface. And is given by, $t_{pm} = 1 + r_{pm}$ and $t_{ma} = 1 + r_{ma}$.

The maximum enhancement factor for the electric field intensity is obtained as,

$$\left(\frac{|H_{ma}|^2}{|H_{pm}|^2} \right)_{\max} = \frac{\varepsilon_a}{\varepsilon_p} \left(\frac{|E_{ma}|^2}{|E_{pm}|^2} \right)_{\max} = \frac{\varepsilon_a}{\varepsilon_p} T_{\max} \quad (2.34)$$

where $T_{\max} = \frac{1}{\varepsilon_a} \frac{2|\varepsilon_{mr}|^2}{\varepsilon_{mi}} \frac{a}{1 + |\varepsilon_{mr}|}$, with $a^2 = |\varepsilon_{mr}|(\varepsilon_p - 1) - \varepsilon_p$

For example, when $\varepsilon_p = 2.2$ (quartz), $\varepsilon_a = 1$ and silver at $\lambda = 450$ nm, 600 nm and 700 nm, the calculated approximate $T_{\max}$ are 100, 200 and 250 respectively [3].

2.6.6 Attenuated total reflection (ATR) principle

Attenuated total reflection (ATR) is a phenomena used to investigate the excitation of SPs. ATR is the principle used to excite SPs in Kretschmann-Raether geometry, which is already discussed in section 2.6.4. When incident light is incident at the prism/metal interface, it is partially reflected from and partially transmitted into the metal as an exponentially decaying field. And at the metal/air interface the field excites SPs. The

internal damping is increased and the degree of SP excitation is decreased when the thickness of the metal film is increased. And then reflection coefficient, R approaches unity. But when the thickness of the film is decreased the radiated field is increased and R is reduced. The reflected field and the radiated field cancel out and R becomes zero, when the metal film thickness is ideal, d_i . The sum of the reflected, transmitted, and absorbed part of the light energy equals unity, $R + T + A = 1$ due to energy conservation principle. When $d = d_i$, then $R = 0$, $T = 0$ and $A = 1$, i.e. all the light energy is absorbed in the metal film.

When the metal film thickness decreases, prism dielectric constant, ε_p approaches that of the metal/air interface and an additional wavevector term Δk_x add to the incident wavevector term k_x . Thus the wave vector term becomes $k_x = k_x^0 + \Delta k_x$. The internal damping in the metal is given by $\Gamma_i = \text{Im}\{k_x\}$. An additional damping term $\Gamma_{rad} = \text{Im}\{\Delta k_x\}$ is added to the total damping, which is due to the radiation caused by SPs on the metal/air interface that escapes the metal film and radiates back into the dielectric medium in the direction of the reflected light. Now the total damping in the metal film becomes [3],

$$\begin{aligned}\Gamma_{total} &= \Gamma_i + \Gamma_{rad} \\ \Gamma_{total} &= \text{Im}\{k_x\} + \text{Im}\{\Delta k_x\}\end{aligned}\tag{2.35}$$

The reflectivity of a prism/metal/air system in terms of damping is obtained as [3],

$$R = 1 - \frac{4\Gamma_i\Gamma_{rad}}{[k_x - (k_x^0 + \Delta k_x)]^2 + (\Gamma_i + \Gamma_{rad})^2}\tag{2.36}$$

At the resonance condition, $k_x = k_x^0 + \Delta k_x$, Eqn.(2.35) reduces to [3],

$$R = 1 - \frac{4\Gamma_i\Gamma_{rad}}{(\Gamma_i + \Gamma_{rad})^2}\tag{2.37}$$

When the internal damping in the metal is equal to the radiation damping, $\Gamma_i = \Gamma_{rad}$, $R=0$. That is R becomes zero and all the light energy is absorbed in the metal. This is the optimal condition for surface plasmon excitation.

2.7 Outcome from literature review

During the literature review, it is observed that plasmonic lithographic techniques have great potential to achieve cost effective high resolution nanoscale patterning. In plasmonic lithography, metal mask based configurations have been reported experimentally and theoretically by many groups. Also, some research groups have numerically and theoretically proposed surface plasmon interference nanoscale lithography based on Kretschmann-Raether attenuated total reflection (ATIR) geometry. However, the experimental demonstration of this configuration has not yet been reported. This scheme uses a prism instead of metallic grating mask as a coupler, which makes the structure of lithographic system simple and reduces the cost of fabrication. The main technical challenges could be: (i) to make the perfect optical contact at the metal/photoresist interface by using refractive index liquid or vacuumpump, which damaged or polluted the used metal and photoresist film, (ii) to control the thickness of matching fluid at the metal/photoresist interface. Hence there is great interest in this area of plasmonic lithography research to realize Kretschmann configuration experimentally for the patterning of large area high resolution periodic nanoscale features. Also, the experimental demonstration of such plasmonic lithography configuration was not realized yet as well.

The damping of light intensity caused by the metal absorption loss also affects the exposure depth and intensity contrast of patterns written by plasmonic lithography. Therefore we need to propose a straightforward solution for this issue by using an optical gain medium in plasmonic lithography configuration to minimize the optical absorption loss. Here also we have to consider several technical challenges. This is another interesting research problem in plasmonic lithography to further improve the exposure depth of SP field and hence to increase the aspect ratio of the features. It is also observed during literature review that not much work is reported on direct patterning based on noble metal nanoparticles. Hence there lie potential research challenges in plasmonic lithography for improving the resolution. This thesis in this

context explains about various plasmonic lithography concepts to achieve the targeted high resolution features as outlined in Chapter 1. The thesis initially investigates the conventional interference lithography and evanescent wave interference lithography before embarking on the plasmonic interference concepts. The next chapter will be discussing about detailed investigation carried out on multiple beam interference lithography.

Chapter 3

Multiple beam interference lithography

In this chapter, single-exposure multiple-beam interference lithography based on conventional laser interference and evanescent wave interference is demonstrated and compared. The proposed two-beam and four-beam interference approaches are carried out theoretically and verified experimentally, employing the proposed configurations so as to realize the patterning of large area one- and two-dimensional periodic features on photoresist medium. The influences of polarization on both techniques are also analyzed.

3.1 Laser interference lithography (LIL)

In laser interference lithography (LIL), the interference of two or more coherent light beams from a single laser source is used to form a horizontal standing wave pattern in the far field, which can be recorded either in a photoresist or directly in the material of interest.

3.1.1 Theoretical analysis

Two beam laser interference

A pair of co-planar beams with amplitude A_1 and A_2 , intersect at a plane with equal oblique angle θ with respect to normal (Z-axis) is illustrated in Fig. 3.1. Consider both plane waves to be s-polarized such that the orientations of electric field amplitude vectors of the plane waves are perpendicular to the (XZ) plane. If δ_1 and δ_2 are initial phases of the individual plane waves, the electric field of the plane waves in the second medium are expressed as,

$$E_s^{(1)} = |\tau_s^{(I,r)}| A_1 \cos\left(-k_r \sin \theta_r' x + k_r \cos \theta_r' z - \frac{2\pi}{T} t + \delta_1 + \chi_s\right) \exp\left(\frac{-k\kappa_r z}{\cos \theta_r'}\right) e_y \quad (3.1)$$

$$E_s^{(2)} = -|\tau_s^{(I,r)}| A_2 \cos\left(k_r \sin \theta_r' x + k_r \cos \theta_r' z - \frac{2\pi}{T} t + \delta_2 + \chi_s\right) \exp\left(\frac{-k\kappa_r z}{\cos \theta_r'}\right) e_y \quad (3.2)$$

Where $|\tau_s^{(I,r)}|$ is the amplitude factor of the transmission coefficient for s-polarized incident electric field, T is the inverse of the source frequency, θ_r' is the angle of refraction and χ_s is the corresponding induced phase shift resulted from the transmission.

Fig. 3.1 Interference between a pair of s-polarized incident plane waves.

The intensity distribution of the interference between the two plane waves measures the square of the total electric field and is given by,

$$\begin{aligned} I &\propto \langle (E_s^{(1)} + E_s^{(2)}) \bullet (E_s^{(1)} + E_s^{(2)}) \rangle \\ &= |\tau_s^{(I,r)}|^2 \left\{ \frac{A_1^2}{2} + \frac{A_2^2}{2} - A_1 A_2 \cos(2k \sin \theta x - \delta_{1,2}) \right\} \exp\left(\frac{-2k\kappa_r z}{\cos \theta_r'}\right) \end{aligned} \quad (3.3)$$

The period (Λ) of the interference pattern, along the x-direction is given by, $\Lambda = \lambda / 2 \sin \theta$. The term $\delta_{1,2}$ in the Eqn. (3.3) is defined by $\delta_1 - \delta_2$, is the phase difference between the incident plane waves, and results in spatial shift of the

sinusoidal intensity distribution. Also, the intensity contrast of the sinusoidal interference intensity at $z = 0$ is given by, $C_{2s} = \frac{A_1 A_2}{A_1^2 + A_2^2}$.

Fig. 3.2 Interference between a pair of p-polarized incident plane waves.

If the incident plane waves are p-polarized and the electric field of p-polarized plane wave is parallel to the (XZ) plane (Fig. 3.2). The expression for the harmonic electric field of the two incident p-polarized plane waves are given as,

$$E_p^{(1)} = |\tau_p^{(I,r)}| A_1 \cos(-k_r \sin \theta'_r x + k_r \cos \theta'_r z - \frac{2\pi}{T} t + \delta_1 + \chi_p) (-\cos \theta'_r x + \sin \theta'_r z) \exp\left(\frac{-k \kappa_r z}{\cos \theta'_r}\right) \quad (3.4)$$

$$E_p^{(2)} = |\tau_p^{(I,r)}| A_2 \cos(k_r \sin \theta'_r x + k_r \cos \theta'_r z - \frac{2\pi}{T} t + \delta_2 + \chi_p) (-\cos \theta'_r x - \sin \theta'_r z) \exp\left(\frac{-k \kappa_r z}{\cos \theta'_r}\right) \quad (3.5)$$

Where $|\tau_p^{(I,r)}|$ is the amplitude factor of the transmission coefficient for p-polarized incident electric field, and χ_p is the corresponding induced phase shift resulted from the transmission. The corresponding intensity distribution of the interference between the two plane waves is obtained by,

$$I \propto |\tau_p^{(I,r)}|^2 \left\{ \frac{A_1^2}{2} + \frac{A_2^2}{2} - A_1 A_2 \cos(2\theta'_r) \cos(2k \sin \theta'_r x - \delta_{1,2}) \right\} \exp\left(\frac{-2k \kappa_r z}{\cos \theta'_r}\right) \quad (3.6)$$

From Eqn. (3.6), it is evident that the interference term is modulated by $\cos(2\theta_r')$, which is defined as $\cos(2\theta_r') = 1 - \frac{\sin^2 \theta}{n_r^2}$. The corresponding contrast at $z = 0$ is

$$\text{given by, } C_{2p} = \frac{2\cos 2\theta_r' A_1 A_2}{A_1^2 + A_2^2}.$$

Four beam laser interference

Consider the four counter propagating incident plane waves are s-polarized such that their electric field vectors are perpendicular to their respective plane of incidence, the general expression for the interference between them is given by,

$$I_{4s} \propto \frac{|\tau_s^{(I,r)}|^2}{T} \int_0^{t_{\text{exp}}} \left[\sum_{l=1}^4 A_l \cos(H_s/2) \sin(\phi_l) \right]^2 + \left[\sum_{w=1}^4 A_w \cos(H_s/2) \cos(\phi_l) \right]^2 \partial t \quad (3.7)$$

where ϕ_l is the azimuthal angle of the individual beam, A_l and A_w are the electric field amplitude of the incident beam and t_{exp} is the exposure duration which is presumably much larger than T , and $H_s = 2(\chi_s + \delta_{1,2}) + 2k_r \cos \theta_r' z + 2k_r \sin \theta_r' \sin \phi_l y + 2k_r \cos \theta_r' \sin \phi_l x - \frac{4\pi}{T}$

If the multiple (four) incident plane waves are p-polarized, the theoretical expression for the intensity distribution is,

$$I_{4p} \propto \frac{|\tau_p^{(I,r)}|^2}{2T} \int_0^{t_{\text{exp}}} \left\{ (1 + \cos(2\theta_r')) \left[\sum_{l=1}^4 A_l \cos(H_p/2) \sin(\phi_w) \right]^2 + \left[\sum_{l=1}^4 A_l \cos(H_p/2) \cos(\phi_l) \right]^2 \right. \\ \left. + (1 - \cos(2\theta_r')) \left[\sum_{l=1}^4 A_l \cos(H_p/2) \right]^2 \right\} \partial t \quad (3.8)$$

Where,

$$H_p = 2(\chi_p + \delta_{1,2}) + 2k_r \cos \theta_r' z + 2k_r \sin \theta_r' \sin \phi_l y + 2k_r \cos \theta_r' \sin \phi_l x - \frac{4\pi}{T}$$

The numerical simulation results (using Eqs. 3.6, 3.7 and 3.8) of two beam and four beam laser interference lithography is shown in the Fig. 3.3 and Fig. 3.4, respectively.

Fig. 3.3 Simulated periodic 1D pattern using two beam LIL (p-polarization).

Fig. 3.4 Simulated periodic 2D pattern using four beam LIL (a) for s-polarization, (b) for p-polarization.

3.1.2 Experimental analysis

A conventional interferometric set up is used for the experimental investigation, which includes a continuous-wave UV argon-ion laser of wavelength 364 nm, an electronic shutter, a cross-phase grating and polarizers. The schematic diagram of the experimental setup for multiple beam laser interference lithography is illustrated in Fig. 3.5. An electronic shutter (Newport, model 845 HP) controlled continuous wave argon-ion laser (Spectra Physics, 2065-7S) of illumination wavelength 364 nm is normally incident on a custom made two-dimensional diffraction grating (Ibsen Photonics Pte Ltd).

Fig. 3.5 Experimental set up for multiple beams LIL.

The two-dimensional diffraction grating is designed in such a way that it can suppress the 0th order beam and generates high diffraction efficiency (17%) four first order beams. A linear polarizer, mounted in custom fabricated rotating mount, is placed in the optical path of each diffracted beam to obtain the respective polarization of light beam. The 0th order beam is blocked with a hard stop and four counter propagating first order beams are made to incident on the sample placed in a sample holder. The diffracted beams are aligned and directed such that they are made to incident 45° on the sample. The average power density of incident beams measured is 334.35 mW/cm². The interference of two and four beams is recorded in AZ7220 positive tone photoresist. In the case of two beam interference, two counter propagating first order beams were used. And four first order beams were used when four beam interference is employed.

The sample configuration of laser interference lithography consists of photoresist layer of chosen thickness (1µm), that is coated on a silicon wafer. The optimum values of exposure duration and development time are taken as 400 ms and 1 min, respectively. The results of interference of two and four p-polarized incident beams are shown in Fig. 3.6 to Fig. 3.9. Figure 3.6 (a) represents the 2D Atomic Force Microscopy (AFM) image of recorded features on the photoresist using two beam interference and Fig. 3.6 (b) shows the corresponding 3D AFM image. Fig. 3.7 represents the AFM sectional analysis of the Fig. 3.6. Exposure duration of 400 ms resulted in periodic grating lines

with average line width ≈ 136 nm, average period ≈ 253 nm and height ≈ 300 nm on the photoresist (Pls. see Appendix G). Figure 3.8 (a) and 3.8 (b), respectively shows the patterned features obtained using four beam laser interference and Fig. 3.9 shows the corresponding AFM sectional analysis. The dots are arranged in a periodic square lattice formation with average diameter 130.8 nm, period 241.5 nm and height ≈ 300 nm on the photoresist.

Fig. 3.6 Experimental results of two beam LIL (using *p*-polarization) (a) 2D AFM image, (b) 3D AFM image.

Fig. 3.7 AFM Sectional analysis. Periodic grating lines patterned in photoresist [period 253 nm, line width 136 nm, exposure time 400 ms, and development time 1 min].

The experiment is then repeated by keeping polarization of incident beams as *s*-polarization. In this case, the exposure time is taken as 500 ms and development time 1 min. The results of two beam and four beam laser interference lithography are shown

in Fig. 3.10 and Fig. 3.11 respectively. Two beam LIL results, periodic grating lines with an average periodicity of 258.8 nm, average line width equal to 136.7 nm and height $\approx$ 200 nm on the photoresist medium. From Fig. 3.9, 2D square array with an average period equal to 241.5 nm, average spot size 130.8 nm, and height $\approx$ 200 nm are obtained by interfering four counter propagating s-polarized incident beams (Pls. see Appendix G). The total area successfully patterned for LIL (using both p and s polarization) is around 100 mm. Theoretically estimated period (using) is 257 nm, it is found to be almost equal to experimentally obtained period of 258 nm.

Fig. 3.8 Experimental results of four beam LIL (using p-polarization) (a) 2D AFM image, (b) 3D AFM image.

Fig. 3.9 AFM Sectional analysis. 2D square array features patterned in photoresist [period 246 nm, spot size 128 nm, exposure time 400 ms, and development time 1 min].

Fig. 3.10 Experimental results of two beam LIL (using s-polarization): periodic grating line with period 258.8 nm and line width 136.7 nm is patterned, exposure time 500 ms and development time 1 min.

Fig. 3.11 Experimental results of four beam LIL (using s-polarization): 2D square array features patterned in photoresist [period 241.5 nm, spot size 130.8 nm, exposure time 500 ms and development time 1 min].

3.2 Evanescent wave interference lithography (EWIL)

In evanescent wave interference lithography (EWIL), a shorter wavelength intensity pattern can be created in the near field of sub-wavelength grooves or prism when two resonantly enhanced, evanescently decaying wave are superimposed. The photoresist medium should be kept in close proximity to either the high refractive index medium or the sub-wavelength mask to capture the exponentially decaying evanescent waves interference.

3.2.1 Theoretical analysis

Interference of two evanescent waves is realized by employing a TIR set-up as shown in the Fig. 3.12. An ideal optical contact between the incident medium (high-index prism) and the second medium (photoresist) is assumed. The interface between the prism medium and the photoresist is represented at $Z=0$. The two plane waves with same incident angle (θ_i) is incident at the interface between a high refractive index glass prism and the photoresist. The incident angle is defined to be larger than the critical angle (θ_c). Also, both the prism and photoresist are assumed to be homogenously isotropic with refractive index represented by n_i and $n_r + j\kappa_r$ respectively.

Fig. 3.12 Schematic illustration of set-up to realize TIR generated EWIL.

If the two incident beams $\mathbf{E}_i^{(1)}$ and $\mathbf{E}_i^{(2)}$ are assumed to be s-polarized plane waves with equal amplitude (A), the theoretical intensity field of the resultant evanescent interference in the photoresist layer is given by,

$$I_e|_{2s} \propto E_e^2|_{2s} = 2A^2 |\tau_p^{(i,r)}|^2 \exp(-2kQz)(1 + \cos(2kn_i \sin \theta_i x)) \quad (3.10)$$

where $Q = n_r \sqrt{q(\theta_r')}$ and $q(\theta_r') = (n_i \sin \theta_i / n_r)^2 - 1$, θ_r' is the angle of refraction.

When the incident plane waves are p-polarized, the theoretical intensity distribution for evanescent interference between two counter-propagating evanescent waves, $E_e^2|_{2p}$, is given by,

$$E_e^2|_{2p} = \frac{1}{2} A^2 \left| \tau_p^{(i,r)} \right|^2 \exp(-2kQ z) \times \left\{ 4G^2 \cos(2kn_i \sin \theta_i x) + 2n_{ir}^2 (1 - \cos 2\theta_i) (1 - \cos(2kn_i \sin \theta_i x)) \right\} \quad (3.11)$$

where in Eq. (3.11),

$$G = \sqrt{\frac{\kappa_r^2 \left(1 + \sqrt{q(\theta_r')} \right)^2 + q^2(\theta_r')}{n_r^2 q(\theta_r')}} \quad (3.12)$$

In the case of interference of four evanescent waves: if the four equal amplitude incident plane waves are s-polarized; the theoretical intensity distribution of the counter propagating evanescent interference is given by,

$$E_e^2|_{4s} = 2A \left| \tau_p^{(i,r)} \right|^2 \exp(-2kQ z) \left\{ \cos(2kn_i \sin \theta_i x) + \cos(2kn_i \sin \theta_i y) - 2 \right\} \quad (3.12)$$

In the case of four p-polarized incident plane waves, the corresponding theoretical intensity distribution of the counter propagating evanescent interference is given by,

$$E_e^2|_{4p} = \frac{1}{2} A \left| \tau_p^{(i,r)} \right|^2 \exp(-2kQ z) \left\{ 4G^2 [\cos(2kn_i \sin \theta_i x) + \cos(2kn_i \sin \theta_i y)] \right. \\ \left. - 4n_{ir}^2 \cos 2\theta_i + 8G^2 + 4n_{ir}^2 + n_{ir}^2 (1 - \cos 2\theta_i) \times \right. \\ \left. [4 \cos(2kn_i \sin \theta_i (x - y)) - 4 \cos(2kn_i \sin \theta_i (x + y))] \right. \\ \left. - 4 \cos(2kn_i \sin \theta_i (x - y)) - 4 \cos(2kn_i \sin \theta_i (x + y)) \right\} \quad (3.13)$$

where $n_{ir} = n_i / n_r$.

The theoretically calculated minimum period for EWIL is given by,

$$\Lambda = \frac{\lambda}{\sqrt{2} n_i \sin \theta_i} \quad (3.14)$$

Furthermore, it is important to understand how intensity distribution correlates to the resultant resist features in the lithography process. In this context, various photoresist models (resist topology) have been proposed to compute the positional intensity values and corresponding photoresist development rate [110].

The numerical simulation result (using Eq. 3.11) of two beam EWIL is shown in the Fig. 3.13. And numerical simulation of four beams (using Eqs. 3.12 & 3.13) EWIL is already carried out by our group and reported in literature [109].

Fig. 3.13 Simulated 1D periodic pattern using two beam EWIL (p-polarization).

3.2.1 Experimental analysis

Experimental arrangement of multiple beam evanescent wave interference lithography is illustrated in Fig. 3.14. The experimental set up is same as mentioned in the section 3.1.2. The sample configuration of EWIL is based on a liquid immersion system. A 60° triangular prism of refractive index 1.745 is placed on top of the photoresist (thickness=240 nm) coated silicon substrate and an index matching liquid is introduced between the prism and photoresist to provide optical contact between them.

The experimental results of two and four beam EWIL using p-polarized incident beam is shown in Fig. 3.15 to Fig. 3.18. Figure 3.15 (a) & (b) respectively, represents the 2D and 3D AFM image of the one-dimensional grating lines patterned on the photoresist and Fig. 3.16 shows the corresponding AFM sectional analysis. From the figures it is evident that 1D periodic line have an average period of $\cong 187$ nm and average line width $\cong 97$ nm is obtained with exposure duration of 300 ms and developing time of 1 min (Pls. see Appendix G).

Fig. 3.14 Experimental set up for multiple beams EWIL.

Fig. 3.15 Experimental results of two beam EWIL (using p-polarization) (a) 2D AFM image, (b) 3D AFM image.

Figure 3.17 illustrates the AFM topography image of four beam EWIL and Fig. 3.18 represents the corresponding sectional analysis. Four beam EWIL generate 2D periodic dot array patterns with an average period of 164 nm and spot size 82 nm for an exposure duration of 300 ms and 1 min development time (Pls. see Appendix G). The maximum height of the obtained features in both cases is found to be equal to 100 nm.

Fig. 3.16 AFM Sectional analysis. Periodic grating lines patterned in photoresist [period 187 nm, line width 97 nm, exposure time 300 ms, and development time 1 min].

Fig. 3.17 Experimental results of four beam EWIL (using *p*-polarization) (a) 2D AFM image, (b) 3D AFM image.

To study the influence of polarization on evanescent wave interference, the experiment is then repeated, using *s*-polarized incident beams. The results of two beam and four beam EWIL are shown in Fig. 3.19 and Fig. 3.20 respectively. Two beam EWIL generates periodic grating lines with an average period 185.5 nm, average line width 87.9 nm and height 80 nm on the photoresist medium (Pls. see Appendix G). From Fig. 3.20, it is evident that 2D square array with period 1649.9 nm, spot size 87.9 nm, and height 30 nm are obtained by interfering four counter propagating *s*-polarized

incident beams. In this case, the optimum value of exposure time and development time is taken as 350 ms and 1 min, respectively.

Fig. 3.18 AFM Sectional analysis. 2D square array features patterned in photoresist [period 164 ± 11 nm, spot size 82 ± 11 nm, exposure time 300 ms, and development time 1 min].

*Fig. 3.19 Experimental results of two beam EWIL (using *s*-polarization): periodic grating lines patterned in photoresist [period 185.5 nm, line width 87.9 nm, exposure time 350 ms, and development time 1 min].*

Fig. 3.20 Experimental results of four beam EWIL (using s-polarization): 2D square array features patterned in photoresist [period 169.9 nm, spot size 87.9 nm, exposure time 350 ms and development time 1 min].

The total area successfully patterned for EWIL (using both p and s polarization) is around 25 μm . It shows that successfully patterned area is limited for EWIL as compared to LIL, because of the near field interference effect. Theoretically estimated period (using Eq. 3.14) is 182 nm, it is found to be almost equal to experimentally obtained period of 185.5 nm.

3.3 Comparison between LIL and EWIL

A comparative analysis between these two techniques is carried out and the results are tabulated in Table. 3.1. From the table, it is evident that near field interference lithography like EWIL provides better resolution and periodicity than LIL. However, the exposure depth of the features generated by EWIL is smaller as compared to LIL, which really affects the aspect ratio of the features. The effect of polarization is not evident from the table because average value of period and resolution is tabulated. The experimental details are tabulated in the Table. 3.2.

Interference lithography		Two beam interference			Four beam interference		
		Average Period (nm)*	Average resolution (nm)*	Maximum height (nm)*	Average period (nm)*	Average resolution (nm)*	Maximum height (nm)*
Laser interference lithography	p-polarization	258.8	136.7	300	241.5	130.8	300
	s-polarization	258.8	136.7	200	241.5	130.8	200
Evanescent wave interference lithography	p-polarization	185.5	88	100	170	88	100
	s-polarization	185.5	88	80	170	88	30

*The value shown in this table represents the average value of 15 data sets. A detailed analysis about this is given in Appendix G.

Table 3.1 Comparison chart for interference lithography using 364 nm incident wavelength.

Interference lithography	Polarization	Resist thickness	Average power density (mW/cm ²)	Exposure time (ms)	Development time (min)
Conventional laser interference	p-polarization	1 μ m	334.35	400	1
	s-polarization	1 μ m	334.35	500	1
Evanescent wave interference	p-polarization	~240 nm	334.35	300	1
	s-polarization	~240 nm	334.35	350	1

Table 3.2 Experimental details.

3.4 Summary

A single exposure multiple beam interference lithography based on conventional laser interference and evanescent wave interference is theoretically presented followed by experimental demonstration and comparison, employing a 364 nm wavelength source. It is inferred that both one-and two-dimensional nanoscale periodic features can be patterned on the photoresist, using the proposed single exposure multiple beam interference. It is experimentally shown that near field interference lithography such as evanescent wave interference lithography provides higher resolution and smaller period (in Table 3.1) as compared to laser interference lithography. The observed variations in the size and height of the periodic features can presumably be attributed to AFM artifacts such as tip-sample convolution, sample drift. A detailed account on these different types of AFM artifacts that can affect the image quality is given in Appendix-F . However, the obtained exposure depth (height) of the patterned features are poor compared to LIL. Therefore, enhancing the decaying evanescent field at the prism/photoresist interface is to be looked into further improving for the exposure depth and intensity contrast of the features. In this context, the following chapter focuses on the proposed concepts and methodologies for achieving that by employing surface plasmons and surface plasmon interference.

Chapter 4

Plasmonic lithography based on surface plasmon interference

This chapter describes the different configurations of plasmonic lithography based on surface plasmon interference generated by a thin metal film. Chapter begins with the investigation of well known metal grating mask based configuration using FDTD simulation. A detailed theoretical analysis of multiple beam surface plasmon interference, based on prism coupling technique is also presented for lithography application, followed by numerical and experimental verification of the proposed concept and configuration. Further, planar layer configuration is proposed and the results are numerically and experimentally verified. Simulated resist profiles, obtained through this proposed configuration is also presented using cellular automata model.

4.1 Metal grating mask based configuration

Metal grating mask based configuration is a commonly used technique for plasmonic lithography [139]. As distinct from a Kretschmann scheme, the mask grating based scheme is much more compact. In this configuration, the period of the grating can be several times greater than the period of the expected interference pattern and interference of various diffraction orders generate the SP interference pattern on the photoresist layer. The optical near field of metallic mask can produce fine features with subwavelength scale resolution. The schematic of plasmonic lithography configuration using metal mask is shown in Fig. 4.1. The metallic mask, which can be fabricated on a thin quartz glass by electron-beam lithography and liftoff process, is brought into intimate contact with a photoresist coated on a silica substrate. Light is incident normally from the top and light tunnels through the mask via SPP and reradiates in to the photoresist

Fig. 4.1 Metal grating mask based configuration.

Fig. 4.2 (a) Electric field distribution below the metallic grating (b) intensity distribution of the interference pattern generated on the photoresist layer.

The distribution of the electric field on a metallic mask is analyzed based on finite difference time domain (FDTD) method [165]. The simulated structure is a 2 by 2 hole array perforated on aluminum film. The boundary condition along Z-directions is set to be perfectly matched layer (PML) and other boundaries set to be periodic [166]. The hole diameter, periodicity, and aluminum film thickness are 50 nm, 200 nm and 50 nm, respectively. The refractive index of quartz glass and photoresist used in the simulation are 1.5 and 1.7, respectively. The wavelength of incident p-polarized light is chosen as 406 nm. Figure 4.2 (a) and Fig. 4.2 (b) respectively show the electric field distribution underneath the metallic mask consisting of an array of holes and the intensity distribution of interference pattern generated on the photoresist layer. The electric field distribution represents the case in which a photoresist layer in the near field of the mask is indexed matched to its supporting substrate. It is evident from Fig.4.2 that the SP interference pattern, with periodicity 100 nm and resolution 50 nm, can be achieved using this configuration.

4.2 Prism based configuration

Prism based configuration (Kretschmann configuration) is a well known method used to excite surface plasmon polaritons, performed with the evanescent field generated by attenuated total internal reflection (ATR) principle and hence for SP interference. Figure 4.3 represents the SP interference lithography technique using prism based configuration, in which the upper layer is a high refractive index isosceles triangle prism, and the coated thin metal layer at the bottom surface of the prism, is in contact with the photoresist layer on a silica substrate.

Fig. 4.3 Prism based configuration for plasmonic lithography.

The dispersion relation for surface plasmon polariton is described as,

$$k_{SP} = k_x = \frac{\omega}{c} \sqrt{\frac{\epsilon_m \epsilon_d}{\epsilon_m + \epsilon_d}} \quad (4.1)$$

where ω the excitation frequency, c is the speed of light in vacuum, ϵ_m is the complex dielectric constant of wavelength dependent metal and ϵ_d is the dielectric constant of the dielectric layer. At the surface plasmon resonance angle, the reflected light by TIR has a minimum value and depends on the characteristics of the dielectric layer. Equation (4.1) can be expressed in terms of surface plasmon resonance angle (θ_{SP}),

$$k_x = k_{SP} = \frac{\omega}{c} \sqrt{\epsilon_d} \sin \theta_{SP} = k_0 n_d \sin \theta_{SP} \quad (4.2)$$

The parameters such as incident angle, wavelength and dielectric constants of metal and dielectric layers are extremely important for obtaining the resonance condition.

The wave vector of surface plasmon wave becomes significantly larger than that of the incident light wave vector, when the real parts of ε_m approaches $-\varepsilon_d$. At this condition, the wavelength of the excited SPs should be shorter compared to the wavelength of illumination light. If ψ_1 and ψ_2 are the two SP waves, then their superposed interference pattern can be expressed mathematically as [169],

$$|\psi_1 + \psi_2|^2 = 2|\psi_0|^2 \left[1 + \cos\left(\frac{4\pi\sqrt{\varepsilon_d} \sin \theta_{sp}}{\lambda} x\right) \right] \quad (4.3)$$

where ψ_0 is the incident wave, ε_d is the dielectric function of photoresist layer, λ is the illumination wavelength and θ_{sp} is the SP resonance angle, and fringe separation is expressed as [167],

$$\Delta x = \frac{\lambda}{2\sqrt{\varepsilon_d} \sin \theta_{sp}} \quad (4.4)$$

4. 2.1 Theoretical analysis of multiple beam SP interference

Fig. 4.4 Schematic diagram of three layer system.

Surface plasmon interference is realized by employing the attenuated total reflection (ATR) principle based three layer configurations as illustrated in the Fig. 4.4. The configuration is shown in the (X Z) plane and is identically represented in the (Y Z) plane. The optical contact at prism/metal and metal/photoresist interface is assumed to be ideal. In this geometry, the interface at the prism/metal or metal/photoresist is represented at $z = d$ and $z = -d$ respectively. The dielectric functions of prism and

photoresist are given by ε_1 and ε_3 respectively, and metal has complex dielectric function, $\varepsilon_2 = \varepsilon_2' + i\varepsilon_2''$.

4.2.1.1 Two beam SP interference

When two p-polarized plane waves with same incident angle and same amplitude were incident at the prism/metal interface, the surface plasmons will propagate in the positive and negative directions of the X-axis. In this case one-dimensional periodic features (grating lines) will be generated on the photoresist (medium 3). The Maxwell's curl equations are,

$$\nabla \times H = \frac{\partial D}{\partial t} \quad (4.5)$$

$$\nabla \times E = -\frac{\partial B}{\partial t}$$

We can write the following set of coupled equations from Eqn. (4.5) by considering

harmonic time dependence, that is $\left(\frac{\partial}{\partial t} = -i\omega\right)$

$$\frac{\partial E_z}{\partial y} - \frac{\partial E_y}{\partial z} = i\omega\mu_0 H_x$$

$$\frac{\partial E_x}{\partial z} - \frac{\partial E_z}{\partial x} = i\omega\mu_0 H_y$$

$$\frac{\partial E_y}{\partial x} - \frac{\partial E_x}{\partial y} = i\omega\mu_0 H_z \quad (4.6)$$

$$\frac{\partial H_z}{\partial y} - \frac{\partial H_y}{\partial z} = -i\omega\varepsilon_0 E_x$$

$$\frac{\partial H_x}{\partial z} - \frac{\partial H_z}{\partial x} = -i\omega\varepsilon_0 E_y$$

$$\frac{\partial H_y}{\partial x} - \frac{\partial H_x}{\partial y} = -i\omega\varepsilon_0 E_z$$

The electromagnetic fields of a single beam in the (X Z) plane of the medium 1 ($Z > d$) is obtained as follows:

When the electromagnetic field propagation is along the X-direction and homogeneity

in the Y-direction, that is $(\frac{\partial}{\partial x} = ik_x)$ and $(\frac{\partial}{\partial y} = 0)$

The coupled equations (4.6) simplifies to get the following equations,

$$\begin{aligned}\frac{\partial E_y}{\partial z} &= -i\omega\mu_0 H_x \\ \frac{\partial E_x}{\partial z} - ik_x E_z &= i\omega\mu_0 H_y \\ ik_x E_y &= i\omega\mu_0 H_z\end{aligned}\tag{4.7}$$

$$\frac{\partial H_y}{\partial z} = i\omega\epsilon_0 E_x$$

$$\frac{\partial H_x}{\partial z} - ik_x H_z = -i\omega\epsilon_0 E_y$$

$$ik_x H_y = i\omega\epsilon_0 E_z$$

When p-polarized plane waves propagate in the X-direction, the electric component has no Y dependence. Therefore the field components are (E_x, H_y, E_z) .

The electric field components in the medium 1 are obtained from Eqn. (3.7) as,

$$E_{x1}(x, z) = -i \frac{1}{\omega\epsilon_1\epsilon_0} \frac{\partial H_{y1}}{\partial z}\tag{4.8}$$

$$E_{z1}(x, z) = -\frac{k_x}{\omega\epsilon_1\epsilon_0} H_{y1}\tag{4.9}$$

The magnetic field component in the medium 1 is given by,

$$H_{y1}(x, z) = A_1 e^{ik_x x} e^{k_{z1} z} \quad (4.10)$$

By substituting Eqn. (4.10) in Eqn. (4.8) and (4.9), we get,

$$E_{x1}(x, z) = -iA_1 \frac{k_{z1}}{\omega \epsilon_1 \epsilon_0} e^{ik_x x} e^{-k_{z1} z} \quad (4.11)$$

$$E_{z1}(x, z) = -A_1 \frac{k_x}{\omega \epsilon_1 \epsilon_0} e^{ik_x x} e^{k_{z1} z} \quad (4.12)$$

$$\text{where } k_{z1} = \frac{2\pi}{\lambda} \left(\frac{\epsilon_2'^2}{\epsilon_2' + \epsilon_1} \right)^{1/2} \text{ and } k_x = \frac{2\pi}{\lambda} \left(\frac{\epsilon_2' \epsilon_1}{\epsilon_2' + \epsilon_1} \right)^{1/2}$$

In the above equations, ω and ϵ_0 are the excitation frequency and free space dielectric constant, respectively. The corresponding field components in the medium 3 ($Z < -d$) are written as,

$$H_{y3}(x, z) = A_3 e^{ik_x x} e^{-k_{z3} z}$$

$$E_{x3}(x, z) = iA_3 \frac{k_{z3}}{\omega \epsilon_3 \epsilon_0} e^{ik_x x} e^{-k_{z3} z} \quad (4.13)$$

$$E_{z3}(x, z) = -A_3 \frac{k_x}{\omega \epsilon_3 \epsilon_0} e^{ik_x x} e^{-k_{z3} z}$$

$$\text{where } k_{z3} = \frac{2\pi}{\lambda} \left(\frac{\epsilon_2'^2}{\epsilon_2' + \epsilon_3} \right)^{1/2} \text{ and } k_x = \frac{2\pi}{\lambda} \left(\frac{\epsilon_2' \epsilon_3}{\epsilon_2' + \epsilon_3} \right)^{1/2}$$

The coupled electromagnetic fields in the medium 2 ($-d < Z < d$) are written as,

$$H_{y2}(x, z) = A_2 e^{ik_x x} e^{k_{z2} z} + A_2' e^{ik_x x} e^{-k_{z2} z}$$

$$E_{x2}(x, z) = -iA_2 \frac{k_{z2}}{\omega \epsilon_2 \epsilon_0} e^{ik_x x} e^{k_{z2} z} + iA_2' \frac{k_{z2}}{\omega \epsilon_2 \epsilon_0} e^{ik_x x} e^{-k_{z2} z} \quad (4.14)$$

$$E_{z2}(x, z) = A_2 \frac{k_x}{\omega \epsilon_2 \epsilon_0} e^{ik_x x} e^{k_{z2} z} + A_2' \frac{k_x}{\omega \epsilon_2 \epsilon_0} e^{ik_x x} e^{-k_{z2} z}$$

$$\text{where } k_{z2} = \frac{2\pi}{\lambda} \left(\frac{\epsilon_1^2}{\epsilon_2' + \epsilon_1} \right)^{1/2} \quad \text{or } k_{z2} = \frac{2\pi}{\lambda} \left(\frac{\epsilon_3^2}{\epsilon_2' + \epsilon_3} \right)^{1/2}$$

In surface plasmon interference lithography, the electromagnetic field underneath the metal layer (medium 3) is interested. Thus surface plasmons propagating along the X-axis have the components, $H_{SP} = (0, H_{y,SP}, 0)$ and $E_{SP} = (E_{x,SP}, 0, E_{z,SP})$ and corresponding electric field components in medium 3 was obtained from Eq. (4.13) as follows,

$$H_{y,SP}(x, z) = A_3 e^{ik_x x} e^{-k_{z3} z} \quad (4.15)$$

$$E_{x,SP}(x, z) = iA_3 \frac{k_{z3}}{\omega \epsilon_3 \epsilon_0} e^{ik_x x} e^{-k_{z3} z} \quad (4.16)$$

$$E_{z,SP}(x, z) = -A_3 \frac{k_x}{\omega \epsilon_3 \epsilon_0} e^{ik_x x} e^{-k_{z3} z} \quad (4.17)$$

The electric field equations can be rewritten as,

$$E_{x,SP}(x, z) = iA_3 \frac{k_{z3}}{\omega \epsilon_3 \epsilon_0} e^{-k_{z3} z} \cos k_x x \quad (4.18)$$

$$E_{z,SP}(x, z) = A_3 \frac{k_x}{i\omega \epsilon_3 \epsilon_0} e^{-k_{z3} z} \sin k_x x \quad (4.19)$$

It is evident from the Eqn. (4.18) to Eqn. (4.19) that the amplitude of E_x and E_z components decreases exponentially with $\exp(-k_{z3} z)$, which indicate that the surface plasmon electric field components are exponentially decaying fields. The amplitude ratio of SP field components are given by,

$$\left| \frac{E_{z,SP}}{E_{x,SP}} \right| = \left| \frac{k_x}{k_z} \right| \approx \left| \frac{\text{Re}(\epsilon_2)}{\epsilon} \right| \quad (4.20)$$

According to Eqn. (4.20), the field component $E_{z,SP}(x, z)$ dominates over the component, $E_{x,SP}(x, z)$ in the field distribution of two beam SP interference. Therefore the SP interference term is determined by $E_{z,SP}(x, y, z)$. Hence the corresponding intensity distribution of the interference between two counter propagating surface plasmon waves to pattern one-dimensional periodic features are given by,

$$I_{x,SP} \propto \langle (E_{x,SP} + E'_{x,SP}) \bullet (E_{x,SP} + E'_{x,SP}) \rangle \quad (4.21)$$

$$I_{z,SP} \propto \langle (E_{z,SP} + E'_{z,SP}) \bullet (E_{z,SP} + E'_{z,SP}) \rangle \quad (4.22)$$

where $E'_{x,SP}(x, z)$ and $E'_{z,SP}(x, z)$ are the $E_{x,SP}$ and $E_{z,SP}$ field components in the negative (X Z) direction.

4.2.1.2 Four beam SP interference

When four counter propagating p-polarized plane waves with same incident angle and same amplitude were incident at the prism/metal interface, the surface plasmons will propagate in both positive and negative directions of the X-axis and Y-axis. In this case two-dimensional periodic features (dot arrays) with square symmetry will be generated on the photoresist (medium 3). For 2D surface plasmon interference generation, the electromagnetic field components in the (YZ) plane of the medium 3 also need to be found out. The electromagnetic fields of a single beam in the (Y Z) plane of the medium 3 (Z<-d) is obtained as follows,

When the electromagnetic field propagation is along the Y-direction and homogeneity in the X-direction, that is $(\frac{\partial}{\partial y} = ik_y)$ and $(\frac{\partial}{\partial x} = 0)$. By following the same procedure, the electric field component in the (YZ) plane of the medium 3 is obtained as,

$$E_{y3}(y, z) = i \frac{1}{\omega \epsilon_3 \epsilon_0} \frac{\partial H_{x3}}{\partial z} \quad (4.23)$$

$$E_{z3}(y, z) = \frac{k_y}{\omega \epsilon_3 \epsilon_0} H_{x3} \quad (4.24)$$

And magnetic field component is given by,

$$H_{x3}(y, z) = A_3 e^{ik_y y} e^{-k_{z3} z} \quad (4.25)$$

For SPs propagating in Y-direction, the SP field components are given by, $H_{SP} = (H_{x,SP}, 0, 0)$ and $E_{SP} = (0, E_{y,SP}, E_{z,SP})$. Substitute Eqn. (4.25) in Eqn. (4.24) and Eqn. (4.23), we get,

$$E_{y,SP}(y, z) = -iA_3 \frac{k_{z3}}{\omega \epsilon_3 \epsilon_0} e^{ik_y y} e^{-k_{z3} z} \quad (4.26)$$

$$E_{z,SP}(y, z) = A_3 \frac{k_x}{\omega \epsilon_3 \epsilon_0} e^{ik_y y} e^{-k_{z3} z} \quad (4.27)$$

Hence the corresponding SP electric field components in the (Y Z) plane is given by,

$$E_{y,SP}(y, z) = -iA_3 \frac{k_{z3}}{\omega \epsilon_3 \epsilon_0} e^{-k_{z3} z} \cos k_y y \quad (4.28)$$

$$E_{z,SP}(y, z) = -A_3 \frac{k_y}{i\omega \epsilon_3 \epsilon_0} e^{-k_{z3} z} \sin k_y y \quad (4.29)$$

Now the total electric field components of four beam SP interference is obtained by adding equations (4.18), (4.19), (4.28) and (4.29), and as follows,

$$E_{x,SP}(x, z) = iA_3 \frac{k_{z3}}{\omega \epsilon_3 \epsilon_0} e^{-k_{z3} z} \cos k_x x \quad (4.30)$$

$$E_{y,SP}(y, z) = -iA_3 \frac{k_{z3}}{\omega \epsilon_3 \epsilon_0} e^{-k_{z3} z} \cos k_y y \quad (4.31)$$

$$E_{z,SP}(x, y, z) = A_3 \frac{k_{SP}}{i\omega \epsilon_3 \epsilon_0} e^{-k_{z3} z} (\sin k_x x - \sin k_y y) \quad (4.32)$$

wherein amplitude term of Eqn. (4.31), we can take $k_x \approx k_y = k_{SP}$

In this case also, the amplitude of E_x , E_y and E_z components decreases exponentially with $\exp(-k_{z3}z)$, which indicate that the SP electric field components are exponentially decaying fields. The amplitude ratio of SP field components are given by,

$$\frac{|E_{z,SP}|}{|E_{x,SP}|} = \frac{|E_{z,SP}|}{|E_{y,SP}|} = \frac{|k_{SP}|}{|k_{z3}|} \approx \left| \frac{\text{Re}(\varepsilon_2)}{\varepsilon_3} \right| \quad (4.33)$$

According to Eqn. (4.33), the field component $E_{z,SP}(x, y, z)$ dominates over the other two components, $E_{x,SP}(x, z)$ and $E_{y,SP}(y, z)$ in the field distribution of four beam SP interference. Therefore the SP interference term is determined by $E_{z,SP}(x, y, z)$. And $E_{x,SP}(x, z)$ and $E_{y,SP}(y, z)$ field components generate equal intensity one-dimensional periodic features (grating lines) on the (X Z) and (Y Z) planes, respectively. However, $E_{z,SP}(x, y, z)$ field component generates high intensity two-dimensional periodic features (dot array) on the (X Y Z) plane. The corresponding intensity distribution of the interference between four counter propagating surface plasmon waves to pattern 2D periodic features are given by,

$$I_{z,SP} \propto \left\langle \left(E_{z,SP}(x, y, z) + E'_{z,SP}(x, y, z) \right) \bullet \left(E_{z,SP}(x, y, z) + E'_{z,SP}(x, y, z) \right) \right\rangle \quad (4.34)$$

where $E'_{z,SP}(x, y, z)$ is the $E_{z,SP}$ field component in the negative (X Y Z) direction.

4.2.1.3 Projection of k-vectors on the substrate surface

Let us consider a four layer configuration as shown in Fig.4.5. In the figure, first and fourth medium is assumed to be prism and substrate layer in which dielectric functions ε_0 and ε_3 , respectively. Second medium is a finite metal with complex dielectric function $\varepsilon_l = \varepsilon'_l + i\varepsilon''_l$ and thickness d_l . And third medium is finite photoresist layer with dielectric function ε_2 and thickness d_2 . Since surface plasmon supports TM waves, it has two electric field components, $E_x(z)$ and $E_z(z)$ and one magnetic field component, $H_y(z)$. The $E_z(z)$ field is proportional to $H_y(z)$ in each one of the four media and $E_x(z)$ field is proportional to the derivative of $H_y(z)$ with respect to z in each one of the four media.

Fig. 4.5 Schematic of multilayer system

The plasmon dispersion equation (k_{spp}) when the metal film thickness and photoresist thickness is finite is given by [3],

$$k_{spp} = k_x^{halfspace} + k_x^{metal} + k_x^{photoresist} + k_x^{radiation} \quad (4.35)$$

where $k_x^{halfspace}$ is the well known plasmon dispersion relation at the interface of metal

halfspace and substrate halfspace and given by, $k_x^{halfspace} = \frac{\omega}{c} \sqrt{\frac{\epsilon'_1 \epsilon_3}{\epsilon'_1 + \epsilon_3}}$

The influence of metal film thickness on SPP dispersion relation is given by,

$$k_x^{metal} = \frac{\omega}{c} r_{01} \left(\frac{2}{\epsilon_3 - \epsilon'_1} \right) \left(\frac{\epsilon'_1 \epsilon_3}{\epsilon'_1 + \epsilon_3} \right)^{3/2} \exp \left(-2 \frac{2\pi d_1}{\lambda} \frac{-\epsilon'_1}{(-\epsilon'_1 - \epsilon_3)^{1/2}} \right) + k_x^{lm} \left[\frac{1}{2 \operatorname{Re}(k_x^{halfspace})} \left(\frac{2\epsilon'_1 + \epsilon_3}{-\epsilon_3} \right) - j \frac{\epsilon'_1}{\epsilon'_1 - \epsilon_3} \right] \quad (4.36)$$

$$\text{where, } k_x^{lm} = \frac{\omega}{c} r_{01} \left(\frac{2}{\epsilon_3 - \epsilon'_1} \right) \left(\frac{\epsilon'_1 \epsilon_3}{\epsilon'_1 + \epsilon_3} \right)^{3/2} \exp \left(-2 \frac{2\pi d_1}{\lambda} \frac{-\epsilon'_1}{(-\epsilon'_1 - \epsilon_3)^{1/2}} \right)$$

And r_{01} is the reflection coefficient at prism/metal interface,

$$r_{01} = \frac{\left(\frac{k_{1z}}{\epsilon_1} - \frac{k_{0z}}{\epsilon_0} \right)}{\left(\frac{k_{1z}}{\epsilon_1} + \frac{k_{0z}}{\epsilon_0} \right)} \quad \text{where, } k_{iz} = (\epsilon_i k_0^2 - k_{spp}^2)^{1/2}$$

Now the influence of photoresist thickness on plasmon dispersion relation is given by,

$$k_x^{photoresist} = \frac{\omega}{c} \left(\frac{\epsilon_2 - \epsilon_3}{\epsilon_2} \right) \left(\frac{\epsilon_1' \epsilon_3}{\epsilon_1' + \epsilon_3} \right)^2 \left(\frac{\epsilon_2 - \epsilon_1'}{\epsilon_3 - \epsilon_1'} \right) (-\epsilon_1' \epsilon_3)^{-1/2} \left(\frac{2\pi d_2}{\pi} \right) + k_x^{1p} \left[\frac{1}{2 \text{Re}(k_x^{halfspace})} \left(2 \frac{2\epsilon_3^2 + \epsilon_2^2}{\epsilon_3(\epsilon_3 - \epsilon_2)} + \frac{\epsilon_1' + \epsilon_3}{-\epsilon_3} \right) - \frac{1}{2} j \frac{\epsilon_1'}{\epsilon_1} \right] \quad (4.37)$$

$$\text{where, } k_x^{1p} = \frac{\omega}{c} \left(\frac{\epsilon_2 - \epsilon_3}{\epsilon_2} \right) \left(\frac{\epsilon_1' \epsilon_3}{\epsilon_1' + \epsilon_3} \right)^2 \left(\frac{\epsilon_2 - \epsilon_1'}{\epsilon_3 - \epsilon_1'} \right) (-\epsilon_1' \epsilon_3)^{-1/2} \left(\frac{2\pi d_2}{\pi} \right)$$

The radiation term describes the change of radiation damping. The influence of radiation term on the plasmon dispersion is given by,

$$k_x^{radiation} = \frac{k_x^{1m} k_x^{1p}}{\text{Re}(k_x^{halfspace})} \left[\frac{-\epsilon_1'}{\epsilon_3} + \frac{2\epsilon_3}{\epsilon_3 - \epsilon_2} + \frac{\epsilon_2}{2\epsilon_3} \right] \quad (4.38)$$

If E_0 is the electric field amplitude of incident wave and E_t , is the transmitted amplitude at photoresist/substrate interface, then the surface plasmon field enhancement factor is given by,

$$T = \left| \frac{E_t}{E_0} \right| \quad \text{where } E_t = (E_x^2 + E_z^2)^{1/2}$$

4. 2.2 Numerical analysis of multiple beam SP interference

Numerical analysis of multiple beam surface plasmon interference is carried out using finite difference time domain (FDTD) method. A schematic view of the multiple beam SP interference lithography configuration is shown in Fig.4.6. The simulated configuration composed of a thin metal film coated at the bottom face of a high refractive index 60° triangular prism, which is in perfect optical contact with a photoresist on silica substrate. The interface between metal and photoresist is represented at $Z=0$. In the simulation, perfectly matched layer (PML) boundary condition is employed along the Z-axis, perpendicular to the propagation direction of the light and periodic boundary conditions along the other axis. The mesh sizes along all directions are taken as 1 nm. In the simulation, the refractive index of photoresist used is 1.7 and wavelength of p-polarized light is taken as 364 nm. The given values correspond to the chosen AZ7220 (AZ Electronic Materials Ltd), positive tone photoresist. The behavior of surface plasmon interference patterns on the photoresist layer by coating aluminum (Al) and silver (Ag) metal films are separately analyzed.

The complex dielectric constants of aluminum and silver at this wavelength are $-19.42+3.606i$ and $-2.5575+0.5989i$ respectively [168]. The dielectric constants of metals at optical frequencies are complex numbers because of absorption and the real part of the most of the dielectric constants are negative at these frequencies. The thickness of photoresist layer and metal film is assumed to be 300 nm and 50 nm, respectively.

Fig. 4.6 Schematic diagram of multiple beam SP interference lithography configuration.

4.2.2.1 Two beam SP interference

In the simulation of two beam SP interference, the refractive index of the prism used with Ag metal layer is 1.745 (NLAK 8 glass) and that with Al metal layer is 1.865 (NLAF 36 glass). Hence the surface plasmon resonance angle at prism/metal interface is 54° and 52.3° (theoretically calculated values) for prism/Ag and prism/Al configuration, respectively. Consider two counter propagating p-polarized plane waves incident at the prism/metal interface at the resonance angle. Figure 4.7 shows the field distributions of the interference pattern generated on the photoresist layer.

Here the Z-axis is considered as the decay direction and metal/photoresist interface is taken as the origin of the decay direction. Figures 4.7 (a) and 4. 7 (b) shows the field distribution of E_x and E_z components obtained respectively for Ag film as the metal medium and figures 4.7 (c) and 4.7 (d) respectively represents the E_x and E_z components obtained for Al film as the metal medium. These field distributions generate one-dimensional periodic grating lines in the Z-directions and maximum

enhancement factor (E_z -field) found to be 21 a.u for Ag and 45 a.u for Al. The normalized intensity is highest at the metal/photoresist interface. The intensity values are normalized with respect to incident light intensity. The normalized intensities of both components decay exponentially from the origin and normalized intensities of E_z components are larger than that of E_x components.

Fig. 4.7. Electric field distribution of the interference pattern generated on the photoresist layer for Ag metal layer system and Al metal layer system (a) Ag- E_x , (b) Ag- E_z , (c) Al- E_x , (d) Al- E_z .

The simulation results show that the surface plasmon interference with Al as the metal medium results in higher intensity at the metal/photoresist interface as well as through the depth of the photoresist medium as compared to Ag metal medium and it can be inferred that the resonant surface plasmon wavelength of Al locates at the UV wavelength range. Furthermore, it is evident from the simulation results that field component dominate over field component in the two beam SP interference configuration. It correlates well with the theoretically obtained results. From simulation, the periodicity and line width of the patterns are found to be approximately equal to 120 nm and 60 nm, respectively.

4.2.2.2 Four beam SP interference

Consider four equal amplitude p-polarized plane waves each with a wavelength of 364 nm are incident on the prism. Metal film is taken as Al, because it is having deep resonant depth at near UV wavelength range. During the analysis, the thickness of the Al film and photoresist are taken as 50 nm and 300 nm, respectively and the four counter propagating beams are incident at an angle of 54° at the prism/metal interface. The obtained simulation results in the photoresist medium are shown in Fig.4.8 and Fig.4.9. Figure 4.8 represent the E_z intensity distributions of two- dimensional periodic patterns generated on the (X Y) plane. It represents a periodic dot array pattern with square lattice symmetry and obtained maximum enhancement factor is 4.2 a.u. Figure 4.9 (a) and Fig. 4.9 (b) respectively show, E_x and E_y intensity distributions in the (X Z) and (Y Z) plane. As shown in the figures, the decay direction is taken as Z-axis and metal/photoresist interface is taken as the origin of the decay direction ($Z=0$). It is visible from the figure that the normalized intensity is highest at the metal/photoresist interface. These field distributions generate one-dimensional periodic grating lines in the Z-directions and maximum enhancement factor (0.007 a. u) is same for both electric field components.

Form the simulation results, it is evident that field component dominates over and field components in the four beam SP interference configuration. These results correlate well with the theoretically obtained results.

Fig. 4.8 E_z -field distribution along the X-Y plane for Al.

Fig. 4.9 (a) E_x -field distribution along the X-Z plane, and (b) E_y -field distribution along the Y-Z plane.

The simulation is then repeated by employing Ag as the metal medium. The field distribution of 2D periodic dot array patterns is shown in Fig. 4.10. As expected, the obtained maximum enhancement factor is 2.8, which is less than the value obtained with Al metal (4.2). Hence it is evident from the two and four beam simulation results that Al metal is a better candidate for surface plasmon generation at near UV wavelength range for lithography applications.

Fig. 4.10 E_z -field distribution along the X-Y plane for Ag.

4. 2.3 Experimental analysis of multiple beam SP interference

A conventional interferometric set up is used for the experimental study of multiple beam SP interference, which includes a continuous-wave UV argon-ion laser of wavelength 364 nm (Spectra Physics, 2065-7S) , electronic shutter (Newport, model 845 HP), custom made cross-phase grating (Ibsen Photonics Pte Ltd.), mirrors and polarizers.

4.2.3.1 Experimental set up

Fig 4.11 Schematic diagram of experimental setup.

The schematic diagram of the experimental setup for multiple beam SP interference lithography is illustrated in Fig. 4.11. The details about the experimental configuration are already discussed in the Sec. 3.1.2.

The prism configuration comprise of a high refractive index 60° triangular prism with flat top as the upper layer; the bottom surface of which is coated with a metal film of a thickness of 50 nm that is in intimate optical contact (using index matching liquid) with a thin positive tone photoresist (AZ7220) layer on a silica substrate. The flat top surface is designed to reflect any stray light incident on the prism. The dimension of the sample is taken as 20 mm X 20 mm.

Resist (AZ7200) (ml)	PGMEA (ml)	Approximate resist thickness (nm)
1	2	240
1	4	150
1	6	100
1	8	70
1	10	40

Table 4.1 Photoresist thickness.

The SP interference patterns are recorded in AZ7220 positive tone photoresist (AZ Electronics Material TM). In order to get thin photoresist thickness, AZ7200 is diluted with PGMEA (EBR solvent, AZ Electronic Material) at different proportions and spin coated at 1500 rpm. The photoresist thickness values at different proportions of AZ7200 and PGMEA are tabulated in Table 4.1. Care has been taken to make the coated resist surface defect free. After exposure, the photoresist is developed in AZ300MIF.

4.2.3.2 Surface roughness studies of metals

In the experiment, the metal films (Ag and Al) of thickness 50 nm are coated using sputtering technique (sputter magnetron) and experiment is done immediately after coating the metal film, in order to avoid the oxide formation (which is relatively a slow process). However, if the surfaces of coated metal films are not smooth enough, the scattering effect caused by the rough metal surface lower the quality of the lithography features. That means, a smooth metal surface is the requirement of SP interference lithography. Hence the surface roughness studies of coated metal films are carried out, in order to get smooth metal surface for SP interference lithography.

Fig. 4.12 Surface roughness analysis of Ag film (a) AFM sectional analysis and (b) 3D AFM image.

The surface roughness is a measure of the texture of the surface. Atomic force microscope (AFM) is used to study the surface roughness of the coated metal films. Figure 4.12 and Fig. 4.13, respectively represent the AFM analysis of coated silver and aluminum films. From the AFM results, the obtained RMS roughness of Ag and Al metals are evaluated as 3.407 nm and 0.616 nm with a vertical distance of 6.876 nm and 2.069 nm, respectively. These results show that coated metal films are smooth enough for SP interference lithography and Ag film is smoother than Al film.

Fig. 4.13 Surface roughness analysis of Al film (a) AFM sectional analysis and (b) 3D AFM image.

4.2.3.3 Two beam SP interference

Fig. 4.14 SP resonance angle calculation using the FDTD method: reflectance versus incident angle.

In the case of two beam SP interference lithography, two counter propagating first-order beams out of four first-order beams coming out of the cross-phase grating are allowed to incident on the prism surface. Here the spin coated photoresist thickness is ~ 100 nm. Initially Ag is used as the metal film and refractive index of high index prism is 1.745(NLAK 8 glass). Hence the theoretically calculated incident angle (SP resonance angle) at the prism/metal interface is 54° .

Fig. 4.15 AFM images of the exposure pattern transferred onto the photoresist film: large-area grating lines at exposure time of 1 s (a) 2D AFM image, and (b) 3D AFM image (for Ag as the metal medium).

Fig. 4.16 AFM image of the developed grating lines on the photoresist. (b) Sectional analysis along the line drawn in (a); periodic patterns with minimum line width of 89 nm on a 172 nm period were obtained (for Ag as the metal medium).

The SP resonance angle is also calculated numerically by finite-difference time-domain method. To find the SP resonance angle, reflectance analysis is carried out as a function of incident angle. Here the incident wavelength is taken as 364 nm. The simulated SP resonance angle plot is shown in Fig. 4.14. From the figure it is evident

that the SP resonance angle is around 53.5° , which correlates with the theoretically obtained value.

During the experiment, exposure time of the sample is kept 1 s and the development time is taken as 2 min. After development, the tapping-mode atomic force microscope (AFM) with high lateral resolution (5 nm) is used to analyze the topography of the recorded features on the photoresist. An AFM image of the lithographic pattern of the SP interference of the two beams is shown in Fig. 4.15. Large-area uniform periodic grating lines were obtained at this exposure dose and exposure time. Figure 4.15 (a) represents the 2D AFM image and Fig. 4.15 (b) represent corresponding 3D image. Figure 4.16 shows a section analysis of the AFM image, and it is found that grating lines with an average fringe separation of 161 nm and average line width of 89 nm were patterned on the photoresist layer (Pls. see Appendix G).

Fig. 4.17 AFM images of the exposure pattern transferred onto the photoresist film: large-area grating lines at exposure time of 15 s (a) 2D AFM image, and (b) 3D AFM image (for Al as the metal medium).

The experiment is then repeated by employing Al film as the metal medium. In this case, the refractive index of prism is 1.865 (NLA 36 glass), the exposure time is taken as 15 s and development time is 2 min. The theoretically calculated SP resonance angle at the prism/ metal interface is 52.3° . The exposed patterns transferred on the photoresist layer using two beam SP interference lithography are shown in Fig 4.17. The 2D and 3D AFM results in Fig. 4.17 show that large-area uniform periodic grating lines were patterned on the photoresist with a single exposure. Figure 4.18 shows the section analysis of the AFM image, and it is found

that grating lines with an average period of 156 nm and average line width of 83 nm were obtained (Pls. see Appendix G).

Fig. 4.18 (a) AFM image of the developed grating lines on the photoresist. (b) Sectional analysis along the line drawn in (a) (for Al as the metal medium).

4.2.3.4 Four beam SP interference

A four beam SP interference lithography experiment is also carried out to pattern 2D periodic features on the recording medium. Four first-order beams from 2D diffraction grating is used for this purpose to generate interference of multiple counter propagating SP waves as a lithographic technique to print periodic 2D features. The result of four beam SP interference lithography using Ag film is shown in Fig. 4.19. Figure 4.19 (a) represents the obtained AFM images of the exposure pattern transferred onto the photoresist layer using four-beam SP interference lithography, and Fig. 4.19 (b) shows the corresponding three dimensional AFM image. The AFM sectional analysis of the exposed dot array on the photoresist film is shown in Fig. 4.20. It is evident from Fig. 4.20 that a large-area periodic dot array with an average spot size 93 nm and average periodicity 173 nm was patterned on the photoresist layer (Pls. see Appendix G).

Fig. 4.19 AFM images of resist features patterned from four beam SP interference using Ag metal (a) 2D image: large area periodic dot array were obtained at exposure duration of 1 s, (b) corresponding 3D AFM image (for Ag as the metal medium).

Fig. 4.20 (a) AFM image of the developed dot array in a $3\ \mu\text{m} \times 3\ \mu\text{m}$ exposed area on the photoresist. (b) Sectional analysis along the line drawn in (a) (for Ag as the metal medium).

Four beam SP lithography by using Al metal also carried out. The exposed patterns transferred on the photoresist layer using four beams SP interference lithography is

shown in Figs. 4.21. From Fig. 4.21 (a), the AFM results show that uniform periodic two dimensional dot arrays are patterned on the photoresist and Fig. 4.21 (b) represents three dimensional AFM image of developed dot array pattern, which belongs to $3\ \mu\text{m} \times 3\ \mu\text{m}$ exposed area. The AFM sectional analysis on $3\ \mu\text{m} \times 3\ \mu\text{m}$ exposed area is shown in Fig. 4.22 and it is evident that two-dimensional dot array that have average period 1751 nm and average spot size 93 nm was transferred fairly well to the photoresist layer (Pls. see Appendix G).

Fig. 4.21 (a) AFM characterization of patterns transferred to photoresist using four beam SP interference lithography at exposure time 15 s, (b) 3D AFM image of the developed dot array in $3\ \mu\text{m} \times 3\ \mu\text{m}$ exposed area (for Al as the metal medium).

The non-uniformity of the exposed dot array patterns can presumably be attributed to (i) the intensity fluctuation of the laser, (ii) due its dependence on the development time, and (iii) the sample drift while doing AFM measurement. While doing the experiment, it was also inferred that the size of the patterns in exposed area depends on the power density and the duration of the exposure. With increase in exposure duration and power density, it can be observed that the spot size of the patterns increases while keeping the period same. The obtained resolution and period in two- and four-beam SP interference lithography for both metal mediums are found to be almost same. But there could be some difference in exposure depth and intensity contrast as evident from the numerical simulations, which was not explored further due to the thin photoresist thickness.

Fig. 4.22 (a) AFM image of the developed dot array in $3 \times 3 \mu\text{m}^2$ exposed area on the photoresist. (b) Sectional analysis along the line drawn in (a) (for Al as the metal medium).

Theoretically estimated period (using Eqn.4.4) of two beam SP interference lithography using Ag and Al metal films are 164 nm and 160 nm, respectively. However, these values are found to be slightly different from the experimentally obtained minimum period of 161 nm and 156 nm for Ag and Al respectively. This discrepancy may be attributed to the calibration error of the AFM device or due to sample drift while doing the AFM measurements.

4.2.3.5 SP interference lithography using thick photoresist film

The plasmonic lithography is then repeated, using thick photoresist film to analyze the metal film dependence on the SP interference. In this case, the photoresist is spin coated at a thickness of 240 nm on the silicon wafer.

Fig. 4.23 2D AFM images of features resulting from two beam SPIL using Ag film.

Fig. 4.24 2D AFM images of features resulting from four beam SPIL using Ag film.

The results of two beam and four beam SP interference lithography by employing Ag metal is shown in Fig. 4.23 and Fig. 4.24, respectively. The samples are exposed for a duration of 3 s followed by 1 min of developing the same. In Fig. 4.23, it is shown that uniform periodic grating lines with average fringe separation of 164 nm and line width of 84.5 nm were obtained at this exposure dose. It is evident from the Fig. 4.24 that periodic square dot array with average spot size of 88 nm and period of 166 nm is patterned on the photoresist layer using four beam SPIL (Pls. see Appendix G). The maximum height of the features obtained with this exposure is 180 nm for two beam SPIL and 160 nm for four beam SPIL.

Fig. 4.25 2D AFM images of features resulting from two beam SPIL using Al film.

Fig. 4.26 2D AFM images of features resulting from four beam SPIL using Al film.

The experiment is then repeated by employing Al film. In this case, the exposure time is taken as 25 s and development time is 2 min. The exposed patterns transferred on the photoresist layer using two beam and four beam SP interference is illustrated in the Fig. 4.25 and Fig. 4.26 respectively. The obtained period and resolution of the features are same as those obtained with Ag metal, but the height of the features are slightly higher (200 nm for two beam SPIL and 180 nm for four beam SPIL). That means SPIL using Al metal gives better exposure depth and good intensity contrast at 364 nm wavelength, because SP resonance wavelength of Al locates at UV wavelength range.

A comparison between the three interference lithography techniques, namely conventional laser interference, evanescent wave interference and surface plasmon

interference are tabulated in the Table 4.2. And Table 4.3 gives the experimental details of these three techniques. From the Table 4.2, it is evident that near field interference lithography techniques such as EWIL and SPIL provides much higher resolution compared to conventional laser interference lithography. Also among other near field optical interference lithography approaches, SPIL provides long exposure depth and good intensity contrast, which can be used for the fabrication of high aspect ratio features. The periodic grating lines with higher aspect ratio of 2.2 and 1.14 are obtained with LIL and EWIL respectively. And four beam LIL and EWIL provide periodic dot array patterns with higher aspect ratio of 2.3 and 1.14, respectively. However, the obtained aspect ratio, by employing SPIL is 2.36 for two beam interference and 2.04 for four beam interference, which is almost same as that obtained with LIL. It shows that SPIL can also provide high aspect ratio features close to LIL by choosing suitable metal at particular wavelength.

Interference lithography	Two beam interference			Four beam interference			Theoretically estimated period (nm)
	Average period (nm)*	Average resolution (nm)*	Maximum height (nm)*	Average period (nm)*	Average resolution (nm)*	Maximum height (nm)*	
LIL (using p-polarization)	258.8	136.7	300	241.5	131	300	257
EWIL (using p-polarization)	185.5	88	100	170	88	100	182
SPIL (using Ag)	164	84.5	180	166	88	160	160
SPIL (using Al)	164	84.5	200	166	88	180	164

*The value shown in this table represents the average value of 15 data sets. A detailed analysis about this is given in Appendix G.

Table 4.2 Comparison chart for interference lithography techniques using 364 nm incident wavelength.

Interference lithography	Polarization	Resist thickness	Average power density	Exposure time	Development time
LIL	p-polarization	1 μm	334.35 mW/cm^2	400 ms	1 min
EWIL	p-polarization	~ 240 nm	334.35 mW/cm^2	300 ms	1 min
SPIL (Ag)	p-polarization	~ 240 nm	334.35 mW/cm^2	3 s	1 min
SPIL (Al)	p-polarization	~ 240 nm	334.35 mW/cm^2	25 s	2 min

Table 4.3 Experimental details.

It can be concluded that surface plasmon interference lithography could be an efficient, cost effective, maskless patterning technique for the fabrication of high resolution, good intensity contrast and high aspect ratio periodic features. The hexagonal periodic structures could be fabricated by using single exposure three beams interference lithography. Future investigations will be along this direction. Also, it is possible to further improve the exposure depth and large area patterning of periodic features by using the concept of long range surface plasmon (LRSP) interference. In this context, next section will be discussing about the large area periodic patterning based on long range surface plasmon interference, using a planar layer configuration.

4.3 Planar layer SP interference lithography

This section describes the periodic patterning based on the interference of long range surface plasmon modes. A planar layer configuration is proposed for this purpose to pattern large area periodic features with high exposure depth on the recording medium.

4.3.1 Theoretical analysis

Fig. 4.27 Planar layer SP interference configuration.

Fig. 4.28 Ray geometry of proposed planar layer configuration.

The proposed planar layer configuration for plasmonic lithography is shown in Fig. 4.27. This is a modification of the above mentioned prism based configuration. It is based on ATR principle, which consists of a high refractive index thin dielectric layer, is kept below the incident planar prism medium. A thin metal film is coated onto the bottom side and in contact with photoresist layer cover on a substrate. The high refractive index thin dielectric layer above the metal layer is used to satisfy the attenuated total reflection (ATR) principle for exciting surface plasmons and bulk prism medium is used to satisfy the momentum matching condition. It should be noted that this configuration supports the interference of long range surface plasmons, because this configuration is an asymmetric system, in which the thin metal layer is sandwiched between semi-infinite dielectric medium (thin dielectric layer and photoresist) and a high refractive index thin dielectric layer with finite thickness. Due

to the high refractive index of the thin dielectric layer, the index matching condition of the dielectric medium at the both sides of the metal film can be satisfied for supporting long range surface plasmon modes.

Let Z-direction as the propagation direction, the evanescent field can be expressed as $E = E_0 \exp[i(k_x x \pm k_z z - \omega t)]$, where wavevector k_z is imaginary, which is responsible for the exponential decay of the E_z field. The surface plasmon wavevector k_x lies parallel to the x direction and continues through the interface. The SP resonance angle can be calculated by applying ray geometry analysis in the Fig. 4.28,

By applying Snell's law at air/prism interface,

$$n_1 \sin \theta_1 = n_2 \sin \theta_2 \quad (4.39)$$

where n_1 and n_2 are refractive index of air and prism respectively. θ_1 is the incident angle at the prism surface and θ_2 refraction angle given by,

$$\theta_2 = \sin^{-1}\left(\frac{\sin \theta_1}{n_2}\right) \quad (4.40)$$

Then the corresponding incident angle at the prism/dielectric layer interface is calculated as α , given by $\alpha = 45 + \theta_2$ (4.41)

Snell's law at prism/dielectric layer interface

$$n_2 \sin \alpha = n_3 \sin \theta_p \quad (4.42)$$

where n_3 is the refractive index of dielectric layer.

The incident angle at the dielectric layer/metal interface or SP resonance angle is given

by,
$$\theta_p = \sin^{-1}\left(\frac{n_2 \sin \alpha}{n_3}\right) \quad (4.43)$$

$$\sin \theta_p = \frac{n_2}{n_3} [\sin(45 + \sin^{-1}(\frac{\sin \theta_1}{n_2}))] \quad (4.44)$$

Therefore SP resonant angle depends on refractive index of both prism and dielectric layer. Hence momentum matching condition is given by,

$$k_x = k_0 n_3 \sin \theta_p = k_{sp} \quad (4.45)$$

Substitute Eqn. (4.44) in (4.45), we get

$$k_x = k_0 n_2 [\sin(45 + \sin^{-1}(\frac{\sin \theta_1}{n_2}))] = k_{sp} \quad (4.46)$$

That is, k_x wavevector mainly depends on the refractive index of prism. It shows that the surface plasmon resonance condition can be controlled by varying only the refractive index of the prism.

4.3.2 Numerical analysis of planar layer configuration

The FDTD method is used to predict the light intensity distribution on the photoresist layer. The perfectly matched layer (PML) boundary condition has been used along the Z-axis, and periodic boundary condition has been used at the other axes. In the simulation, the refractive index of the prism, dielectric layer, and photoresist are 1.745 (NLK 8 glass), 1.94 (NLASF31A glass) and 1.53 (AZ9200 from AZ Electronic Material) respectively and the chosen wavelength of p-polarized light is 427 nm. The metal layer is silver, whose frequency-dependent dielectric constant is $-5.082+0.7232i$ at this wavelength [168].

Fig. 4.29 Reflectance vs. incident angle of dielectric layer coated with silver film.

To find the resonance angle, the minimum reflectance of light at the same wavelength to excite the surface plasmon waves, reflectance analysis is carried out as a function of the incidence angle. The thickness of dielectric layer is assumed to be 80 nm and that of silver film is taken as 20 nm. From Fig. 4.29, it is evident that the resonance angle is 59.5° and this angle is used as the incident angle for the surface plasmon interference.

Fig. 4.30 Electric field distribution of the interference pattern generated by the field components on the photoresist layer (a) E_x -field (log scale), (b) E_x -interference pattern, (c) E_z -field (log scale), and (d) E_z -interference pattern.

When two p-polarized plane wave incident on the configuration at the resonance angle, the electric field of E_z relative to E_x , has high relative strength. Figure 4.30 shows the field distributions of the interference pattern generated on the photoresist layer. Here the Z-axis is considered as the decay length and metal/photoresist interface is taken as the origin of the decay length. Fig. 4.30 (a) and Fig. 4.30 (c) respectively shows, the E_x and E_z components of long range surface plasmon interference with 80 nm thickness thin layer.

Figure 4.31 represents the normalized intensities of the electric field components, E_x and E_z as a function of the decay length from the origin. The normalized intensity, $|E|^2/|E_0|^2$ in the near field of the metal layer determines the exposure depth in the photoresist, where E_0 is the intensity of the incident beam. The normalized intensities of both electric field components decay exponentially from the origin and normalized intensity of E_z component is larger than that of E_x component. Therefore the total intensity is dominated by E_z component. The normalized intensities of E_x and E_z component calculated along $Z=50$ nm is 680 a.u and 3700 a.u, respectively. Both intensity component of the proposed configuration at this point is very high compared to Kretschmann configuration (Prism based configuration). Numerical simulation results show that the exposure depth larger than 400 nm is possible for this proposed scheme, which is found to be higher than Kretschmann configuration with the same conditions.

The intensity contrast is defined by $V = (I_{\max} - I_{\min}) / (I_{\max} + I_{\min})$, where $I_{\max} = E_z^2$ and $I_{\min} = E_x^2$. The variation of intensity contrast as a function of distance from the origin is shown in Fig. 4.32 and is compared with Kretschmann configuration. The contrast along the Z-direction is expected to be higher than the Kretschmann configuration.

Fig. 4.31 Normalized intensities of the electric field components as a function of the decay direction from the origin.

Fig. 4.32 Intensity contrast as a function of decay length from the origin.

The thickness of dielectric layer and metal film is also an important factor for the surface plasmon resonance. Hence the dependence of normalized intensity on thin dielectric and metal layer thickness is also investigated separately by keeping one of them constant. Fig. 4.33 (a) illustrates the variation of normalized intensities with various dielectric layer thicknesses along $Z=50$ nm when metal thickness is kept constant as 20 nm. It is evident from the figure that there is an optimum value of dielectric thickness equal to 80 nm at which maximum intensity is obtained. Fig. 4.33 (b) shows the variation of normalized intensities as a function of metal thickness along $Z=50$ nm when dielectric layer thickness is 80 nm. The metal layer thickness is varied

from 10 nm to 50 nm and maximum intensity is obtained when thickness is 20 nm. It is also evident from Fig. 4.33 that there is a large intensity variation when dielectric layer thickness is varied from 70 nm to 90 nm and metal layer thickness is varied from 15 nm to 25 nm. Therefore by using 80 nm dielectric layer thickness and 20 nm metal film thickness, it is possible to achieve the maximum intensity for this configuration.

Fig. 4.33 Normalized intensities of the electric field components calculated at $Z=50$ nm as a function of (a) dielectric layer thickness (b) metal layer thickness.

4.3.3 Resist dissolution process

To compute the positional development rates of the photoresist domain in response to the normalized intensity profile, a value of $1\text{mW}/\text{cm}^2$ for unit normalized intensity is adopted. The development process is then simulated, employing the modified CA method, to obtain the subsequent post-development resist profile. During the development process, the developing reagent dissolves the exposed photoresist in an isotropic manner. Various forms of cellular automata (CA) numerical technique have been reported for simulating photoresist development process in both two dimensional and three dimensional spatial domain, showing good agreement between the simulated and experimental results [169]. In addition to the proven level of accuracy, the CA technique is straightforward in implementation it allows user to employ regular and uniform spatial and temporal discretization in modeling the physical system.

Fig.4.34 Two-dimensional resist profile cross section at exposure times: (a) =50 s, (b) =70 s, (c) =100 s, (d) =150 s.

In this work, a modified three dimensional CA algorithm is used that follows closely, to the one proposed by Karafyllidis [170]. The exposed photoresist domain is divided into identical cubic CA cells, each with edge length ‘a’. Unlike previous works, the algorithm implemented in this work considers all the neighbouring cells in the computation sub-domain when solving for the local state of the concerned cell. The CA model simulates the isotropic nature of the resist etching mechanism during the resist development process. Theoretical analysis of CA model is presented in Appendix-E.

Fig. 4.35 Simulated 3D cross sectional resist profile at exposure times: (a) =100 s, (b) =150 s.

Fig. 4.34 shows the two dimensional resist profiles and Fig. 4.35 represents the three dimensional resist profiles of obtained interference pattern on the photoresist layer by using the proposed planar layer configuration at different exposure times. The zero value along the vertical axis corresponds to the metal/photoresist interface. The obtained results show that with increase in exposure time, the line width of the pattern decreases and exposure depth increases. Further, it correlates well with the results obtained through FDTD simulations.

4.3.4 Effect of metals on UV excited plasmonic lithography

This section describes and compares the effect of metal films, such as aluminum (Al) and silver (Ag) on UV excited two beam surface plasmon interference nanolithography. The proposed planar layer configuration has been employed to study the light intensity distribution on the recording medium.

4.3.4.1 Numerical investigation

Finite Difference Time Domain methods with perfectly matched boundary condition is employed along Z-axis, perpendicular to the propagation direction of the light and periodic boundary condition has been used in the other axis to simulate the field distribution on the photoresist layer. In the simulation, the refractive index of dielectric layer and photoresist are 1.939 (NLASF31 glass) and 1.7 (AZ7220) respectively. The refractive index of upper prism medium is assumed to be 1.865 (NLAF36 glass) and wavelength of p-polarized light is taken as 364 nm. The behavior of surface plasmon interference patterns on the photoresist layer by coating aluminum (Al) and silver (Ag) metal films are separately analyzed. The complex

dielectric constants of aluminum and silver at this wavelength are $-19.42+3.606i$ and $-2.5575+0.5989i$ respectively [168]. The thickness of the dielectric layer and metal film is assumed to be 50 nm and 20 nm respectively. The incident angle at prism surface is assumed to be 45° and corresponding surface plasmon resonance angle at dielectric layer/metal interface is 62° .

Fig. 4.36 Electric field distribution of the interference pattern generated on the photoresist layer of planar layer configuration with Al and Ag as metal medium (a) Al- E_x , (b) Al- E_z , (c) Ag- E_x , (d) Ag- E_z .

Figure 4.36 shows the electric field distributions of the interference pattern generated on the photoresist layer at the incident wavelength of 364 nm. Figures 4.36 (a) and 4.36 (b) shows the field distribution of E_x and E_z component respectively for Al film and figures 4.36(c) and 4.36(d) respectively represents generated E_x and E_z component for Ag film. In the figures, Z-axis is considered as the decay direction and metal/photoresist interface is taken as the origin of the decay direction. From the Fig. 4.36, it is evident that high electric field distribution throughout the photoresist layer is achieved for Al film compared to Ag film at the same condition. The reason could be that resonant surface plasmon wavelength of Al locates at the UV wavelength range while that of Ag locate in visible wavelength range. Also, the surface plasmon propagation length of Al is longer than that of Ag at UV excitation. The simulation results show that the obtained periodicity and line width on the photoresist layer is approximately 100 nm and 50 nm respectively. Furthermore, the intensity transmission calculated at metal/photoresist interface is 46% for Ag metal film compared to that of 100% for Al metal film. The exposure depth higher than 250 nm is possible when Al metal film is used, whereas Ag metal film can give approximately 200 nm.

Fig. 4.37 Intensity contrast as a function of decay direction from the origin.

The variation of intensity contrast as a function of distance from the origin is shown in Fig. 4.37. It is observed that the contrast is constant throughout the Z-direction for both metals and it is also clear that Al film gives better contrast than Ag film at this wavelength. Therefore long exposure depth and good intensity contrast is possible by using Al film as the metal layer at 364 nm wavelength compared to Ag film. The

thickness of the metal film also effects the intensity distribution on the photoresist layer. Figure 4.38 shows the variation of normalized intensities as a function of metal thickness along $Z=5$ nm when dielectric layer thickness is 50 nm. Both metal film thicknesses are varied from 5 nm to 40 nm and maximum intensity is obtained for 20 nm thickness.

Fig. 4.38 Normalized intensity variation with metal film thickness.

4.3.4.2 Experimental investigation

An experimental investigation is carried out for planar layer configuration by employing Ag and Al metal film, using the conventional set up mentioned in the section 3.1.2. A test sample of dimension 20 mm X 20 mm is designed for SP interference lithography at 364 nm wavelength in which the upper layer is a square prism of refractive index 1.856; a metal film (Ag and Al) coated high refractive index (1.939) dielectric layer is placed at the bottom surface of the prism with index matching liquid. And they are brought into intimate optical contact with a thin photoresist (AZ7220) layer on a silica substrate. The thickness of coated metal film is 50 nm and photoresist thickness is around 100 nm.

Two counter propagating first order beams of 2D diffraction grating was made to incident on the sample placed in a sample holder. The polarization of the incident light beam was set to p-polarization and the incident angle of the two beams at the prism side is set at 45° . The theoretically estimated SP resonance angle at dielectric layer/ metal interface is 62° . The p-polarized incident beams at the prism surface has a

targeted power density of 334.35mW/cm^2 and the sample was interrogated with exposure duration of 5s (for Ag) and 15s (for Al). The atomic force microscopy (AFM) images of exposed patterns transferred on the photoresist layer using two beam SP interference lithography is shown in Fig.4.39. The nanoscale grating lines with minimum line width of 70 nm and 78 nm are obtained for Ag and Al metals respectively, which is different from the simulated value of 50 nm. The discrepancy between simulated and experimentally obtained resolution is presumably attributed to the inherent calibration error of AFM device or to the sample drift occurred while doing AFM measurements. The obtained resolution through numerical simulation and experiment is almost same for both metals, but there could be some difference in exposure depth and intensity contrast as obtained in numerical simulations. However, this problem could not be investigated clearly as thin photoresist layer was used.

Along with these grating lines, we could also obtain nanoscale pillars simultaneously as shown in Fig. 4.39. The observation of simultaneous nanopillar patterning can be attributed presumably to the formation of hyperbolic or diverging phase fronts occurring at the interfaces [171]. The multiple interference of back reflected beams generated at prism/dielectric layer interface may also be one of the reasons for the simultaneous patterning of gratings and pillars. In future we will be investigating these issues.

Fig. 4.39 AFM images of exposure pattern transferred on the photoresist film (a) using Ag film and (b) using Al film.

Four beam SP interference lithography, using planar layer configuration is also carried out to pattern two dimensional features. Four first order beams of 2D diffraction grating were used for this purpose to generate interference of multiple counter

propagating surface plasmon waves as a lithographic technique to print periodic two dimensional features. Figure 4.40 represents obtained AFM images of exposure pattern transferred on the photoresist layer using four beam SP interference lithography. It is found that large exposed area is possible for this configuration compared to Kretschmann configuration. It means that the beam at the metal/photoresist interface is highly divergent and planar layer configuration supports the propagation of long range surface plasmons. Therefore there is a high chance for SP interference to pattern large area nanoscale features. The non-uniformity of the exposed patterns can presumably be attributed to the intensity fluctuation from laser or depends on the development time. The advantage of this configuration is that it can provide large area low cost plasmonic lithographic technique without using any complex mask fabrication techniques.

Fig. 4.40 AFM image of periodic dot array pattern.

4.4 Summary

Different concepts of plasmonic lithography techniques based on surface plasmon interference on a thin metal film are investigated and analyzed. A multiple beam (two and four) surface plasmon (SP) interference generation based on prism coupling technique is theoretically analyzed. The configuration is then numerically and experimentally analyzed by employing aluminum and silver metal at 364 nm illumination wavelength to realize high resolution and good aspect ratio one- and two-dimensional periodic nanoscale features on the recording medium. Also, a comparative analysis between three interference lithography techniques such as

conventional laser interference, evanescent wave interference, and surface plasmon interference is presented. It is experimentally shown that among near field interference lithography, SPIL provide long exposure depth and good intensity contrast as compared to evanescent wave interference lithography. Further, SPIL can provide low-cost plasmonic lithographic fabrication doing away with complex mask fabrication techniques that are associated with the conventional approaches.

A planar layer concept for surface plasmon interference lithography for fabricating large area periodic features beyond the diffraction limit is proposed. High electric field distribution compared to conventional prism based configuration is found to be achievable with this and hence facilitate high contrast and high resolution features with good exposure depth. The simulation results indicate that, the feature size approximately at 60 nm is achievable by using silver metal layer and a p-polarized 427 nm wavelength illumination. Simulated resist profiles, using cellular automata model, obtained through this proposed concept is also presented. The effect of metal films, such as aluminum and silver on UV excited two beam surface plasmon interference nanolithography is investigated using planar layer configuration. The grating lines with 100 nm periodicity and 50 nm linewidth have been demonstrated numerically at 364 nm illumination wavelength. It is also found that the obtained periodic feature shows good exposure depth and high intensity contrast when Al is used as the metal film. The experimental results of proposed planar layer configuration using both metals are also presented. The advantages of this concept and methodology are the good mechanical control and strong enhanced field to give shorter wavelengths of surface plasmons. The observed variations in the size and height of the periodic features can presumably be attributed to AFM artifacts such as tip-sample convolution, sample drift. A detailed account on these different types of AFM artifacts that can affect the image quality is given in Appendix-F.

Localized surface plasmons associated with a metal nanoparticle can be used for further improving the resolution and exposure depth of the periodic nanoscale features. In this context, the following chapter focus on the localized surface plasmon assisted periodic nanopatterning.

Chapter 5

Periodic nanopatterning by localized surface plasmons

In this chapter, localized surface plasmons associated with a metal nanoparticle is investigated for periodic nanopatterning. Initially, periodic nanoparticle array based plasmonic lithography configuration has been demonstrated. A near field optical excitation of gap modes in a metal particle-surface system for patterning one- and two- dimensional periodic nanostructure is proposed and numerically demonstrated. The existence of gap modes in metal particle-surface based plasmonic lithography configuration is investigated for improving the resolution and exposure depth. 2D and 3D resist profile cross section using modified cellular automata model, obtained through this proposed configurations are also presented.

5.1 Metal nanoparticle array for plasmonic lithography

A periodic metal nanoparticle array assisted plasmonic lithography technique is proposed and discussed in this section. This is realized by employing a closely spaced periodic metal nanoparticle array. The basic principle of the concept is the electromagnetic energy (local plasmon mode) transfer via periodic array of metal nanoparticles. That means an array of metal nanoparticle act as a waveguide for surface plasmon propagation.

5.1.1 Localized surface plasmons

The collective oscillations of the conduction electrons in a metal nanoparticle is known as localized surface plasmon (LSP), whose resonance frequency is the plasma frequency determined by the shape and size of the metal nanoparticle [172]. It can find in engineered nanostructures as well as the aggregates of nanoparticles.

Figure 5.1 represents a silver nanoparticle of size 20 nm. When the nanoparticle is exposed with an external electric field, the field can penetrate into the volume of the nanoparticle and shift the oscillating conduction electrons with respect to the particles metal- ion lattice. A restoring local field can be produced within the particle (as shown in Fig.5.1) due to the resulting surface charges of opposite sign at the opposite

surface elements of the particles. This local field rises with increasing shift of the electron gas relative to the ion background and consequently represents an oscillator. The behavior of oscillator is defined by the electron's effective mass and charge, the electron density and geometry of the particles. Both linear and nonlinear optical responses of nanoparticles are significantly enhanced when the local fields are concentrated on the spot.

Fig. 5.1 Schematic of a metal nanoparticle (a) exposed to an electric field, (b) and (c) the electrons are shifted with respect to the ion-lattice [172].

Based on the point dipole approximation theory, the absorption and scattering cross sections of a nanoparticle is written as [172],

$$C_{abs} = \frac{2\pi}{\lambda} \text{Im}[\alpha] \quad (5.1)$$

$$C_{sca} = \frac{1}{6\pi} \left(\frac{2\pi}{\lambda} \right)^4 |\alpha|^2 \quad (5.2)$$

With polarizability of the nanoparticle,

$$\alpha = (4\pi)^{-1} \frac{(\epsilon_m - \epsilon_d)}{(\epsilon_d + p(\epsilon_m - \epsilon_d))} \quad (5.3)$$

Where p is the depolarization factor, and ϵ_m and ϵ_d are dielectric function of metal and surrounding medium. The scattering efficiency of the nanoparticle is given by,

$$Q_{sca} = \frac{C_{sca}}{(C_{sca} + C_{abs})} \quad (5.4)$$

Near the surface plasmon resonance, the polarizability of the nanoparticle becomes

very high. At this condition the incident light may interact with the nanoparticle over a wide cross sectional area, which is larger than the geometric cross sectional area of the particle. Light scattering and absorption from a nanoparticle depends on the size and shape of the particle. When the metallic nanoparticle size is much smaller than the wavelength of the light, absorption in the nanoparticle is more compared to scattering. This property of metallic nanoparticle can be utilized for the transferring of electromagnetic energy below the diffraction limit and hence utilized for nanoscale lithography.

5.1.2 Electromagnetic energy transfer via periodic metal nanoparticle array

As mentioned in the previous section, at the plasmon resonance condition the metal nanoparticles show strong light absorption. That means nanoparticle is an efficient converter of light to local plasmon mode, which is the requirement of a waveguiding structure for efficient coupling of light energy. The theoretical and experimental demonstration of this concept is already reported by many authors [173, 174]. The numerical simulation of localized surface plasmon mode transport via periodic chain of metal nanoparticle is carried out using FDTD method. A finite periodic array of identical silver nanospheres with constant nanoparticle spacing is considered as a waveguiding structure and surrounding medium is assumed to be SiO_2 . The light field is assumed to be irradiated on the first nanosphere in the periodic array only. But all other nanospheres get field distribution by coupling their local plasmon oscillation energy.

In the simulation, a periodic array of Ag nanosphere with diameter 20 nm and constant spacing (period) of 20 nm, 70 nm, 120 nm, and 220 nm are used. The wavelength of the irradiation light is assumed to be 436 nm, which is the particle resonance wavelength of Ag nanosphere with size 20 nm. The spatial field distribution of calculated intensity from the beginning of nanosphere chain with different nanosphere spacing is shown in Fig. 5.2. It is evident from the figure that at smaller period, strong electromagnetic energy transport is possible. That is, when the particles are very close to each other that their enhanced local fields overlap, and are strongly squeezed between the particles. However, when the particle period increases the

electromagnetic energy transport decreases and additional to that, fringes (scattered field) further away from the particle can be seen. This is due to the interference of exciting evanescent field with the grating orders of linear chain scattered parallel to the SiO_2 substrate [175].

It is also evident from the simulation results that when the nanoparticles in the periodic array are close to each other that absorb more light and scattered field can become negligible. In short, the efficient coupling of local plasmon mode and hence electromagnetic energy transport is possible by using a periodic array of metal nanoparticle with smaller period as a waveguiding structure.

Fig. 5.2 Simulation results of electromagnetic energy transfer via periodic array of Ag nanoparticles with different nanoparticle spacing (a) 20 nm, (b) 70 nm, (c) 120 nm and (d) 220 nm.

5.1.3 Metal nanoparticle array based plasmonic lithography

Above mentioned concept and methodology can be utilized in nanoscale patterning beyond the diffraction limit. In this context, Fig. 5.3 shows the schematic diagram of the proposed plasmonic lithography configuration based on periodic nanosphere array. It consists of a high refractive index prism in contact with periodic monolayer of either Ag metal or Al metal nanospheres. They are brought into intimate contact with a photoresist on a silica substrate. For a spherical particle, the surface plasmon resonance occurs at the wavelength λ for which $\varepsilon_{particle}(\lambda) = -2\varepsilon_{medium}(\lambda)$ with $\varepsilon_{particle}$ and ε_{medium} , the real part of the dielectric functions of the metal particle and the surrounding medium respectively. The optical near field of metal nanoparticle arrays mainly depends on the particle periodicity and size. In this configuration, the nanoparticle size and period is chosen that can subdue the scattering effects and absorb maximum incident light to transport the local plasmon mode. When two counter propagating beams incident on the configuration at resonance angle, the local plasmon mode could propagate along the positive and negative direction of X-axis and superposition of these two coupled waves generate the interference patterns on the photoresist medium.

Fig. 5.3 Schematic diagram of proposed plasmonic lithography configuration.

5.1.4 Numerical simulation results

The numerical analysis is performed based on finite difference time domain method. The perfectly matched layer boundary condition has been used in the boundaries perpendicular to the propagation direction of the light and Bloch boundary condition

has been used in the other boundary. In the simulation, the refractive index of the prism and photoresist layer are 1.745 and 1.7 respectively. The behavior of intensity distribution on the photoresist layer is analyzed by using array of silver (Ag) and aluminum (Al) nanoparticles separately.

As a first case, the numerical calculation is performed based on a periodic array of mono-layer Ag nanospheres, which is placed in between prism and lower photoresist layer. The diameter and periodicity of Ag nanospheres are assumed to be 20 nm each. The resonant wavelength of p-polarized light is taken as 451 nm and incident resonance angle is 60° (The reason behind will be explained by figures 5.4 (a) and 5.4 (c) as given below). Similar analysis is repeated by replacing Ag nanospheres with Al nanospheres of same diameter and periodicity. In this case, the incident resonant wavelength and resonant angle are kept 413 nm and 56° respectively (The reason behind will be explained by figures 5.4 (b) and 5.4 (d) as given below). The complex dielectric constants of silver and aluminum at their resonant wavelength are $-6.06+0.197i$ and $-24.97+5.26i$ respectively [168].

Figure 5.4 shows the variation of normalized intensities with incident wavelengths and incident angles for both Ag and Al nanosphere array. Figure 5.4 (a) represents the normalized intensity measured along the metal nanoparticle array/photoresist interface as a function of incident wavelength for Ag nanosphere array, where incident angle is assumed to be 60° . It is evident from the Fig. 5.4 (a) that the maximum intensity is obtained when incident resonance wavelength is 451 nm and for Al nanosphere array, Fig. 5.4 (b) shows that the incident angle is 56° . It is also evident from the Fig. 5.4 (b) that the maximum intensity is possible when incident resonance wavelength is 413 nm. Figures 5.4 (c) and 5.4 (d) respectively illustrates the variation of normalized intensities for both Ag and Al nanosphere array with various incident angles measured along the metal nanoparticle array/photoresist interface. In the case of Ag nanosphere array, normalized intensity is maximum when the incident resonance angle is 60° , where incident wavelength is assumed to be 451 nm and for Al nanosphere array, maximum normalized intensity is obtained when the incident resonance angle is 56° , where incident wavelength is assumed to be 413 nm.

(a)

(b)

(c)

(d)

Fig. 5.4 Normalized intensity (I) variation as a function of incident wavelength (λ) and incident angle (θ) measured along the metal nanoparticle array/photoresist interface (a) I vs λ for Ag nanosphere array, (b) I vs λ for Al nanosphere array, (c) I vs θ for Ag nanosphere array and (d) I vs θ for Al nanosphere array.

The electric field distributions of the interference pattern generated on the photoresist layer is illustrated in Fig. 5.5. Figure 5.5 (a) shows the field distribution of component for Ag nanospheres and Fig. 5.5 (b) represents corresponding component for Al nanosphere. And Fig. 5.6 (a) and 5.6 (b) represents the normalized intensity variation with decay direction from the origin of Ag nanosphere array and Al nanosphere array, respectively. In the Fig. 5.5 and 5.6, Z-axis is considered as the decay direction and nanoparticle array/photoresist interface is considered as the origin

of the decay direction. The normalized intensity is highest at the metal nanoparticle array/photoresist interface and it decay exponentially from the origin. The simulation results show that SP interference with the Ag nanosphere array results in higher intensity at the metal nanoparticle array/photoresist interface as well as through the depth of the photoresist medium as compared to Al nanosphere array. Furthermore, the intensity transmission calculated at metal nanoparticle array/photoresist interface is 10% for Al nanosphere array to that of Ag nanospheres array. It is also observed that exposure depth higher than 350 nm is possible by using Ag nanoparticle array, whereas Al nanoparticle array can gives approximately 300 nm. The simulation results show that the obtained period of intensity distribution on the photoresist layer is approximately 120 nm.

Fig. 5.5 Electric field distribution on the photoresist layer generated by the field components (a) E_z -Ag, and (b) E_z -Al.

Figure 5.7 shows the variation of intensity contrast as a function of decay direction from the origin. It is observed that the contrast is constant throughout the Z-direction for both configurations though array scheme with Al nanoparticles gives better contrast compared to the array scheme with Ag nanoparticles. A modified cellular automata (CA) model has been used to analyze the development of resist dissolution process. Figure 5.8 shows the 2D resist profile cross-section of obtained interference pattern on the photoresist layer by using the proposed schemes at exposure time of 100 s. Fig. 5.8 (a) shows resist profile cross section obtained by using Ag nanosphere array and Fig. 5.8 (b) corresponding pattern obtained by using Al nanosphere array.

The zero value along the vertical axis corresponds to the metal nanoparticle array/photoresist interface. The obtained result shows that Ag nanosphere array provide high exposure depth compared to Al nanosphere array at same exposure duration. The obtained linewidth and exposure depth at 100 s exposure time are 40 nm and 160 nm for Ag nanospheres, and 40 nm and 130 nm for Al nanospheres.

Fig. 5.6 Normalized intensity variation with decay direction (a) for Ag nanospheres, (b) for Al nanospheres.

Fig. 5.7 Intensity contrast variation as a function of decay direction from the origin.

Fig. 5.8 2D resist profile cross section at exposure time 100 s: (a) for Ag nanospheres (linewidth ~ 40 nm, exp. depth=160nm) (b) for Al nanosphere (linewidth ~ 40 nm, exp. depth=130nm).

Fig. 5.9 2D interference pattern generated on the photoresist layer by irradiating four counter propagating beams, (a) for Ag nanospheres and (b) for Al nanospheres.

The proposed configuration is also numerically investigated (using FDTD) for 2D nanoscale patterning by employing four counter propagating incident beams. In this case, four counter propagating beams with same wavelength are irradiated on the configuration at the resonant angle. The coupled local plasmon modes propagate along the positive and negative direction of both X- and Y-axis. The superposition of these four plasmon waves generates the corresponding 2D interference patterns on the

recording medium. Fig. 5.9 (a) and Fig. 5.9 (b) respectively represent the 2D interference pattern generated on the photoresist by employing Ag and Al nanospheres. Here also Ag nanosphere array provide high electric field distribution as compared to Al nanosphere array.

5.2 Gap modes assisted plasmonic lithography concept

In this section, the focus will be on a new plasmonic lithography concept for high resolution nanolithography based on the excitation of gap modes in a metal particle-surface system. The principle, the excitation of gap modes in a metal particle-surface system and excitation of surface plasmon polaritons mediated by gap modes are illustrated and analyzed theoretically from a lithography point of view.

5.2.1 Gap modes in a metal-particle surface system

At the nanoscale, mainly electric oscillations at optical frequency contribute the optical fields, but the magnetic field component does not contribute significantly due to weak field component. The existences of localized optical modes on dimensions much smaller than the optical wavelength are responsible for such fields to concentrate and support the nanostructured materials. These energy concentrating modes are called surface plasmons (SPs) and it is well known that a system should contain both negative and positive dielectric permittivities to support surface plasmons. The shape of the metal nanoparticle and metal surface thickness is an important factor for the surface plasmon resonance. A thin metal surface is associated with surface plasmon polariton (SPP) modes, which are coupled modes of photons and plasmons. Since the SPP modes are nonradiative electromagnetic modes, to excite them the incoming beam has to match its momentum to that of the plasmons. It is possible by passing the incident photons through a bulk dielectric layer to increase the wavevector component and achieve the resonance at the given wavelength. But a fine metal particle is associated with localized surface plasmon (LSP) modes, which are collective oscillations of the conduction electrons in a metal nanoparticle. The LSP modes can be excited directly by incident photons since they are radiative electromagnetic modes.

Fig. 5.10 schematic of metal particle-surface system.

When a system consisting of a fine metal particle placed near to a metal surface, an electromagnetic interaction between LSP modes associated with metal nanoparticle and SPP modes associated with metal surface is possible. This interaction plays an important role to enhance the light emission from metal-insulator-metal tunnel junction, mediated by metal nanoparticles [176-178]. Due to this electromagnetic interaction there exist new types of localized electromagnetic normal modes, called gap modes in the space between the nanoparticles and the surface [179, 180]. Figure 5.10 represents an isolated metal sphere (Al) of dielectric function $\varepsilon(\omega)$ embedded in a surrounding medium (SiO_2) of dielectric function ε_m , that is placed close to a metal surface (Ag). The retardation effects of electromagnetic fields can be neglected when the radius (R) of the sphere is small and resonant frequencies corresponding to the excitation of LSP are expressed as [181],

$$\varepsilon(\omega) = -\varepsilon_m(l+1)/l \quad (5.5)$$

Where $l = 1, 2, \dots$ is an integer. If the sphere is much smaller than the wavelength of the incident light, the dipole mode with $l = 1$ is mainly excited.

Theoretically, this concept can be explained by approximating the LSP modes as a dipole and considering its interaction with image dipole induced inside the metal surface. This dipole-dipole interaction may greatly modify the LSP mode and hence the resonance frequency and field distribution. In other way, new electromagnetic modes are expected to appear by change in symmetry of the system. It means the spherical symmetry of the isolated sphere translate to cylindrical symmetry for a sphere-surface system. These modes also correspond to polarization modes parallel and perpendicular to the symmetry axis. When the particle-surface distance is

sufficiently small ($D/R < 1$), this system can support a series of gap modes and the electric field becomes more and more localized at the gap between the particle and the surface. When the gap mode is excited, the intensity of the electric field is enhanced relative to that of the excitation field and these modes are believed to play an important role in the light emission process. It is reported that the maximum enhancement factor is larger than that achieved with an isolated particle (LSP excitation) or a surface alone (SPP excitation) system [182].

In the case of metal sphere-surface system, the translation invariance is broken, and the surface plasmon modes become localized under the particle. These modes are localized over a distance set by the geometric mean of the sphere radius (R) and the particle-surface distance (D). Hence the wavevector of the gap mode is given by,

$$k_g = (DR)^{-1/2} \quad (5.6)$$

The corresponding frequency of the gap mode is given by,

$$\omega_g = \varpi_p \left(\frac{D}{R} \right)^{1/4} (\varepsilon_0)^{-1/2} \quad (5.7)$$

where ϖ_p the average plasma frequency of the two metals and ε_0 is the dielectric constant of the surrounding medium.

The metal particle-surface system supposed to find variety of potential applications in near field optics, although the roles played by the gap modes have not yet been fully explored. One of the promising applications in scanning tunneling microscope (STM) in which the tunneling current are excited by gap modes [183]. In STM, SPP modes in a metallic surface are excited by ATR method. To obtain images with high lateral resolution, the intensity of the reflected and scattered light can be enhanced by placing a sharpened metallic tip very close to a surface. Theoretical treatments of this problem is already reported, in which tip is often modulated by a sphere [184]. The direct evidence of the existence of gap modes is experimentally demonstrated by Hayashi's group [182]. The authors performed a systematic absorption measurement on Ag island particles placed above an Al surface and realized strong localization and strong enhancement of electromagnetic field under the conditions of resonant excitation of gap modes.

FDTD simulation results of a metal particle-surface system (Fig. 5.10) are shown in Fig. 5.11. The local field (LSP) around an Al nanoparticle at 427 nm incident wavelength is shown in Fig. 5.11. Figure 5.11 (a) represents the field in the absence of Ag surface and Fig. 5.11 (b-d) shows the enhanced local field in the presence of Ag surface at various particle-surface distances. It is visible from the figure that field distributions (gap modes) are generated in the space between nanoparticle-surface when Ag surface is placed at the distances (b) $D=3$ nm, (c) $D=5$ nm and (d) $D=10$ nm. That is, a particle-surface system supports series of gap modes when the particle-surface distance is sufficiently small ($D/R < 1$). The basic idea is that by exciting the gap modes in the space between nanoparticle and surface, enhanced local field around the Al nanoparticle is possible. In other way the enhanced intensity is possible by modifying the LSP modes around the nanoparticle.

Fig. 5.11 Numerical demonstration of gap modes: Electric field distribution around an Al nanoparticle (a) absence of Ag-surface, (b-d) presence of Ag-surface: (b) $D/R=0.3$, (c) $D/R=0.5$, and (d) $D/R=1$.

The field localization and enhancement can be expected even when the metal sphere and/or the metal substrate are replaced by a dielectric sphere and/or a dielectric substrate. But the degree of localization and enhancement is smaller than that for a metal sphere–metal surface system.

The main features of gap modes are as follows [182],

1. When the particle-surface distance is sufficiently small ($D/R < 1$), the configuration can support a series of gap modes.
2. The resonant frequencies of the gap modes shift to lower frequencies as the particle–surface distance decreases
3. The electric field becomes more and more localized at the gap between the particle and the surface, when D is very small.
4. Strong localization and strong enhancement of electromagnetic field are possible, at the resonant excitation of the gap modes
5. When the gap mode is excited, the intensity of the electric field is enhanced relative to that of the excitation field and maximum enhancement factor is larger than that achieved with an isolated particle (LSP excitation) or a surface alone (SPP excitation).
6. The enhancement factor is larger for an excitation field perpendicular to the surface than for an excitation field parallel to the surface.

5.2.2 Gap modes excited plasmonic lithography configuration

Schematic diagram in Fig. 5.12 represents the plasmonic lithography configuration based on the excitation of gap modes in metal particle-surface system. It consists of a high refractive index thin dielectric layer kept below the incident prism medium, which is in contact with periodic Al metal nanospheres. Period of Al nanosphere array is taken as 24 nm. These Al nanospheres are embedded in a lower refractive index surrounding medium (SiO₂). A thin Ag metal film is coated at distance D from the Al nanospheres in the surrounding medium and kept in contact with photoresist layer on a silica substrate. The diameter of Al nanospheres is taken as 20 nm and thickness of Ag film is 10 nm.

Fig. 5.12. Schematic diagram of gap modes excited plasmonic lithography configuration.

The basic idea of the technique is that the excited gap modes above the metal surface can greatly enhance the surface plasmons on the metal surface and superposition of two excited SP modes generates the interference patterns on the photoresist layer. Furthermore, the modes responsible for the field distribution could be weakly coupled gap modes of single particle-film systems. By applying the appropriate boundary condition at the metal surface/photoresist interface, the dispersion relation for surface plasmon polariton is described as,

$$k_{SP} = \frac{\omega_g}{c} \sqrt{\frac{\epsilon_m \epsilon_d}{\epsilon_m + \epsilon_d}} \quad (5.8)$$

where ω_g is the gap mode excitation frequency, c is the speed of light in vacuum, ϵ_m is the complex dielectric constants of metal surface and ϵ_d is the dielectric constants of photoresist layer. Here, the excitation frequency of gap mode is always greater than that of the excitation frequency of illumination light. Hence we can achieve much higher resolution compared to other existing plasmonic lithography techniques. The wavevector of surface plasmon wave becomes significantly larger than that of the incident light wavevector, when the real parts of ϵ_m approaches $-\epsilon_d$. At this condition, the wavelength of the excited SPs get normally shorter compared to the wavelength of gap modes.

5.2.3 Electric field distribution

The finite difference time domain method is used to predict the light intensity distribution on the photoresist layer. The simulation region is terminated with perfectly matched layer (PML) boundary condition on the boundaries perpendicular to the propagation direction of the light and Bloch boundary condition on the other boundaries. The refractive index of the upper prism, dielectric layer and photoresist layer are 1.745 (NLK8 glass), 1.939 (NLAF31A glass) and 1.53(AZ9200 from AZ Electronic Material) respectively. The dielectric layer thickness is assumed to be 90 nm. The wavelength of p-polarized light is taken as 427 nm (as shown in Fig. 5.13) and incident resonant angle is 56° at this wavelength. The complex dielectric constants of aluminum and silver at this wavelength are $-26.728+5.8i$ and $-5.082+0.7232i$ respectively [168].

Fig. 5.13 Variation of normalized intensity with incident wavelength.

The normalized intensities measured along the metal surface/photoresist interface as a function of incident wavelength is shown in Fig. 5.13, where incident angle is assumed to be 56° . It is evident from the figure that the intensity distribution is possible for a band of wavelength and maximum intensity is obtained when the incident resonance wavelength is 427 nm. It is also evident that there is a large intensity variation when the incident wavelength varies from 413 nm to 442 nm. It could be due to large gap mode excitation at that wavelength range and peak at 427 nm. When two p-polarized 427 nm illumination light beam incident at the dielectric layer/nanosphere interface, the field intensity distribution developed on the photoresist surface is shown in Fig.5.14. Figures 5.14 (a) and 5.14 (b) respectively shows the field distribution of

and components, when particle-surface distance $D=0$ nm. And Figures 5.14 (c) and 5.14 (d) respectively represents that of conventional prism based configuration in which high refractive index prism with an Ag metal film coated onto the bottom side and in contact with photoresist layer on a silica substrate. Here the thickness of the Ag film is taken as 20 nm and remaining parameters are same as the proposed configuration. It should be noted that Ag film thickness of 10 nm for proposed configuration and 20 nm for the prism layer configurations are the required respective Ag film thickness for obtaining maximum intensity.

Fig. 5.14. Electric field distribution of the interference pattern generated by the field components on the photoresist layer (a) E_x (b) E_z of proposed configuration and (c) E_x (d) E_z of prism based configuration.

Figure 5.15 represents the normalized intensity variation, $(|E|^2/|E_0|^2)$ (where E_0^2 is the incident intensity) with decay direction. Here Z-axis is considered as the decay direction. The exposure fields E_z and E_x represents the longitudinal and transverse components respectively. The E_z component is much stronger than the E_x component and these components have $\pi/2$ phase difference in both configurations. The electric field distribution show that interference patterns with approximate periodicity of 120 nm is formed at the interface for both configurations. From the Fig. 5.14 and Fig. 5.15, it is evident that the proposed configuration gives high electric field distribution compared to conventional prism based configuration. The intensity transmission calculated at metal surface/photoresist interface is 4% for conventional prism based configuration to that of the proposed configuration. Therefore the maximum enhancement factor is much larger for this configuration compared to that achieved with conventional prism based configuration. From Fig 5.15, it is clear that the exposure depth above 350 nm is achieved for the proposed scheme, but prism based configuration gives around 250 nm. The fringe visibility or contrast can be expressed as $V = (I_{\max} - I_{\min}) / (I_{\max} + I_{\min})$, where $I_{\max} = E_z^2$ and $I_{\min} = E_x^2$. The intensity contrast calculated is around 0.90 for both configurations within the exposure depth of 200 nm, which is sufficiently high for the realization of interference patterns and much higher than the exposure threshold of common negative optical resists.

Fig. 5.15. Normalized intensity variation with decay direction.

The metal particle-surface distance (D) is an important factor for the gap mode excitation. Therefore the variation of normalized intensities with D needs to be analyzed. Figure 5.16 shows the variation of normalized intensities of E_x and E_z component calculated along the metal surface/photoresist interface as a function of metal particle-surface distance D . The distance, D is varied from 0 to 30 nm and interference patterns are observed in all cases. From the figure it is clear that when $D=0$ nm, maximum intensity is obtained and both intensity components decreases when the distance increases. It is also evident from the figure that there is a large intensity variation when D varies from 0 to 5 nm. That is when D decreases; the field becomes more and more localized at the gap between the particle and the surface. The localization and excitation of electromagnetic normal modes are caused by resonant excitation of electromagnetic normal modes of the particle-surface system. It correlates well with theory.

Fig. 5.16 Normalized intensity variation as a function of metal particle-surface distance (D).

Numerical analysis of four beam surface plasmon interference lithography based on gap mode excitation is also carried out. In this case, four counter propagating TE-polarized illumination beams, each with a wavelength of 427 nm is incident on the proposed configuration. Figure 5.17 represents the obtained 2D dot array patterns on the recording medium with different particle-surface distance. It is also visible from the counter plot that there is large intensity variation (in the scale bar) when the

particle-surface distance increases from 1 nm to 5 nm. It shows the existence of gap modes in the four beam interference lithography configuration.

Fig.5.17 Electric field distribution of the 2D interference pattern generated on the photoresist layer, when (a) $D=1$ nm and (b) $D=5$ nm.

5.2.4 Resist features

The modified CA modal is adopted in order to obtain the resultant resist features, as discussed in the previous Sect. 3.3.3.

Fig. 5.18 2D resist profile cross section at exposure time: (a) =100s, and (b) =150s.

Figures 5.18 and 5.19 respectively show 2D and 3D resist cross-section profiles obtained on the photoresist layer by employing the proposed concepts and configuration at different exposure times. The zero value along the vertical axis corresponds to the metal/photoresist interface. The obtained results show that with increase in exposure time, the line width of the pattern decreases and exposure depth increases. Fig. 5.18 (b) shows that, obtained line width, periodicity and exposure depth are around 25 nm, 120 nm and 180 nm, respectively at 150 s exposure duration. Therefore approximate resolution of 25 nm is achievable by this configuration, which is generally not possible with conventional prism based configuration. Also, the advantage of this configuration is that it can provide much larger enhanced fields to give shorter wavelengths of surface plasmons compared to that achieved with an isolated metal particle or a metal surface alone configuration.

Fig. 5.19 3D resist profile cross section at exposure time: (a) =100s, (b) =150s.

5.3 Summary

A new concept for high resolution nanoscale surface plasmon interference lithography is proposed (numerical simulation) using periodic metal nanoparticle array. To support the concept, electromagnetic energy transport via periodic chain of metal nanoparticle is demonstrated. It is found that the proposed configuration gives very high electric field distribution, and good exposure depth and contrast are achievable by using Ag and Al nanoparticle array. In short, this proposed concept and methodology promises good potential for nanolithography at high resolution to fabricate sub-40 nm periodic nanostructures. Resist profile cross section using modified cellular automata model, obtained through this proposed configurations are also presented.

A novel plasmonic lithographic technique based on the excitation of gap modes in a metal particle-surface system beyond the diffraction limit is proposed and numerically illustrated. The existence of gap modes in a metal particle-surface system is theoretically and numerically analyzed. The FDTD simulation results show that this configuration can provide strong enhanced field to give shorter wavelengths of surface plasmons to fabricate sub-30 nm size periodic structures, by employing Al nanosphere-Ag surface system. Therefore it promises the lithography at high resolution, good exposure depth and good contrast to fabricate one-dimensional periodic nanostructures for various applications. Two-dimensional periodic feature patterning based on proposed concept is also demonstrated. Also, as an advantage it can provide much larger enhanced field compared to that achieved with an isolated metal particle or a metal surface alone configuration.

The two proposed concepts reported in this chapter were not experimentally validated due to the lack of periodic nanoscale particles embedded medium. Hence this will be one of the focuses of the future work direction.

Chapter 6

Conclusion and Future works

This chapter concludes the major research contents with a summary of work done in this thesis, followed by future work directions. The initial studies conducted to meet the objectives of planned future work directions are also briefly presented in this chapter. Finally, the major research contributions made during the period are highlighted.

6.1 Conclusions

Various plasmonic lithography concepts and configurations for obtaining nanoscale features beyond the conventional free space diffraction limit were explored and analyzed in this thesis. Initially, the conventional laser interference lithography (LIL) was investigated both theoretically and experimentally. Periodic features with half-pitch resolution of 136.7 nm were experimentally obtained using 364 nm illumination wavelength. It can be inferred from the obtained results that LIL was unable to pattern high resolution (sub-100 nm) periodic features using near UV illumination wavelength sources. In this context, near-field interference lithography configuration such as evanescent wave interference lithography (EWIL) was proposed for high resolution nanopatterning. Both theoretical and experimental investigation was carried out and analyzed employing the proposed optical configurations. Using this technique, periodic nanoscale features with an average resolution of 88 nm was obtained by employing an incident wavelength of 364 nm. The obtained results show that it can be used for the fabrication of sub-100 nm periodic features. However, the experimentally obtained exposure depth and intensity contrast were found to be poor as compared to LIL. Hence, it was clear that EWIL is not a good choice for the fabrication of good aspect-ratio periodic features. A possible solution to overcome this problem is suggested by enhancing the decaying evanescent field at the prism/ photoresist interface. This is possible by exploring the concept of surface plasmon resonance, due to its enhanced transmission at the near field.

In this context, various configurations for plasmonic lithography was proposed and investigated for high resolution periodic nanoscale feature patterning. Initially, the theoretical simulation results of commonly used grating mask based configuration were analyzed. A detailed theoretical and experimental demonstration of single exposure prism based (maskless) plasmonic lithography concept for one-and two-dimensional periodic feature patterning was presented. The theoretical formulation for multiple beam (two and four) surface plasmon interference was developed by solving the Maxwell's curl equations in three dimensional space, using harmonic time dependent analysis. Numerical simulation of multiple beam SP interference was carried out and the results were compared with theory. The results were then experimentally verified by employing aluminum and silver as metal medium at 364 nm illumination wavelength so as to realize high resolution 1D (grating lines) and 2D (dot array) periodic nanoscale patterns on the recording medium. Large-area periodic grating lines and dot array features with an average resolution of 84.5 nm on a 164 nm period and 88 nm on a 166 nm period were achieved. A comparative analysis between the different multiple beam interference lithography techniques proposed in this thesis was experimentally carried out. It is also experimentally shown that among the different near field interference lithography techniques, surface plasmon interference lithography provides long exposure depth and good intensity contrast (i.e. even when compared to EWIL). This technique is expected to provide a convenient route for patterning high-throughput nanometer-scale structures without employing expensive equipment or complex mask fabrication approaches.

To further improve the exposure depth and large-area patterning of periodic nanoscale features, a planar layer configuration was proposed for surface plasmon interference lithography. The proposed configuration was then investigated theoretically and experimentally. Simulation results show that it gives very high electric field distribution on the recording medium as compared to Kretschmann configuration and hence facilitates high resolution with good exposure depth and good intensity contrast. The resist dissolution process was analyzed using a cellular automata model to obtain the subsequent post-development resist profile. The proposed configuration is then used to investigate the effect of metal films, such as aluminum and silver on UV excited two beam surface plasmon interference nanolithography. Numerical simulation results show that one-dimensional periodic nanoscale structures with a line

width of 50 nm were achievable by employing the above said metal films when interrogated with p-polarized, 364 nm illumination wavelength source. It is also found that the obtained periodic feature shows good exposure depth and high contrast when Al is used as the metal film. The experimental result of proposed configuration was also presented. The nanoscale grating lines with minimum linewidth of 70 nm and 78 nm were obtained for Ag and Al metals, respectively. It is also found that this configuration can provide large area patterning as compared to Kretschmann (prism based) configuration. In short, this proposed concept and methodology promises good potential for nanolithography to obtain high resolution, good exposure depth and good intensity contrast so as to fabricate sub-wavelength periodic nanostructures.

Recently, the research has focused on metal nanoparticles, due to its localization and enhancement of electromagnetic wave at plasmon resonance condition for high resolution nanoscale feature patterning. In this context, localized surface plasmons associated with metal nanoparticles assisted plasmonic lithography concepts were proposed and theoretically investigated. Firstly, a concept of periodic metal nanoparticle array based plasmonic lithography configuration has been investigated to realize periodic nanoscale structures. The fundamental concept of the technique is the electromagnetic energy transfer via periodic metal nanoparticle array. The proposed concept and methodology promise to have good potential for nanolithography to fabricate sub-40 nm periodic nanostructures using Ag and Al nanoparticle array. Secondly, a novel plasmonic lithography technique was proposed based on the excitation of gap modes in a metal particle-surface system. Numerical simulation results show that by employing Al nanosphere-Ag surface system, this configuration can provide strong enhanced field to give shorter wavelength of surface plasmons to fabricate sub-30 nm periodic structures. It can also provide much larger enhanced field compared to that achieved with an isolated metal particle or a metal surface alone configuration. Both one-and two-dimensional periodic feature patterning was demonstrated using the above mentioned concepts. Further, 2D and 3D resist profile cross sections, which are obtained using a cellular automata model, are also analyzed and compared.

6.2 Future work directions

6.2.1 Significance of future works

As mentioned earlier, due to the lack of nanoscale size of metal nanoparticle embedded layer, only the theoretical investigation of metal nanoparticle assisted plasmonic lithography concepts were presented in this thesis. Therefore the first focused work in the future will be to do experimental investigations of the proposed concepts. Secondly, it should be noted that the damping of light intensity caused by the metal absorption loss affects the exposure depth (aspect ratio) and intensity contrast of the written periodic nanoscale features. A straightforward solution to overcome this issue is by using an optical gain medium in the plasmonic lithography configuration to overcome the absorption loss. Hence this work to be a future work direction of the thesis to realize high aspect ratio periodic nanoscale features. Thirdly, the main objective of the thesis is the patterning of one- and two-dimensional periodic nanoscale features on the recording medium. However, the patterned 1D and 2D periodic nanoscale features can also find variety of other potential applications such as biosensors, solar cell, etc. In this context, the future work directions and some of the application oriented research challenges ahead are discussed briefly in the following sections.

6.2.2 Experimental investigation of nanoparticle assisted plasmonic lithography concept

The experimental evidence of the proposed gap modes-assisted plasmonic lithography concept and periodic metal nanoparticle assisted plasmonic lithography technique need to be investigated further. The previous experimental set up discussed in the Sec 3.1.2 will be employed towards conducting the relevant experiment. However, as such sample was not available; one need to prepare, which itself is a challenging task ahead. For gap modes assisted scheme, suggested experimental methodology are given below,

1. Al nanoparticles and Ag films can be deposited by vacuum evaporation technique.
2. SiO₂ film can be deposited by sputtering technique.
3. The thickness of the nanoparticles, metal film and distance 'D' can be monitored by quartz microbalance.

In the case of periodic metal nanosphere assisted scheme, the periodic metal nanoparticle array can be fabricated on a substrate by electron beam lithography followed by metal coating and subsequent lift-off process.

Once such samples are prepared, the experimental investigation can be carried out, which will be the first in the list of future planned works.

6.2.3 Investigation into compensation of LSP loss by optical gain medium for metal nanoparticle assisted plasmonic lithography

As mentioned in the literature review section, metal absorption loss affects the damping of localized surface plasmons in a nanoparticle, and propagating surface plasmon polaritons in a metal film. This problem can be compensated by using an optical gain medium such as organic dye in the dielectric medium surrounding the metallic nanostructures.

Figure 6.1 shows the localized electric field distribution around an 60 nm (optimized) diameter gold nanoparticle, when a TE-polarized illumination light incidents on the nanoparticle surface. Figure 6.1(a) represents E_z -field component of TE-polarized light in logarithmic scale. When the Rhodamine 6G dye is placed at distance 'D' from the gold nanoparticle, the enhanced localized field distribution around the nanoparticle is shown in Fig. 6.1(b). From the figure it is visually clear that there is an increase in electric field distribution due to the presence of dye molecule. This enhancement of LSP can be experimentally validated by pump-probe Rayleigh scattering and fluorescence lifetime measurement experiments. This approach can be used to improve further the exposure depth and intensity contrast when introduced to LSP assisted plasmonic lithography. [See Appendix-A for more details]

Fig. 6.1 Local field enhancement around an 60 nm gold nanoparticle (a) absence of dye and (b) presence of dye.

6.2.4 Experimental demonstration of metal nanograting (1D) based SPR sensors

One of the application oriented research that can be derived from the proposed concepts will be on this SPR sensor based on nanoscale metal grating. Numerical investigation of this concept is already discussed in the appendix section (Appendix-D). The patterned 1D periodic (grating lines) features can be used for this purpose to fabricate metal nanogratings. The proposed SPR biosensor chip configuration based on metal nanograting is shown in Fig.6.2. The SPR biosensor chip consists of four components, (1) optoelectronic system for excitation and detection of SPR, (2) microfluidic system for sample handling, (3) biointerface functionalized with surface receptors, and (4) data analyzing system to extract relevant information. The research challenges are, (1) to bring these components together to form a miniaturized biochip, the practical design issue should be considered and (2) a tradeoff between reusability and disposability must be analyzed. [See Appendix-D for more details]

Fig. 6.2 Schematic diagram of metal nanograting based SPR sensor.

6.2.5 Fabrication of 2D plasmonic crystals using patterned dot array features for biochip and solar cell applications

Another future work direction will be the fabrication of plasmonic crystal using the 2D patterned features, which can find potential biochip and solar cell applications. Plasmonic crystal fabrication process is briefly described below,

1. Four beams SP interference lithography could be used to pattern two-dimensional periodic nanopillars on the photoresist layer.

2. Reactive ion etching (RIE) technique could be used to transfer the patterns to the substrate.
3. Electron beam evaporation or sputtering technique could be used to coat metal on the etched patterns.

A biochip platform using plasmonic crystal is shown in Fig.6.3 (a). Plasmonic crystals based sensors have gained much attention recently, due to their potential to enable label-free biological and chemical detection. Plasmonic crystals based solar cell geometry is shown in Fig. 6.3 (b), where plasmonic crystals are used at the bottom side of the absorbing layer instead of periodic metal corrugation to trap and guide the light inside the absorbing layer.

Fig. 6.3 (a) Schematic diagram of plasmonic crystal based (a) biochip platform, and (b) solar cell geometry.

An advantage of plasmonic crystals over periodic metal corrugation is that the plasmon resonance can be tailored by changing the shape of the unit cell, tuning the lattice periodicity, and varying the crystal symmetry. Hence improved light absorption is expected by tuning these parameters. About 28% increment in light absorption compared to bare thin film silicon solar cell is obtained in the wavelength range of 400 nm to 1200 nm and enhanced light absorption at longer wavelength range is also observed as well. [See Appendix-C for more details]

It should be mentioned here that a detailed account on these initial studies carried out are given in the Appendix- A, C and D.

6.3 Major contributions

Surface plasmon enabled lithography, which is not restricted by free space diffraction limit, is one of the potential research thrust areas as it offers the possibility for high resolution nanopatterning. Since 2004, two well known configurations based on grating mask and prism based technique have been reported. Grating mask based configuration is a well established configuration for this lithography technique and many authors have already theoretically and experimentally demonstrated the concept. However, this technique requires the fabrication of a fine-period mask grating and is found to be not cost effective. The prism based configuration is a cost effective plasmonic lithography technique for large area patterning. But, only theoretical and numerical demonstration of this concept was so far reported. In this context, we have experimentally realized this concept for large area one-and two-dimensional periodic nanoscale feature patterning. This work is the first major contribution of this thesis. Also, a new theoretical formulation for multiple beam surface plasmon interference generation was developed. We have proposed a planar layer configuration for plasmonic lithography, which is a modification of prism based configuration. Both theoretical and experimental demonstration of this configuration was carried out. Also, we have experimentally realized that surface plasmon interference lithography can provide good aspect ratio and high resolution periodic nanoscale features as compared to other interference lithography techniques.

Recently, research has focused on noble metal nanoparticles because of their localization and enhancement of electromagnetic waves at plasmon resonance condition. In this context, we have proposed a new high resolution plasmonic lithography concept based on gap mode excitation. This is the second major contribution of this thesis. Another novel plasmonic lithography concept based on periodic metal nanoparticle array was proposed. The basic principle of the technique is the recently proposed electromagnetic energy transfer via periodic metal nanoparticle array. Only theoretical and numerical evidence of these concepts are carried out. Experimental evidence needs to be investigated further as mentioned in the “future work directions”.

Now researchers are concentrating how to compensate the surface plasmon loss in a metal nanoparticle and metal surface for various applications. Many groups have already proposed some solutions for this issue [123-125]. In this thesis, the compensation of LSP loss in a gold nanoparticle by placing an optical gain medium such as dye in the surrounding dielectric medium is demonstrated. Both numerical and experimental evidence of the concept was demonstrated in Appendix-A. This contribution in the plasmonic lithography field is expected to further improve the aspect ratio of the patterned features.

The major contributions of the project can be grouped as:

- Experimental demonstration of prism based plasmonic lithography for obtaining one- and two- dimensional periodic nanoscale feature.
- Theoretical formulation for multiple (two and four) beam surface plasmon interference generation.
- A planar layer surface plasmon interference lithography configuration for large area periodic nanoscale feature patterning.
- Gap modes assisted plasmonic lithography concept for high resolution (sub-30 nm) periodic nanoscale feature patterning.
- Periodic nanoparticle array based plasmonic lithography concept.
- Compensation of LSP loss by gain medium for nanoparticle assisted plasmonic lithography.

Appendix

Appendix-A

Compensation of LSP loss by optical gain medium

In the case of a nanoparticle, it is needed to calculate the critical gain to compensate the absorption loss in LSP. The polarizability of a nanoparticle is given by Eq. (5.3). It is well known from Eq. (5.3) that at the surface plasmon resonant condition, the real part of dielectric constant of surrounding dielectric medium equal to negative of the dielectric constant of metal involved function. That is,

$$\varepsilon_d' = -p(\varepsilon_m' - \varepsilon_d') \quad (1)$$

However, the imaginary part of the denominator of Eqn. (5.3) becomes zero, when the surrounding dielectric medium has critical optical gain at the resonant condition [123].

$$\varepsilon_d'' + p(\varepsilon_m'' - \varepsilon_d'') = 0 \quad (2)$$

From Eqn. (2),

$$\varepsilon_d'' = \frac{-p\varepsilon_m''}{(1-p)} \quad (3)$$

The gain coefficient is given by [123],

$$g = (2\pi / \lambda) \frac{\varepsilon_d''}{\sqrt{\varepsilon_d'}} \quad (4)$$

Now the gain needed to compensate the LSP loss is calculated by substituting Eqn. (3) in Eqn. (4) and obtained as,

$$g = -(2\pi / \lambda n) \left[\frac{p}{(1-p)} \right] \varepsilon_m'' \quad (5)$$

Where in Eqn. (5), $\sqrt{\varepsilon_d'} \approx n$

As mentioned earlier, the size of metal nanoparticle is an important factor for the LSP enhancement. Hence the variation of normalized intensity with nanoparticle diameter has been investigated. The FDTD software is used for the present numerical study. A Perfectly Matched Layer (PML) is employed as boundaries in all the direction to terminate the simulation. The smallest spatial grid size (1 nm) has been used for the

iteration to maintain the accuracy and stability of FDTD calculations. The simulation is performed for gold (Au) nanoparticle of various sizes ranging from 30 nm to 100 nm and excitation wavelength is taken as 532 nm.

Figure A-A-1 illustrates the variation of normalized intensities with respect to size of gold nanoparticle. It is evident from figure that there is a large intensity variation when Au diameter is varied from 40 nm to 70 nm. At that diameter range there is a large localization of conduction electrons within the nanoparticle. It can also be observed that the gold nanoparticle of size 60 nm shows improved localized surface plasmon enhancement as compared to other size. This is attributed to resonant surface plasmon wavelength of this gold nanoparticle, which locates at 532 nm wavelength.

Fig. A-A-1 Normalized intensity variation with nanoparticle diameter for Au nanoparticle.

Experimental details and discussions

The gold nanoparticles are synthesized by citrate reduction of chloroauric acid in water. 250 ml of 0.01% HAuCl₄ solution (0.01gm of HAuCl₄ in 100ml water) and 5 ml of 1% sodium citrate solution in water are prepared as precursor for nanoparticle synthesis. The auric solution is divided into five equal amounts (each of about 50 ml) and subjected to boiling. A few hundred μ ml of 1% sodium citrate solution of five different proportions are added to the boiling solution in order to obtain gold nanoparticles of various sizes (Table A-A-1). After the addition of citrate solution, the

solution is continued to boil for 10 more minutes with constant stirring. The sizes of the nanoparticles were determined using Atomic Force Microscope (AFM) studies. Figure A-A-2 represents the TEM picture of gold nanoparticles (sample B in table A-A-1) of average size 60 nm.

Fig. A-A-2 TEM picture of Au nanoparticles of average size of 60 nm.

Label	Citrate amount	Approximate nanoparticle size (nm)	Absorption Peak (nm)
A	230 μ l	83	540.50
B	280 μ l	63	542.50
C	350 μ l	40	538
D	5 ml	29	521.58

Table A-A-1 Average size of Au nanoparticles with different proportional of citrate solutions.

The optical absorption spectrums of samples are shown in Fig. A-A-3. Optical absorption spectrum of these four samples A, B, C, and D shows peak around 540.50 nm, 542.50 nm, 538 nm and 521.58 nm respectively. These peaks correspond to

characteristic surface plasmon absorption band of the gold nanoparticles of various sizes.

Fig. A-A-3 Optical absorption spectra of four samples (A, B, C, & D).

The excited localized surface plasmon in the metallic spherical nanoparticles suffers significantly from the intrinsic loss associated with the metal and will exhibit singularity due to the cancellation of this loss by an infinite gain medium. The field inside the particle is given by [123],

$$E = E_0 \left(\frac{\epsilon_2 - \epsilon_1}{\epsilon_1 + 2\epsilon_2} \right) \quad (6)$$

where ϵ_1 and ϵ_2 are the complex relative dielectric constants of the metal and surrounding medium respectively, and E_0 is the incident electric field. Singularity arises when the real and imaginary parts in the denominator of the equation vanish simultaneously and can be confirmed experimentally by pump-probe Rayleigh experiment. The damping of surface plasmon is characterized by an exponential decay $e^{-\gamma x}$ of its intensity away from the metal surface. The damping constant γ contains

contributions due to dissipation in the metal γ_m and to radiative loss γ_r . The radiative loss is due to plasmon re-emits as light and metal dissipation loss is given by,

$$\gamma_m = \frac{2\pi}{\lambda_e} \frac{\epsilon_m''}{(\epsilon_m')^2} \left(\frac{\epsilon_m' \epsilon_d'}{\epsilon_m' + \epsilon_d'} \right)^{3/2} \quad (7)$$

where ϵ_m' and ϵ_m'' denote the real and imaginary part of the dielectric constant of the metal, where ϵ_d' is the real part of surrounding dielectric medium (methanol). The refractive index of methanol and dielectric constant of gold at $\lambda_e = 532$ nm are ~ 1.329 and $-6.289996 + 2.04216i$ respectively [168]. Using these values, the obtained damping loss, γ_m is about $1.49636759 \times 10^6 \text{ m}^{-1}$ at 532 nm. This loss can overcome by gain medium such as dye at optimum concentration [185, 186]. Rhodamine 6G is considered as the gain medium and it is prepared in methanol. The gain γ_g needed to compensate for the SP loss is given by,

$$\gamma_g = \frac{2\pi}{\lambda_e} \frac{\epsilon_d''}{(\epsilon_d')^2} \left(\frac{\epsilon_m' \epsilon_d'}{\epsilon_m' + \epsilon_d'} \right)^{3/2} \quad (8)$$

Here ϵ_d'' is the imaginary part of the dielectric constant of dye medium which is the function of dye concentration (N) and emission cross section (σ_e). We assume the dye as a four level system and consider the fluorescence transition occurs between the energy levels 3 and 2. For the system which attains population inversion, the dye medium acquires an imaginary part of the dielectric constant at the emission wavelength (λ_e), which is given by,

$$\epsilon_d'' = \frac{n\lambda_e}{2\pi} (N_3 - N_2) \sigma_e = \frac{n\lambda_e}{2\pi} N \sigma_e \quad (9)$$

where n is the refractive index of gain medium, and N_2 & N_3 represent the dye concentrations at the energy level 2 and 3 respectively. For maximum population inversion, $N_3 \gg N_2$, and assumed that the concentrations at all other energy levels are negligible then $(N_3 - N_2) \approx N$ (total concentration of the system). The emission cross section of the Rhodamine 6G at 532 nm is $\sigma_e \approx 3 \times 10^{-16} \text{ cm}^2$. Using this value of

emission cross section, we obtain the concentration of dye molecules approximately

$$1.43 \times 10^{20} \text{ cm}^{-3} \text{ to get the gain coefficient } \alpha = \frac{\epsilon_d''}{\epsilon_m''} \left(\frac{\epsilon_m'}{\epsilon_d'} \right)^2 = 1.$$

The effect of lifetime of Rhodamine 6G in the presence of the Au particles is studied. Table A-A-2 represents the life time measurements of Rh6G and Rh6G-Au nanoparticles (60 nm size) composites. Rh6G-Au nanoparticles composites such as 280 μ lAu-Rh6G(II), 280 μ lAu-Rh6G(III), and 280 μ lAu-Rh6G(IV) are prepared by mixing 3 ml of as prepared gold nanoparticles (sample C) with 2 ml of 10^{-6} M, 10^{-7} M, and 10^{-8} M Rhodamine 6G solutions respectively. The Rhodamine 6G solutions are prepared in methanol. Nanoparticle of size 60 nm is considered in the present case as it exhibits maximum LSP enhancement. It has been found that life time of Rh6G decreased in the presence of Au nanoparticles. The sample containing dye concentration of about 10^{-8} M exhibits lowest excited state life time and it is found to increase with dye concentration [for samples 280 μ lAu-Rh6G (III) and 280 μ lAu-Rh6G (II)]. The sample 280 μ lAu-Rh6G (II) containing the dye concentration of about 10^{-6} M exhibits excited state life time equal to that of bare dye. This could be due to dominance of Rh6G dye molecules in 280 μ lAu-Rh6G (II) composite. The hypothetical optimum concentration at which the SP loss is just balanced by gain medium can be obtained from the lifetime data of Au-Rh6G composites. The value is found to be about 2.41×10^{-7} M.

Sample Name Au-Rh6G composites	Concentration of Rh6G in methanol	Lifetime
Rh6G (I)	10^{-7} M	4.4ns
280 μ lAu-Rh6G (II)	10^{-6} M	4.4ns
280 μ lAu-Rh6G (III)	10^{-7} M	3.3ns
280 μ lAu-Rh6G (IV)	10^{-8} M	2.6ns

Table A-A-2 Life time data of gold nanoparticle with various concentration of Rh6G dye.

Figure A-A-4 represents the fluorescence lifetime measurements of the Rhodamine 6G dye solution with and without gold nanoparticles. The data is fitted using $I(t) = I_0 \exp(-t/\tau)$, where I_0 is the intensity at time zero. The lifetime is given by the inverse of the total decay rate, $\tau = (\Gamma + k_{nr})^{-1}$, where Γ is the emissive rate and k_{nr} is the nonradiative decay rate. The fluorescence lifetime is obtained from the slope of a plot of $\log I(t)$ versus t . The measured excited singlet state life times of 280 μ lAu-Rh6G (IV) and Rh6G are found to be 2.6 ns and 4.4 ns, respectively. The decrease in lifetime of 280 μ lAu-Rh6G (IV) could be attributed due to quenching effect caused by direct stimulation of plasmon (instead of fluorescence emission) by excited dye molecules.

Fig. A-A-4 Fluorescence lifetime measurements of bare Rhodamine 6G (Rh6G (I), $\tau = 4.4$ ns) and a mixture of Rhodamine 6G and Au nanoparticles (Sample-280 μ lAu-Rh6G (IV), $\tau = 2.6$ ns).

Singularity due to the cancellation of SP loss by an infinite gain medium can be studied experimentally by pump-probe Rayleigh experiment [123]. The experimental set-up to study the Rayleigh scattering behavior of the sample is illustrated in the Fig. A-A-5. The linearly polarized pump light beam from the diode laser is made normal incident on the cuvette containing sample (Rh6GAu). The wavelength of the light employed for the excitation is 532 nm. The probe beam wavelength is fixed at 557 nm as the sample has maximum emission at this wavelength. The intensity of the probe beam is maintained constant throughout the experiment. The thickness of the cuvette used is 2.5 mm. Probe beam is incident obliquely. The pump beam is intensity

modulated by mechanical chopper and corresponding probe beam scattering is detected by optical fiber, monochromator, PMT and lock-in amplifier (SR830) set-up.

Fig. A-A-5 Schematic diagram represents the pump-probe Rayleigh scattering experiment.

Fig. A-A-6 Pump-probe Rayleigh scattering experimental result of sample B (60 nm).

The experiment is performed by maintaining probe beam intensity constant and increasing pump beam intensity linearly. A sudden increase in the scattering intensity at threshold power of about 500 μW pump power has been observed for sample C (Fig. A-A-6). The reason could be due to the gain provided by the surrounding dielectric medium to compensate the plasmonic loss associated with the metal and thereby improving Q factor of the system. The excited fluorophore in the gain medium emits plasmon instead of photon due to strong interaction between the excited dye molecules and electron vibration energy of SP. About 12.5 fold enhancement of Rayleigh scattering is observed. The experiment is also performed to study the effect of sizes on plasmonic enhancement. The experiment is repeated on sample A, C, and

D and Table A-A-3 represent the obtained gain and threshold power for scattering of various sizes of nanoparticles.

Au nanoparticle size (nm)	Gain	Threshold (μW)
Sample-A (83)	1.37	1050
Sample-B (63)	12.5	500
Sample-C (40)	1.50	1020
Sample-D (29)	1.48	963

Table A-A-3 Gain and threshold power for scattering of various sizes of Au-nanoparticles.

Figure A-A-7 represents the study of enhancement of Rayleigh scattering as the function Au nanoparticle size in the presence of gain medium. The plot almost resembles the plot obtained by numerical simulation (Fig. A-A-1). It exhibits the peak around 60 nm. Experiment is repeated with pure dye solution and no such scattering behavior is observed. In short, the achieved singularity by the sample is confirmed with the sudden increase in the Rayleigh scattering of the probe light beam with increase in pump light intensity.

Fig. A-A-7 Enhancement of Rayleigh scattering as the function Au nanoparticle size.

Appendix-B

Multiple beam surface plasmon interference generation-an alternate theoretical analysis

Here also, surface plasmon interference is realized by employing the attenuated total reflection principle based three layer configuration as illustrated in the Fig. A-B-1. The dielectric functions of prism and photoresist are assumed to be same, which is $\epsilon_1 = \epsilon_3 = \epsilon$ and metal has complex dielectric function, $\epsilon_2 = \epsilon'_2 + i\epsilon''_2$. The interface between the prism and metal is represented at $Z=0$. The surface plasmons will propagate in the positive and negative directions of X-axis, when two p-polarized plane waves with same incident angle and same amplitude incident at the prism/metal interface. In this case, one-dimensional interference patterns (grating lines) will be generated on the photoresist medium.

Fig. A-B-1 Schematic of three layer SP interference configuration.

The SPs propagating along the X-axis has the components, $H_{SP} = (0, H_{y,SP}, 0)$ and $E_{SP} = (E_{x,SP}, 0, E_{z,SP})$. The electromagnetic fields of a single beam in the (XZ) plane of three mediums are written as follows,

Medium 1: $Z > 0$,

$$E_1(x, z) = (E_{x1}, 0, E_{z1}) \exp i(k_{x1}x + k_{z1}z - \omega t) \quad (1)$$

$$H_1(x, z) = (0, H_{y1}, 0) \exp i(k_{x1}x + k_{z1}z - \omega t)$$

Medium 2: $Z < 0$,

$$E_2(x, z) = (E_{x2}, 0, E_{z2}) \exp i(k_{x2}x - k_{z2}z - \omega t) \quad (2)$$

$$H_2(x, z) = (0, H_{y2}, 0) \exp i(k_{x2}x - k_{z2}z - \omega t)$$

Medium 3: $Z < 0$,

$$E_3(x, z) = (E_{x3}, 0, E_{z3}) \exp i(k_{x3}x - k_{z3}z - \omega t) \quad (3)$$

$$H_3(x, z) = (0, H_{y3}, 0) \exp i(k_{x3}x - k_{z3}z - \omega t)$$

where k_{z2} and k_{z3} are the wave vector component parallel to the X-direction in the medium 2 and medium 3 respectively. It can be calculated as follows,

The field amplitude of SPs decreases exponentially, normal to the surface. Thus the value of skin depth (depth at which field falls to $1/e$) is given by,

$$z = \frac{1}{|k_{zi}|}$$

$$\text{In the medium 2 with } \varepsilon_2 = \varepsilon_2' + \varepsilon_2'', \quad z_2 = \frac{\lambda}{2\pi} \left(\frac{\varepsilon_2' + \varepsilon}{\varepsilon^2} \right)^{1/2} \quad (4)$$

$$\text{In the medium 3 with } \varepsilon, \quad z_3 = \frac{\lambda}{2\pi} \left(\frac{\varepsilon_2' + \varepsilon}{\varepsilon_2'^2} \right)^{1/2} \quad (5)$$

$$\text{Therefore,} \quad k_{z2} = \frac{2\pi}{\lambda} \left(\frac{\varepsilon^2}{\varepsilon_2' + \varepsilon} \right)^{1/2} \quad (6)$$

$$k_{z3} = \frac{2\pi}{\lambda} \left(\frac{\varepsilon_2'^2}{\varepsilon_2' + \varepsilon} \right)^{1/2} \quad (7)$$

In the Eqn. (2) and (3), k_{x2} and k_{x3} are the wave vector component of the electromagnetic field in the medium 2 and 3, respectively along the X-direction and given by,

$$k_{x2} = k_{x3} = k_x = \frac{2\pi}{\lambda} \left(\frac{\epsilon'_2 \epsilon}{\epsilon'_2 + \epsilon} \right)^{1/2} \quad (8)$$

It is required that k_{z2} and k_{z3} is purely imaginary for the fields in Eqn. (2) and (3) to be surface wave. This is possible when $k_x^2 > \epsilon k^2$, which gives,

$$k_{zi} = i(k_x^2 - \epsilon k^2)^{1/2} \quad (9)$$

When this condition is satisfied, the obtained wave from Eqn. (2) and (3) is a trapped surface wave or evanescent wave, with exponential decay into both media.

In the SP interference lithography, the electromagnetic field underneath the metal film (medium 3) is interested. In medium 3, the relationship between the X-and Z-component of the amplitude of the electric field is calculated by using Maxwell's equations,

$$\nabla \cdot E = \frac{\partial E_{x3}}{\partial x} + \frac{\partial E_{z3}}{\partial z} = 0 \quad (10)$$

Substitute Eqn. (3) in Eqn. (10), which gives,

$$ik_{x3} E_{x3} \exp i(k_{x3}x - k_{z3}z - \omega t) - ik_{z3} E_{z3} \exp i(k_{x3}x - k_{z3}z - \omega t) = 0$$

$$k_{x3} E_{x3} = k_{z3} E_{z3}$$

$$E_{z3} = E_{x3} \frac{k_{x3}}{k_{z3}} \quad (11)$$

The relationship between electric field and magnetic field in the medium 3 is obtained by solving the Maxwell's equation,

$$\nabla \times E_3 = -\frac{1}{c} \frac{\partial H_3}{\partial t} \quad (12)$$

$$\nabla \times E_3 = j \left(\frac{\partial E_{x3}}{\partial z} - \frac{\partial E_{z3}}{\partial x} \right) = j(-ik_{z3} E_{x3} - ik_{x3} E_{z3}) \exp i(k_{x3}x - k_{z3}z - \omega t) \quad (13)$$

$$-\frac{1}{c} \frac{\partial H_3}{\partial t} = j\epsilon_0 \frac{\omega}{c} H_{y3} \exp i(k_{x3}x - k_{z3}z - \omega t) \quad (14)$$

By equating (13) and (14), gives

$$E_{x3}k_{z3} + E_{z3}k_{x3} = -\frac{\omega}{c} H_{y3} \quad (15)$$

Substitute Eqn. (11) into (15), we get

$$E_{x3} \left[\frac{k_{z3}^2 + k_{x3}^2}{k_{z3}} \right] = -\frac{\omega}{c} H_{y3} \quad (16)$$

Where $k_{z3}^2 + k_{x3}^2 = k_3^2 = k_0^2 \epsilon = \epsilon \omega^2 / c^2$ (17)

In Eqn. (17), k_0 is the free space wave vector and ϵ is the dielectric function of the medium 3. Substitute Eqn. (17) in Eqn. (16), we get

$$E_{x3} = \frac{-ck_{z3}H_{y3}}{\epsilon\omega} \quad (18)$$

To find E_{z3} , substitute Eqn. (18) in Eqn. (11)

$$E_{z3} = \frac{-ck_{x3}H_{y3}}{\epsilon\omega} \quad (19)$$

Hereinafter we will consider $E_{x3} = E_{x,SP}$, $H_{y3} = H_{y,SP}$, $E_{z3} = E_{z,SP}$, $k_{x3} = k_x$ and $k_{z3} = k_z$.

From Eqn. (3), SP magnetic field component along (XZ) plane is given by,

$$H_{y3} = H_{y,SP}(x, z) = |H_{y3}| \exp(-ik_z z) \exp i(k_x x - \omega t)$$

$$H_{y,SP}(x, z) = |H_{y3}| \exp(-ik_z z) \cos(k_x x - \omega t) \quad (20)$$

To find corresponding SP electric field component of single beam in the X-Z plane, substitute Eqn. (20) into Eqn. (18) and Eqn. (19), we get

$$E_{x,SP}(x, z) = \frac{-ck_z}{\epsilon\omega} |H_{y3}| \exp(-ik_z z) \cos(k_x x - \omega t) \quad (21)$$

$$E_{z,SP}(x, z) = \frac{ck_x}{i\epsilon\omega} |H_{y3}| \exp(-ik_z z) \sin(k_x x - \omega t) \quad (22)$$

It is evident from the above equations that the amplitude of both E_x and E_z components decreases exponentially with $\exp(-ik_z z)$. The amplitude ratio of field components are given by,

$$\frac{|E_{z,SP}|}{|E_{x,SP}|} = \frac{|k_x|}{|k_z|} \approx \left| \frac{\text{Re}(\epsilon_2)}{\epsilon} \right| \quad (23)$$

According to Eqn. (23), the field component $E_{z,SP}$ dominates in the surface plasmon field distribution.

Two beam SP interference

For two beam SP interference, second beams with electric field components are given by,

$$E'_3(x, z) = (E'_{x3}, 0, E'_{z3}) \exp i(-k_{x3}x - k_{z3}z - \omega t) \quad (24)$$

The corresponding electric field component of the second beam, when surface plasmon propagates in negative X-direction is given by,

$$E'_{x,SP}(x, z) = \frac{ck_z}{\epsilon\omega} |H'_{y3}| \exp(-ik_z z) \cos(k_x x - \omega t) \quad (25)$$

$$E'_{z,SP}(x, z) = \frac{ck_x}{i\epsilon\omega} |H'_{y3}| \exp(-ik_z z) \sin(k_x x - \omega t) \quad (26)$$

Hence the corresponding intensity distribution of the interference between the two SP waves measures the time averaged of the square of the total electric field and is given as,

$$I_{x,SP} \propto \left\langle (E_{x,SP} + E'_{x,SP}) \bullet (E_{x,SP} + E'_{x,SP}) \right\rangle \quad (27)$$

$$I_{z,SP} \propto \langle (E_{z,SP} + E'_{z,SP}) \cdot (E_{z,SP} + E'_{z,SP}) \rangle \quad (28)$$

In two beams SP interference, the intensity term $I_{z,SP}$ dominates over the term $I_{x,SP}$.

Four beam SP interference

To find the electric field intensity of four beam SP interference, the electromagnetic field components in (YZ) plane also need to be found out. For surface plasmons propagating in the Y-direction, the SP field components are given as,

$$H_{SP} = (H_{x,SP}, 0, 0) \quad (29)$$

$$E_{SP} = (0, E_{y,SP}, E_{z,SP}) \quad (30)$$

By following the same procedure, the SP electromagnetic field components of single beam in the (YZ) plane are obtained as,

$$H_{x,SP}(y, z) = |H_{x3}| \exp(-ik_z z) \cos(k_y y - \omega t) \quad (31)$$

$$E_{y,SP}(y, z) = \frac{ck_z}{\epsilon\omega} |H_{x3}| \exp(-ik_z z) \cos(k_y y - \omega t) \quad (32)$$

$$E_{z,SP}(y, z) = -\frac{ck_y}{i\epsilon\omega} |H_{x3}| \exp(-ik_z z) \sin(k_y y - \omega t) \quad (33)$$

When the SP propagates in the negative Y-direction, surface plasmon electric field components are given by,

$$E'_{y,SP}(y, z) = -\frac{ck_z}{\epsilon\omega} |H'_{x3}| \exp(-ik_z z) \cos(k_y y - \omega t) \quad (34)$$

$$E'_{z,SP}(y, z) = -\frac{ck_y}{i\epsilon\omega} |H'_{x3}| \exp(-ik_z z) \sin(k_y y - \omega t) \quad (35)$$

Therefore the total SP electric field components in a four beam configuration is obtained by adding Eqns. (21), (22), (32) and (33),

$$E_{x,SP}(x, z) = \frac{-ck_z}{\epsilon\omega} |H_{y3}| \exp(-ik_z z) \cos(k_x x - \omega t) \quad (36)$$

$$E_{y,SP}(y, z) = \frac{ck_z}{\omega} |H_{x3}| \exp(-ik_z z) \cos(k_y y - \omega t) \quad (37)$$

$$E_{z,SP}(x, y, z) = \frac{ck_{SP}}{i\omega} |H_3| \exp(-ik_z z) [\sin(k_x x - \omega t) - \sin(k_y y - \omega t)] \quad (38)$$

In Eqn. (38), we assumed that $|H_{x3}| \approx |H_{y3}| = |H_3|$ and the magnitude of $k_x \approx k_y = k_{SP}$. Here also the field component $E_{z,SP}(x, y, z)$ dominates over other two components, $E_{x,SP}(x, z)$ and $E_{y,SP}(y, z)$.

Hence the corresponding intensity distribution of the interference between four counter propagating surface plasmon waves are given by,

$$I_{z,SP} \propto \left\langle \left(E_{z,SP}(x, y, z) + E'_{z,SP}(x, y, z) \right) \bullet \left(E_{z,SP}(x, y, z) + E'_{z,SP}(x, y, z) \right) \right\rangle \quad (39)$$

Where in Eqn. (39), $E'_{z,SP}(x, y, z)$ represents the $E_{z,SP}$ field component in the negative (X Y Z) direction.

Appendix-C

Gap modes assisted enhanced broadband light absorption in plasmonic thin film solar cell

In this section, gap modes assisted enhanced broadband light localization in a planar thin film solar cell is presented and results are compared with that of bare thin film silicon solar cell and particle plasmon (LSP) enhanced thin film silicon solar cell. Gap modes are the localized electromagnetic normal modes that exist in the space between the metal nanoparticle and surface. The excitation of the gap modes strongly depends on the distance of the nanoparticle from the surface. When the particle-surface distance is sufficiently small ($D/R < 1$), the system can support a series of gap modes and the electric field becomes more and more localized at the gap between the particle and the surface.

Fig. A-C-1 Schematic diagram of gap modes assisted thin film solar cell.

Figure A-C-1 shows the proposed basic device structure used in the simulation for the gap modes assisted light localization in thin film solar cell, where silver (Ag) nanoparticles of diameter 20 nm are periodically embedded inside the silicon (Si) absorbing layer of thickness 200 nm. A thin aluminum (Al) surface of thickness 10 nm is coated at a distance 'D' from the Ag nanoparticles and Indium Tin Oxide (ITO) layer of thickness 50 nm is taken as the transparent electrode. The plane waves of sun light are taken as TE-polarized light with wavelength ranging from 400 nm to 1200 nm. The numerical analysis is performed based on finite difference time domain method (FDTD). The simulation region is terminated with perfectly matched layer boundary conditions on parallel to the direction of propagation of light and periodic boundary conditions on other axes. The smallest spatial grid size (1 nm) has been used for the iteration to maintain the accuracy and stability of FDTD calculations. The numerical simulation for bare thin film silicon solar cell (with Al reflector) and LSP excited light trapping in thin film solar cell is also carried out to compare the results. The basic idea is that by exciting the gap modes in the space between nanoparticles and surface, enhanced local field around the nanoparticle is possible, thereby increased absorption is achievable.

To calculate the power absorbed in the silicon substrate, two power monitors were used: one at the top of the silicon and the other at the bottom surface. Amount of power transmitted through each surface normalized to source power was then calculated. Power absorbed is obtained by subtracting the transmitted power through each monitors. The variation of normalized absorption with incident wavelength of proposed geometry is shown in Fig. A-C-2. Along with this, normalized absorption of bare silicon thin film solar cell (with Al reflector) and particle plasmon (LSP)

enhanced thin film silicon solar cell is also plotted for comparison. In the case of particle plasmon enhanced solar cell, the Al reflector of thickness 10 nm is placed at a distance 100 nm from the Ag nanoparticles. It should be noted that in all three cases, the silicon thickness is kept constant. It is clear from the figure that enhanced absorption is possible in the case of proposed configuration (particle-surface distance is taken as 1 nm) compared to other two cases. The maximum absorption is obtained at 618 nm incident wavelength, which represents the gap mode resonance wavelength of the Ag particle- Al surface system. However, in the case of particle plasmon enhanced solar cell, maximum absorption is obtained at 525 nm incident wavelength, which represents the surface plasmon resonant wavelength of Ag nanoparticles. It represents a red shift in the resonance wavelength when the Al layer is placed at a distance $D=1$ nm from the Ag nanoparticles. Therefore the obtained local field enhancement could be due the formation of new localized electromagnetic normal modes (gap modes) in the space between the nanoparticle and the surface. That is, the gap modes enhance or modify the local field (LSP) around the nanoparticles. About 10.2% increment in absorption compared to bare thin film silicon solar cell and 3.7% increment in absorption compared to particle plasmon (LSP) enhanced thin film silicon solar cell is obtained using this configuration for the wavelength band of 400 nm-1200 nm. Also, enhanced light localization and absorption is observed at longer wavelength range, which is not possible with bare Si thin film solar cell because of the indirect bandgap of Si. It shows that broadband light localization and hence improved absorption is possible using this technique.

Fig. A-C-2 Variation of normalized absorption with incident wavelength.

Fig. A-C-3 Percentage absorption enhancement variation with particle-surface distance (D).

The variation of percentage absorption enhancement with particle-surface distance is shown in Fig. A-C-3. From the figure, it is clear that there is a large variation of percentage enhancement when D varies from 1 nm to 10 nm. Calculated percentage absorption enhancement (compared to bare silicon thin film solar cell) for particle-surface distances of 1 nm, 3 nm, 5 nm, 7 nm and 10 nm are 10.2 %, 9.7%, 9.1%, 8.3% and 7.1% respectively. There is a 3.1% reduction in normalized absorption when the particle-surface distance is varied from 1 nm to 10 nm. It should also be noted that at D=10 nm, the obtained absorption enhancement is close to that of particle plasmon enhanced solar cell, which is 6.3% (compared to bare silicon thin film solar cell). It clearly shows that gap mode effect exists only when $D/R < 1$.

Fig. A-C-4 Absorption variation with particle-surface distance (D).

The influence of particle-surface distance (D) on absorption is also investigated and plotted in Fig. A-C-4. It is found that when the particle surface distance increases, there is a decrease in absorption at shorter wavelength range (400 nm-800 nm) and absorption is almost same at longer wavelength range (800 nm-1200 nm). This result represents that at longer wavelength range particle-surface distance does not have much effect on the absorption, which shows gap mode contribution is more at shorter wavelength range. It is reported that gap modes resonance wavelength shifts to longer wavelength when D decreases²¹. From the figure, it is found that there is a red shift in the resonance wavelength as D decreases. The obtained gap mode resonance wavelengths at the particle-surface distances of 1 nm, 5nm, and 10 nm are found to be 618 nm, 613 nm and 610 nm respectively. This also proves the existence of gap modes in the space between the nanoparticle and surface. Here the gap mode resonance wavelength is considered as the wavelength at which maximum normalized absorption is obtained. However, the obtained wavelength shift is small. This can be attributed to the dependence of gap mode excitation on the surrounding dielectric medium.

The plasmon resonance can be tuned by selecting appropriate metal particle-surface system and particle-surface distance. Therefore the optimizations of nanoparticle size, metal film thickness, and particle-surface distance are important to improve the light absorption for the design of efficient solar cell geometry. Furthermore, the photocarrier generation is an important consideration for this configuration. In materials with small carrier diffusion length, the photogenerated electron-hole pair should be very close to the junction to minimize losses due to recombination. In this context, the metal-particle surface systems can be placed closer to the junction area to maximally utilize the advantages of this configuration. This concept is also extendable to the design of solar cell geometry using other active absorbing materials such as GaAS, CdTe and organic polymers.

Appendix-D

Numerical simulation of metal nanograting based SPR sensors

As already discussed in the literature review section, the metal nanogratings are widely using for SPR sensors applications, especially for biosensing. The primary advantage of metal nanograting based SPR sensors are to effect miniaturization and to make the size of the chips even smaller for commercial applications including antigen-antibody, protein, and chemicals detection. In this section, a metal nanograting based SPR sensor configuration is proposed and numerically investigated for refractive index sensing applications. It should be noted that this work is one of the future work directions of this project, in which one- and two-dimensional periodic nanoscale features patterned using various interference lithography techniques can be used for the fabrication of metal nanogratings.

Fig. A-D-1 Proposed SPR sensor configuration.

Figure A-D-1 illustrates the simulated metal nanograting based SPR sensor configuration, and its working principle is described as: when a p-polarized light is incident at a certain angle on the grating surface, whose electric field vector is oscillating parallel to the plane of incidence is coupled to the surface plasmons due to grating coupling principle. And these coupled surface plasmons result in the optical power loss of the reflected light intensity. Since SPR condition depends on the properties of metal nanograting (metal, period, resolution, thickness), surrounding

refractive index medium, and incident angle and wavelength of the illumination light. Hence, a shift in wavelength or incident angle can occur at the SPR condition when the refractive index of surrounding medium changes. The surface plasmon coupling condition for gratings, when grating grooves are perpendicular to the plane of incident light is given by,

$$k_0 n_s \sin \theta + \frac{2\pi m}{\Lambda} = k_0 \left(\frac{\epsilon'_m n_s^2}{\epsilon'_m + n_s^2} \right)^{\frac{1}{2}} \quad (1)$$

where, $k_0 = 2\pi/\lambda$, λ wavelength of illumination light, Λ is the period of grating, ϵ'_m is the real part of the dielectric constant of metal, n_s is the refractive index of surrounding medium (analyte), θ is the incident angle and m is the diffraction orders.

In the simulation, gold is taken as the metal and SiO₂ as the grating substrate. The grating periods and line widths are taken as (200 nm, 300 nm) and (100 nm, 150 nm), respectively. This is the required value of grating periods to satisfy the Eq. (1) for surface plasmon excitation. The wavelength of incident light is assumed to be 500 nm and the dielectric constant of gold at 500 nm is taken from Ref. [170]. The refractive index values of surrounding medium (analyte) are varied from 1.5 to 1.52 with a step of 0.001. In this study, shift in incident angle (SP resonance angle) is calculated with surrounding refractive index change. Figure A-D-2 shows the SP resonance angle plot, where variation in reflected light intensity is calculated with incident angle. The incident angle (in this case, 51°) at which minimum reflection (maximum absorption) obtained represents the SP resonance angle.

The calculated SP resonance angle shift with surrounding refractive index change is shown in Fig.A-D-3. A linear shift in SP resonance angle is observed when the refractive index is varied from 1.5 to 1.52. In the simulation, different grating periods have been considered for surface plasmon excitation and hence for refractive index sensing. However, a linear change in SPR angle shift is obtained by using 200 nm and 300 nm grating periods. That means, these periods only support the corresponding modes to excite the plasmons. From Fig.A-D-3, it is also evident that resonance angle increases with grating period and there is a large difference in SP resonance angle for these two periods. The reason could be that different diffraction orders of nanogratings (with different period) contribute to the surface plasmon excitation.

Furthermore, the ratio of change in SPR angle to the refractive index change of analyte calculated for 200 nm and 300 nm grating periods are 1.22 and 1.4, respectively. It shows that 300 nm grating period is more sensitive than 200 nm grating period at 500 nm incident wavelength. Therefore 300 nm is the optimum period for simulated nanograting to satisfy Eq. (1) at which maximum surface plasmon excitation is possible. It shows that grating periods have great importance in the design of metal nanograting for the fabrication of efficient SPR sensors.

Fig. A-D-2 SP resonance angle calculation.

Fig. A-D-3 SP resonance angle shift with refractive index variation.

Appendix-E

Cellular Automata (CA): Theoretical modal

A modified three dimensional CA algorithm is employed here. The exposed photoresist medium is divided into identical cubic CA cells and each cell with edge length a . The local state of each CA cell is considered as the ratio of its etched volume to its total volume. The respective computation sub-domain is shown in Fig. A-E-1. The amount of each cubic cell set at the position (i, j, k) , dissolved at time instant t by its local state $(C_{i,j,k}^t)$, defined as,

$$C_{i,j,k}^t = h_{diss} / a \quad (1)$$

where h_{diss} is the height dissolved in the development process. Based on the definition of CA cell, the initial value for $C_{i,j,k}^t$ is assigned zero and when the computed value for which exceeds one, a value of one would be assigned. Further introduce the differential cell state terms, dC_{adj} , dC_{edg} and dC_{vtx} . These terms represent the change of the central cell state due to the flow of the developer from adjacent, edge and vertex cells positions at the new time instance, after one time step of dt from the time instance t_0 .

Fig. A-E-1. The neighbourhood of the (i, j, k) cell.

The adjacent neighboring cell shares one face with the central cell, edge neighboring cell shares an edge with the central cell and vertex neighboring cell shares a corner vertex with the central cell. Hence, the central cell state at the new time instance is given as,

$$C_{i,j,k}^{t_0+dt} = C_{i,j,k}^{t_0} + dC_{adj}^{dt} + dC_{edg}^{dt} + dC_{vtx}^{dt} \quad (2)$$

Letting the dissolution rate of the central cell to be $R_{i,j,k}$, terms would be defined as follow,

$$dC_{adj}^{dt} = \frac{((C_{i+1,j,k}^{t_0} + C_{i-1,j,k}^{t_0} + C_{i,j+1,k}^{t_0} + C_{i,j-1,k}^{t_0}) + B_{i,j,k+1}^{t_0} + B_{i,j,k-1}^{t_0})R_{i,j,k}}{a} dt \quad (3)$$

$$dC_{edg}^{dt} = \gamma_{edg} ((C_{i+1,j+1,k}^{t_0} + C_{i-1,j+1,k}^{t_0} + C_{i+1,j-1,k}^{t_0} + C_{i+1,j-1,K}^{t_0}) \dots + B_{i+1,j,k+1}^{t_0} + B_{i-1,j,k+1}^{t_0} + B_{i,j+1,k+1}^{t_0} + B_{i,j-1,k+1}^{t_0} \dots) \quad (4)$$

$$+ B_{i+1,j,k-1}^{t_0} + B_{i-1,j,k-1}^{t_0} + B_{i,j+1,k-1}^{t_0} + B_{i,j-1,k-1}^{t_0}) \frac{2R_{i,j,k}^2 t_0 dt}{a^2}$$

$$dC_{vtx}^{dt} = \gamma_{vtx} (B_{i+1,j+1,k+1}^{t_0} + B_{i-1,j+1,k+1}^{t_0} + B_{i+1,j-1,k+1}^{t_0} + B_{i+1,j-1,k+1}^{t_0} \dots + B_{i+1,j+1,k-1}^{t_0} + B_{i-1,j+1,k-1}^{t_0} + B_{i+1,j-1,k-1}^{t_0} + B_{i+1,j-1,k-1}^{t_0}) \frac{3\sqrt{3}R_{i,j,k}^2 t_0^2 dt}{8a^3} \quad (5)$$

where $B_{I,J,K}^{t_0}$ is defined as,

$$B_{I,J,K}^{t_0} = \begin{cases} 1 & C_{I,J,K}^{t_0} = 1 \\ 0 & \text{otherwise} \end{cases}$$

where I represents $i-1, i$, or $i+1$ and same for J and K . As shown in Eq. (4) to Eq. (5), the binary switch function is implemented at those cell positions with $K = k-1$ or $K = k+1$. dt is the time step, defined as, $a/4R_{\max}$, where $R_{\max}$ refers to largest elemental development rate value in the simulation domain. In this modal, the terms γ_{edg} and γ_{vtx} are parameters used to model the indirect flow of developer from the edge cell positions and from the vertex cell positions.

Appendix-F

AFM Artifacts

As mentioned earlier, some of the AFM images are affected by artifacts. Since the basic principle of the AFM imaging depends on the interaction between the tip and sample surface, the most of the AFM artifacts are due to the size, shape, and contamination of AFM tip. The tip-sample convolution is the main AFM tip artifacts and this artifacts has the ability to make protruding features appear wide and holes appear smaller. In addition, other artifacts such as scanner artifacts, sample drift, electronics artifacts, piezo drifts and laser interference patterns can also affect the AFM imaging.

The basic thumb rule of AFM imaging is that the image will exactly reproduce the surface structure only when the difference in the image of the radius of curvature of the tip is one-tenth the radius of the imaged structure [187]. Schematic diagram of AFM tip artifacts of imaging a periodic surface structure with a lateral distance ' L ' and a height ' h ' is shown in Fig. A-F-1. It should be note that the interaction between the tip and sample surface gives the vertical resolution of AFM image and size of the tip determines the lateral resolution. From the figure it is clear that the tip is not able to image the bottom of the structure (Fig. A-F-1(a)) and corner of the structure (Fig. A-F-2(b)). The AFM produced image is represented by dotted line. Hence the actual height and size of the periodic features may be greater than the observed height by AFM.

Fig. A-F-1. Schematic of AFM tip artifacts.

There are various solutions for avoiding artifacts in AFM imaging. The most of the AFM tip artifacts can be reduced by using sharpened (high aspect ratio) tip, deconvolution techniques and clean tip with UV/ozone or piranha solution. Other artifacts at some extent can be minimized by : (i) using smaller force during imaging, (ii) using cantilever with smaller spring constant, (iii) slow down imaging speed, (iv) change scan direction, (v) rescan area of interest, (vi) remove vibrations form room, and (vii) decrease gains on control system [188].

Appendix-G

AFM Sectional Analysis

Interference lithography		Average period (nm)	Average resolution (nm)
LIL	Two Beam [1]	258.8	136.7
	Four Beam [2]	241.5	131
EWIL	Two Beam [3]	185.5	88
	Four Beam [4]	170	88
SPIL	Two Beam [5]	164	84.5
	Four Beam [6]	166	88

Table A-G-1 AFM sectional analysis results.

[1]

(a)

(b)

(a) : Average period = 258.8 nm, Standard Deviation : ± 6 nm

(b): Average resolution = 136.7 nm, Standard Deviation : ± 1 nm

[2]

(a)

(b)

(a): Average period = 241.5 nm, Standard Deviation : ± 5 nm

(b): Average resolution = 131 nm, Standard Deviation : ± 4 nm

[3]

(a)

(b)

(a) : Average period = 185.5 nm, Standard Deviation : ± 10 nm

(b): Average resolution = 88 nm, Standard Deviation : ± 10 nm

[4]

(a)

(b)

(a) : Average period = 170 nm, Standard Deviation : ± 6 nm

(b): Average resolution = 88 nm, Standard Deviation : ± 6 nm

[5]

(a)

(b)

(a) : Average period = 164 nm, Standard Deviation : ± 11 nm

(b): Average resolution = 84.5 nm, Standard Deviation : ± 9 nm

[6]

(a)

(b)

(a) : Average period = 166 nm, Standard Deviation : ± 9 nm

(b): Average resolution = 88 nm, Standard Deviation : ± 6 nm

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