High-precision measurement of plasmonic phase change in metal nanostructures

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**HIGH-PRECISION MEASUREMENT OF
PLASMONIC PHASE CHANGE IN METAL NANOSTRUCTURES**

NGUYEN DUY ANH
SCHOOL OF MECHANICAL AND AEROSPACE ENGINEERING
2020

**HIGH-PRECISION MEASUREMENT OF
PLASMONIC PHASE CHANGE IN METAL NANOSTRUCTURES**

Nguyen Duy Anh

School of Mechanical and Aerospace Engineering

A thesis submitted to the Nanyang Technological University in partial fulfilment of the
requirement for the degree of Doctor of Philosophy

2020

Statement of Originality

I hereby certify that the work embodied in this thesis is the result of original research, is free of plagiarised materials, and has not been submitted for a higher degree to any other University or Institution.

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Date

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Associate Professor SU Pei-Chen

Authorship Attribution Statement

This thesis contains material from 3 papers published in the following peer-reviewed journal(s) / from papers accepted at conferences in which I am listed as the lead (first) author.

Chapter 3 and 4 are published as Nguyen Duy Anh, Byung Jae Chun, Sungho Choi, Dong-Eon Kim, Seungchul Kim, and Young-Jin Kim, 'Plasmonic Dynamics Measured with Frequency-Comb-Referenced Phase Spectroscopy', *Nature Physics*, 15 (2019), 132-37.

The contributions of the co-authors are as follows:

- I, Prof Seungchul Kim and Prof Young-Jin Kim planed and overseen the project.
- I, Dr. Sungho Choi, Dr. Dong-Eon Kim, and Prof Seungchul Kim was designed, prepared and characterized the plasmonic sample.
- I, Dr. Byung Jae Chun, Prof Seungchul Kim, and Prof Young-Jin Kim performed the Frequency-comb-referenced plasmonic spectroscopic experiments.
- I, Prof Seungchul Kim, and Prof Young-Jin Kim analysed the data.
- All authors contributed to the manuscript preparation.

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- [1] D. A. Nguyen, B. J. Chun, and Y. Kim, 'Plasmonic Phase Change Measurement in Metal Nanostructures by Frequency-Comb-Based Spectrally Resolved Interferometry', in 2017 Conference on Lasers and Electro-Optics Pacific Rim (CLEO-PR) (2017), pp. 1-2.
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- I and Dr. Byung Jae Chun performed the experiment.
- I analysed the data.
- I wrote the drafts of both manuscripts. The manuscripts were revised together with Prof Young-Jin Kim.
- I was a presenter in CLEO-PR 2017.
- Prof Young-Jin Kim was a presenter in CLEO 2019.

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Abstract

The plasmonic phenomenon of Extraordinary Optical Transmission (EOT) refers to the interaction of the light and a subwavelength hole array perforated on metallic film. It provides a larger transmission of electromagnetic fields than the transmission predicted from a small aperture by the classical optics. Many of initial research works on this topic have focused on studying the intensity behavior (the transmittance) on several sample parameters such as hole size, the period of the array, the thickness of the metallic film, metal type, and the hole shape. The phase behavior has, to date, not been much explored although it is important for the process of plasmonic.

In optical spectroscopy, broadband phase spectra are known to provide richer, linear, and more direct sources of information on target samples compared to traditional intensity spectra. However, the direct acquisition of broadband phase spectra has proven difficult in plasmonics, owing to the critical requirements for highly stabilized light sources, coherent optical interferometers, and stable optical paths that are impervious to environmental changes. Hence, to contribute to a full understanding of the EOT, this thesis developed two interferometric approaches for the plasmonic EOT phase measurement: spectrally resolved interferometry and heterodyne interferometry. Both methods use frequency comb laser, which is considered as a novel light source for plasmonics. Therefore, they are named as frequency comb referenced (FCR) plasmonic phase spectroscopy.

A femtosecond frequency comb laser including millions of optical frequencies, which phase-locked to an atomic clock of a time standard, has a broad spectrum and high phase stability. It can transfer the phase information in the optical domain to the radio-frequency domain, thereby enable broadband plasmonic phase spectroscopy to have a higher speed, higher precision, and direct traceability to the time standards.

Due to plasmonic field enhancement during the extraordinary transmission, the phase retardation is hundred times stronger than the interaction of the frequency comb with the physical bulk material, which drastically increased the attainable resolution. With a carefully developed plasmonic phase measurement scheme, a 1.94 Å dynamic motion of a pair of nanoholes was measured with a 1.67 pm resolution in the feasibility test experiment, which shows the ability of plasmonic phase spectroscopy to function as a high precision plasmonic ruler.

Furthermore, surface-plasmon resonance (SPR), which is coherent oscillations of the free electrons at the metallic-dielectric interface excited by the incident light, has proven itself to be applicable in biological and chemical sensors. The high sensitivity of the method is caused by the dependence of SPR on the refractive index of the dielectric material on the metallic surface. In the case of subwavelength holes array on Au film, hundreds of such nanostructures, which help to enhance fluorescence or the weak signals from detected molecules, acting as an independent detector for the sensitivity enhancement. Consequently, in the refractive index measurement, the developed plasmonic phase measurement technique successfully detected the gas refractive index change of $\Delta n = 4.6$

$\times 10^{-9}$ RIU (refractive index unit) with the resolution of $\delta n = 1.6 \times 10^{-11}$ RIU, which is three order improvement compared to the commercial SPR devices.

With this superior performance, the future work will focus on understanding and describing in detail the fundamental physics underlying the performance. More theoretical investigation will be conducted to verify the universality of FCR - plasmonic phase spectroscopy for other plasmonic structures: nanorods, two nano-slits, and sub-wavelength slit-groove. It will be the fundamental for applying the FCR plasmonic phase spectroscopy into various applications such as single molecular detection, plasmonic ruler, and precision calibration of nano-instruments.

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List of symbols

Symbols	Description
c	Speed of light
d	Hole diameter
E	Electric field
f	Optical frequency
f_0	Carrier envelop frequency
f_{AOM}	Frequency shifted by Acousto-optic modulator
f_r	Repetition rate frequency
k	Wavenumber
l	Pitch
n	Refractive index
r	Hole radius
t	Au film thickness
Δn	Refractive index change
ε	Relative permittivity
λ	Optical wavelength
ω	Angular frequency

List of Abbreviations

2D	2-dimentional
3D	3-dimentional
AC	Alternating current
AOM	Acousto-optic modulator
APD	Avalanche Photodetectors
CE	Carrier envelope
CEO	Carrier envelope offset
CW	Continuous wave
DC	Direct current
EDFA	Er-doped fibre amplifier
EOT	Extraordinary optical transmission
FCR	Frequency comb referenced
FDTD	Finite-difference time-domain
LSP	Localized surface plasmon
OPD	Optical path difference
OSA	Optical spectrum analyzer
RA	Rayleigh anomaly
REP	Repetition rate
RF	Radio frequency
SEM	Scanning electron microscope
SERS	Surface enhanced Raman scattering
SP	Surface plasmon
SPP	Surface plasmon polaritons
SPR	Surface plasmon resonance
TEC	Thermo-electric heating element
THz-TDS	Terahertz time-domain spectroscopy

Chapter 1. Introduction

1.1. Background

Diffraction occurs when a wave encounters an obstacle or a slit. This behaviour is presented when an obstacle or a slit that is comparable in size to the wavelength. The diffraction of light was demonstrated through the experiment of Thomas Young with two closely spaced slits. In 1944 Hans Bethe [1] introduced a theory that the transmittance of light through a subwavelength hole is very low. In 1998, the plasmonic phenomenon of extraordinary optical transmission (EOT) was discovered by Ebbesen's group [2]. When the light impinged to an array of nanoholes perforated periodically on a metallic film, they observed that the transmission per hole was larger than the prediction by Bethe's theory at some wavelength position. Many promising applications based on this EOT phenomenon have been introduced such as polarization control, filtering and switching, chemical sensing, and surface-enhanced Raman scattering [3].

A femtosecond frequency comb laser including millions of optical frequencies which phase-locked to an atomic clock of a time standard has a broad spectrum with high phase stability [4, 5]. It has many outstanding advances in high-resolution spectroscopy [4, 5], optical clock [6], time/frequency measurement [7-11], length/distance metrology [12-15], broadband calibration of astronomical spectrographs [16], and physical measurements [17]. The frequency comb also made the realization of broadband phase spectroscopy of gaseous constituents simpler, more precise, and more straightforward. Its high inter-modal

1 coherence and short pulse duration have expanded to fast molecular detection by coherent
2 Raman spectroscopy [18].

3 Spectrally resolved interferometry is a technique using frequency-domain
4 interferences between two beams of different optical paths. It has been shown many
5 advantages to be of great use in distance and displacement measurements [19-21], optical
6 profilometry [22-24], dispersion characterization of optical specimens [25-28], and the
7 group refractive index dispersion measurement in glass samples [29]. Spectrally resolved
8 interferometry can measure the complex transfer function of optical elements by using a
9 broadband light source such as a femtosecond laser [13, 29] or an incoherent white light
10 source. The interferogram can be obtained by using different optical setups, for example,
11 Mach-Zehnder, Michelson, Sagnac or Twyman-Green interferometers.

12 As an intensity-detection based method, spectrally resolved interferometry suffers
13 from the DC offset error which obstructs realizing high-speed and high-resolution
14 measurements [30]. Most of the commercial laser interferometers are based on heterodyne
15 interferometry [31, 32], in which the frequency difference can be generated by the Zeeman
16 effect [33] or an acousto-optical modulator [34, 35]. It overcomes the shortcomings of the
17 DC drift of the single-frequency laser and has the advantages of low noise and strong anti-
18 interference ability [36]. The heterodyne interferometer uses the dual-frequency beam with
19 a certain frequency difference Δf as a carrier signal. With the rapid development of
20 electronic phase measurement technology, the resolution of the displacement measurement
21 of the heterodyne interferometry has reached subnanometer [37].

1.2. Motivation

To date, most of the research works on the EOT have focused on the dependence of the intensity behaviour (the transmittance) on several sample parameters such as hole size, the period of the array, the metallic film thickness, metal type, and the hole shape. The phase behaviour has, however, not been much explored although it is an important feature for plasmonic processes. This is the motivation to do this study. In the field of optical spectroscopy, broadband phase spectra are known to provide richer and more direct sources of information on target samples [38]. However, despite its fundamental importance, direct acquisition of broadband phase spectrum has not been easy due to its critical requirements of broadband or widely tuneable light sources, coherent optical interferometers, and stable optical paths robust to environmental changes [39, 40]. Therefore, most broadband spectrometers have relied on intensity information. In plasmonic, there have been also attempts of broadband phase spectroscopy, but only with limited structural conditions and performance. For example, polarization plasmonic interferometry was first implemented in quantitative phase spectroscopy for refractive index sensing [41]. Then, plasmonic interferometry based on two nano-slits into a thin metal film was integrated into a microfluidic chip for label-free biosensing of streptavidin-biotin specific binding [42]. In addition, sub-wavelength slit-groove corrugation was recently introduced for evaluating the spatial degree of coherence at the sub-micrometer level [43].

While the frequency comb was proven to be a promising light source for advanced plasmonics, no demonstrations had been provided. Recently, the interrelation between the

frequency comb and surface plasmon was revealed; the superior performances of the frequency comb, such as absolute frequency uncertainty, high stability, and narrow linewidth, are well maintained with negligible degradations less than 6.5×10^{-19} in absolute frequency position, 2.9×10^{-19} in stability and 1 Hz in linewidth [44]. The frequency comb is now ready as the light source for high-resolution broadband phase spectroscopy in plasmonics. But the phase information when the frequency comb interacts with the EOT has not been considered.

1.3. Objective

The main objective of this research is to demonstrate two interferometric approaches to investigate the phase characteristics of plasmonic EOT: spectrally resolved interferometry and heterodyne interferometry. Both methods use frequency comb laser, which is considered as a novel light source for plasmonics. Then apply the methods for some applications such as the plasmonic ruler and gas sensing. The detail objectives are:

- Simulating the plasmonic phenomenon: using finite-difference time-domain (FDTD) solution for analyzing the plasmonic phenomenon in several structures such as the array of subwavelength holes (EOT sample), two nano-slits, sub-wavelength slit-groove, which used as the reference to evaluate the experimental result. Then, optimizing the EOT sample design for the fabrication.
- Experimental investigation of the plasmonic EOT phase spectrum based on spectrally resolved interferometry using frequency comb as the light source. Spectrally resolved interferometry converts the spectral phase distribution to

spectral amplitude distribution. A series of data processing - Fourier transform, data filtering, inverse Fourier transform, and phase unwrapping - are used for the full reconstruction of amplitude and phase spectrum over a wide spectral range.

- Experimental investigation of the plasmonic EOT phase spectrum based on heterodyne interferometry using frequency comb as the light source. Frequency comb can transfer the phase information in the optical domain to the radio-frequency (RF) domain, clean phase information can be selected from a heterodyne frequency by way of narrow-bandwidth RF filters and lock-in detection. Thereby, it enables broadband plasmonic phase spectroscopy having a higher speed, higher precision, and direct traceability to the time standard.
- Applying plasmonic phase measurement in various applications: plasmonic ruler, gas detection.

1.4. Scope

The scope of the research is described as follows:

- Doing the review of the Extraordinary Optical Transmission (EOT) phenomenon as well as the principle of the frequency comb laser system.
 - Building a computer program to reconstruct the phase and intensity information from the obtained spectral interferograms. It is a series of data processing: Fourier transforms, data filtering, inverse Fourier transform, and phase unwrapping.
 - Configuring and experimentally characterizing the Mach-Zehnder interferometer for both spectrally resolved interferometry and heterodyne interferometry.
-

- Experimentally investigating the interaction between the frequency comb and EOT sample using spectrally resolved interferometry.
- Experimentally investigating the interaction between the frequency comb and EOT sample using heterodyne interferometry.
- Demonstrating the application based on plasmonic EOT phenomenon: plasmonic ruler, gas sensing.

The research roadmap of the project is shown in Figure 1.1.

Figure 1.1. Research road map.

1.5. Report structure

The report is organized as follow:

Chapter 2 reviews the frequency comb and EOT, which are the background of this research. It briefly introduces the overview of femtosecond frequency comb as well as EOT.

Chapter 3 presents the experiment measured the plasmonic phase using spectrally resolved interferometry. From the obtained interferogram, the intensity and phase spectrum were reconstructed by the series of data processing. Comparing the characteristics of the light before and after the interaction with the sample, the intensity and phase changes caused by the plasmonic EOT phenomenon were derived.

Chapter 4 demonstrates the ability of the heterodyne interferometry in measuring the plasmonic EOT phase change. The spectrally resolved interferometry method shows some limitations in the resolution and time response, therefore it requires a technique that can measure the phase with higher speed and higher resolution. The frequency comb is divided into reference and measurement beams, the reference beam is transmitted through an acousto-optic modulator (AOM) for a frequency shift and the measurement beam is passed through the plasmonic sample. At the detection, both beams are combined generating the RF (radio frequency) heterodyne frequency. The phase information was measured by a phase meter.

1 Chapter 5 is the application of the plasmonic phase spectroscopy. In this experiment,
2 I succeed in measuring the gas refractive index with high speed and high resolution.

3 Chapter 6, the last chapter, gives the conclusion for the research along with the plan
4 for future work. It explains the contributions of this research. Also, certain suggestions are
5 provided for extending the application areas of the proposed frequency comb referenced
6 plasmonic phase spectroscopy technique.

Chapter 2. Literature review

2.1. Frequency comb

2.1.1. Overview

In 1960, the International System of Units (SI) was published. It has been modified many times from then. This system of units has been adopted by most developed countries. The length and time unit are defined as: “Metre (1983) is the distance the light propagates in the vacuum in $1/299.792.458$ second” and “Second (1967) the interval of $9.192.631.770$ ($\approx 9,193$ GHz = $9,193 \times 10^6$ Hz) periods of the radiation of Cesium 133 atom”. In the 21st century, it is the revolution in communicating technology, space science and nanotechnology where the scientist and the engineer who need to measure the frequency can reach to terahertz (10^{15} Hz). How can we measure accurately these frequencies when they are faster than the atomic clocks million times? Femtosecond-laser frequency combs can be used to solve this problem [4, 5, 45].

Frequency measurement means counting the number of cycles over a given period. Electronic counters that work with microwave frequencies have long been available. But they are not fast enough to measure the optical frequencies. The frequency comb acts as a set of large gears as found in a clock. It converts the fast oscillations of an optical signal down to a slowly oscillating microwave signal that can be directly counted and/or compared with other transitions (Fig. 2.1). It becomes a very precise tool for optical

1 frequency measurement. Commercially available frequency comb has been widely used in
 2 laboratories for measurement and physical research.

3
 4 **Figure 2.1.** Optical frequency comb acts as a gear for linking optical frequency and microwave frequency
 5 (Ref. [46]).

6 Some metrology applications of the frequency comb are shown in Fig. 2.2a. This is
 7 the only available tool which has the ability to measure the frequency with the accuracy of
 8 10^{-17} correspond to the 10^{-8} accuracy of available wavelength meters [47, 48]. The concept
 9 of the frequency comb has been exploited for the calibrating the absolute length of gauge
 10 blocks with the final wavelength uncertainty attained 1.9×10^{-10} [49]. Frequency combs
 11 are studied as a broadband calibration source for astronomical spectrographs. The
 12 expanded history of the universe can be studied by observing the cosmic movement of
 13 distant objects in real time. This requires Doppler velocity measurements of about one
 14 centimeter per second per year, however, astronomical telescopes have not been calibrated
 15 with this tolerance. In 2008, the frequency comb was first used to correct the wavelength
 16 of an astronomical telescope [16]. Another application of frequency comb is optical

frequency generation, which the output signals preserved the properties of the selected modes [50].

Figure 2.2. a, Some of the metrology application of the frequency comb (Ref. [51]). **b,** Milestones in the development of optical interferometers for distance measurements (Ref. [52]).

Optical distance measurement is one of the fields that has been influenced significantly by the advent of the femtosecond frequency comb [51-54]. By connecting the optical and microwave domain of the electromagnetic spectrum, the frequency comb provides a straight relation between the meter and the second. One of the first distance measurements with the comb was based on synthetic wavelength generation using the high harmonics of the repetition frequency within the comb bandwidth [55]. Other schemes based on cross-correlation between pulses emitted by the frequency comb laser [56-58], spectral interferometry [59, 60], or multiheterodyne interferometry using two frequency combs with a slightly different repetition frequency [12, 61]. A noninterferometric approach based on time-of-flight measurements has also been reported [62].

2.1.2. Principle of operation

Traditional frequency combs are based on mode-locked femtosecond pulse lasers [53]. Mode-locked lasers create ultrashort pulses in just 5 femtoseconds (fs) in duration [63] by fixing the phase relationship across multiple frequencies (Fig. 2.3).

Figure 2.3. Mode-locked lasers create ultrashort pulses by fixing the phase relationship of multiple frequencies (Ref. [64]).

How frequency comb can link optical frequencies to microwave or radio frequencies? The basic idea behind is the result of the Fourier transform relationship, which relates a signal measured in time to its corresponding frequency distribution. For example, the pure sinusoidal oscillation of the electric field with 2.1 fs period domain as plotted in the left-hand side of Fig. 2.4a. This sinusoidal waveform corresponds to a frequency of 474×10^{12} Hz in the frequency domain, or a wavelength of 633 nm. Next considering a single light pulse as shown in Fig. 2.4b. This pulse has the same carrier frequency as in Fig. 2.4a, but is strongly amplitude-modulated by a pulse envelope such that the waveform only lasts for $\Delta t \sim 8$ fs, in this example. The corresponding frequency spectrum for this pulse is still centered at 474×10^{12} Hz, but due to the short pulse envelope, the spectrum is very broad. This is also a result of the mathematical properties of the Fourier transform, which tell us that the spectrum width is inversely proportional to the pulse duration. Considering a pair of pulses shown in Fig. 2.4c. In this example, the pulses have a time delay T between them that is exactly 13 periods of the laser carrier frequency.

Figure 2.4. Time (left column) and frequency (right column) relationship of the laser electric field (in blue). Black lines are for reference only. Coherent light emitted from (a) a single frequency CW laser, (b) a single laser pulse, (c) a pair of laser pulses, and (d) 4 laser pulses separated with equal time delays (Ref. [65]).

Note that the two pulses are identical in this example. In this case, we can see that they are “phase coherent” with the continuous-wave (CW) field of Fig. 2.4a, in the sense that the field nodes and antinodes of the second pulse are still aligned with the original CW carrier frequency. Each pulse individually has the same spectral amplitude (as shown in Fig. 2.4b). However, the mathematical property of the Fourier transform tells us that, because one pulse is delayed in time relative to the other, there will be a linear phase shift across the spectrum of the second pulse relative to the first, given by $\Phi(f) = 2\pi T \times f$ where f is frequency. The spectral components from each pulse will constructively interfere only when this relative phase shift is an integer multiple of 2π . Spectral interference peaks, therefore, occur at $2\pi T \times f = 2\pi n$, or when $f = n/T$, where n is an integer.

If instead of a pulse pair we have four pulses, as shown in Fig. 2.4d, or better yet, an *infinite* train of equally spaced pulses, the constructive interference peaks will simply

become sharper and sharper until each resembles a narrow frequency like that of a CW laser, as in Fig. 2.4a. The above equation, which determines the location of these peaks, is often written in the following form:

$$f_n = n \times f_r \quad (2.1)$$

Where f_r is the repetition rate frequency of pulse train, f_n corresponds to one of the lasing frequencies. Modern laser systems are now capable of generating trains of pulses so short that the resulting “comb” of precisely spaced frequencies can span the entire visible spectrum. The simple expression of Eq. 2.1 is quite powerful, as it directly relates the individual optical frequencies of the femtosecond comb $f_n \sim 10^{15}$ to the easily measured microwave/radio frequency of the pulse repetition rate $f_r \sim 10^7$ - 10^9 by multiples of some large integer n . Now, to measure a frequency of the CW laser, first compared with a single “tooth” of the femtosecond frequency comb to measure the difference in their frequencies. Then, the frequency of that comb tooth can be determined by simply recording the repetition rate of the pulse train with a standard electronic counter.

The concept of the frequency comb may seem simple, but the full realization of this powerful technique took nearly thirty years to develop. Many of the basic concepts were explored in early experiments conducted in the 1970s by Theodor Hänsch and colleagues [66, 67]. However, the laser technology at that time was not sufficiently advanced to solve the problem regarding shortening the laser pulse, intrinsic noise of the laser, which could affect each pulse differently (timing jitter). Another issue was the pulse trains from mode-locked lasers, in fact, do not normally look like the pulse train shown in Fig. 2.4d. Due to

intracavity dispersion and there are no locking mechanisms, a phase shift $\Delta\phi_{ce}$ between the carrier and the envelope (CE) fluctuated randomly. Until 1999, with improving laser technology, different methods for controlling the carrier–envelope offset were suggested [68].

Figure 2.5. (a) The phase shift $\Delta\phi_{ce}$ between the carrier and the envelope in the time domain (b) Each mode of the spectrum in the frequency domain are spaced f_{rep} and the entire comb is offset by an offset frequency f_0 (Ref. [69]).

The change of the CE phases from pulse-to-pulse modifies the simple expression given in Eq. 2.1. In that expression, the spectrum from successive pulses will only constructively interfere at frequencies where their relative phase shift is an integer multiple of 2π . In this analysis not only the relative phase shift due to the pulse delay is included, but also that due to the change in the CE phase. The relative phase shift of the spectrum between each pulse is therefore given by $\Phi(f) = 2\pi T \times f + \Delta\Phi_{CE}$, where $\Delta\Phi_{CE}$ is the change in the CEO phase from pulse to pulse. Setting this value to a multiple of 2π results in a new expression for the position of the frequency comb teeth, that is:

$$f_n = n \times f_r + f_0 \quad (2.2)$$

Where $f_0 = \Delta\Phi_{CE} / (2\pi T)$ is known as the carrier-envelope offset frequency. This extra frequency shift of the entire comb (see Fig. 2.5) is just a result of the time changing phase from pulse to pulse.

To define each frequency, both f_r and f_0 must be measured accurately. The frequency f_r can be directly detected by a fast photodiode with bandwidth exceeding f_r from the beat signal generated by a pair of consecutive comb mode or a pair of comb mode that are separated by a harmonic of the repetition rate [69]. The other side, measurement of f_0 is more complicated requires interferometric measurement. The heterodyne beat between a mode, with index n , is doubled by a second harmonic crystal, and the other mode with index $2n$ returns the offset frequency, $2\nu_n - \nu_{2n} = 2(nf_r + f_0) - (2nf_r + f_0) = f_0$. This technique called “Self-referencing” [11] (Fig. 2.6a).

Figure 2.6. Two schemes measured f_0 using an optical octave. a) Self-referencing approach, (b), the fundamental frequency (ν_{standard}) and its second harmonic are used to determine f_0 (Ref. [70]).

Other method used to measure the f_0 shown in Fig. 2.6b, $f_{beat1} = \nu_s - (nf_r + f_0)$ is the heterodyne beat between the standard frequency, ν_s , and the mode n . While $f_{beat2} = 2\nu_s - (2nf_r + f_0)$ is between the second harmonic of the ν_s and the mode $2n$. Doubling the f_{beat1} then mixing with f_{beat2} gives: $f_{beat2} - 2f_{beat1} = 2\nu_s - (2nf_r + f_0) - (2\nu_s - 2(nf_r + f_0)) = f_0$

2.1.3. Frequency comb generator

Base on the concepts, one of possible frequency comb generators is shown in Fig. 2.7.

Figure 2.7. An example of femtosecond comb generator schematic. AOM: acousto-optic modulator; SHX: second-harmonic-generation crystal (Ref. [70]).

The main part of the generator is a KLM Ti: sapphire laser. The repetition rate is measured from a part of the output by a high-speed photodiode. A servo loop controls f_r by comparing the difference between this signal and a microwave clock. To measure f_0 , an v -to- $2v$ interferometer is used with the concept explained in Fig. 2.6. The measured f_0 signal becomes the feedback in a closed loop to stabilize f_0 . The end mirror in the arm of the laser cavity that includes the prism pair, which is used to compensate the intracavity phase dispersion, is swiveled properly to control the f_0 [11, 53]. Pump power also can be used to control f_0 [71].

2.1.4. Frequency comb spectroscopy

Frequency comb spectroscopy was the first application of a frequency comb in the 1970s [72-74]. In the 2000s, after self-referencing [11] of femtosecond laser synthesizers established the power of frequency comb techniques for comb-assisted precision spectroscopy, frequency comb spectroscopy began to attract the interest of a few research groups [39, 40, 75, 76]. Initially invented for frequency metrology, such combs enable new approaches to spectroscopy over broad spectral bandwidths, of particular relevance to molecules [77]. Most spectrometers such as crossed dispersers employing, or Michelson-based Fourier transform interferometers have a limited dynamic range and therefore combs with a flat intensity spectral distribution are also beneficial, and dramatically enhance their performance. A new class of instruments, such as dual-comb spectrometers without moving parts [78], enables fast and accurate measurements over broad spectral ranges. Stimulated by a number of intriguing proof-of-principle demonstrations, the field has grown to become a hot research topic and, with new research groups constantly getting involved, novel, clever and unforeseen applications are emerging.

2.2. Extraordinary optical transmission

2.2.1. Overview

In 1907, An abnormal absorption referred to the Wood's Anomaly was described Lord Rayleigh [79]. He found that the light could not transmit through a hole array in a metallic plate which had the distance between the holes approaches the wavelength. He did not deliberate abnormal resonance in the transmission which resulted in wavelengths only

longer than the array period. In Bethe's theory given in 1944 [1], the transmission through a single hole proportions to the ratio $\left(\frac{r}{\lambda}\right)^4$, where r is the hole radius (Ep. 2.3, Fig. 2.8). Therefore, they expected that near-impossible light would pass through an array of holes.

$$\eta_B = \frac{64 (kr)^4}{27 \pi^2} \quad (2.3)$$

Figure 2.8. Diffraction and the transmittance through a small hole (Ref. [80]).

The Extraordinary Optical Transmission (EOT) phenomenon of a subwavelength holes arrays was first reported in 1998 by Ebbesen [2], illustrated in Fig. 2.9. When the light impinged to a periodic nanoscale hole arrays drilled on a metallic film, instead of the low transmission predicted by the Bethe's theory they observed that at some wavelength position the transmission higher than the calculation using Eq. 2.3 (Fig. 2.9b). Fig. 2.10 displays the transmission spectrum of tubular holes array $N \times N$ in an Ag film on fused-silica glass. In Fig. 2.10d, when N increases from 1 to 19, the peaks intensity increase until the full saturation when $N = 15$. Fig. 2.10e is the transmission coefficient for each hole corresponding to selected N ($T_{R,N}(\lambda)$). Compared to $T_{R,1}(\lambda)$, $T_{R,N>1}(\lambda)$ is annihilated at some wavelengths, while enhanced at other wavelengths.

Figure 2.9. a) SEM image of an array of circular holes drilled on a metallic film (Ref. [81]); b) Zero-order transmission spectrum of an Ag array (Ref. [2]).

Figure 2.10. (a,b,c) SEM image of array for $N = 1, 4$, and 9 , respectively; (d) Transmission spectra of an $N \times N$ array; (e) Corresponding per-hole transmission coefficient for selected N (Ref. [82]).

The theoretical understanding of EOT has advanced considerably and it is widely accepted that surface plasmon resonant (SPR) leads to EOT. Ebbesen and his team have been leading the basic research in EOT. In 1998, they demonstrated the peak wavelength of transmission spectrum varies with incident light's angle (Fig. 2.11), which is highly similar to the properties of SPR and verifies that SPR is of great significance for EOT's generation [2, 83]. Many other research teams accept and extend the theory. In 2004,

Moreno studied the optical transmission of a round nano-hole array perforated silver film and pointed out that EOT occurred through two LSP's weak coupling and subsequent continuous coupling [84]. In 2006, Hanwei Gao demonstrated the contribution of surface plasmons in enhancing the light transmission over a metallic subwavelength hole array [85]. The evanescent waves has also been considered for the enhanced transmission [81, 82].

Figure 2.11. Transmission spectra with different light incident angle (Ref. [2]).

When the light illuminates to the metallic surface, it excites the free electrons there produces a wave travel along the interface of the metal-dielectric interface called surface plasmon-polariton waves. The electromagnetic field intensity decreases exponentially with the distance away from the interface is shown in Fig. 2.12.

Figure 2.12. A plasmon-polariton wave along a metal – dielectric interface (Ref. [86]).

A surface plasmon wave vector obeys the following dispersion relation (ϵ_d , ϵ_m : dielectric and metal permittivity respectively):

$$k_{SP} = \frac{\omega}{c} \sqrt{\frac{\epsilon_m \epsilon_d}{\epsilon_m + \epsilon_d}} \quad (2.4)$$

Most researchers think when the light impinges onto the metal film the incident light and surface plasmons (SPs) meet the momentum matching condition and then create traveling surface plasmon polaritons (SPP) or localized surface plasmon (LSP) that bind the energy of the light field into one side of the metal surface with the help of reciprocal lattice vector provided by the periodic nano-hole array. Finally, the trapped energy spreads to the other surface of the metal film and the radiates inversely. When the metal film is thin enough, the coupling between plasma waves on both metal surfaces develops hole-tunnel effect into the resonance mode, resulting in enhances transmittance at some specific wavelength (λ_{max}) given by:

$$\lambda_{max} = \frac{P}{\sqrt{\frac{4}{3}(i^2 + ij + j^2)}} \sqrt{\frac{\epsilon_m \epsilon_d}{\epsilon_m + \epsilon_d}} \quad (2.5)$$

where P is the period of the array, i, j are the scattering orders of the array. It does not consider the interference among the holes that give rise to a resonance shift [38]. Therefore, the calculated peak positions are a bit shorter than the measured results shown in Fig. 2.13.

Figure 2.13. the Peak positions at wavelengths slightly shorter than the prediction (Ref. [80])

2.2.2. The dependence of EOT on the material properties and geometric parameters

Many studies have been conducted to studying the dependence of EOT on various structure properties including material and geometry characteristics, such as the distance between two adjacent holes (period), hole shape, film thickness.

Referring to the material, both experimental and simulation result shown that that noble metals (Au and Ag) give better performance for EOT than others (Ni, Co) (Fig. 2.14) [2, 83, 87, 88].

Figure 2.14. Optical response of subwavelength hole array drilled on different metallic film. a) Simulation result based on finite difference time domain method (Ref. [87]), b) Experimental results (Ref. [88]).

In Fig. 2.15, it shows clearly the peak blue-shifts when the period reduces as expected. Because of the period effects to the phase matching between the incident light and the SP waves. Furthermore, the hexagonal array showed better transmission 40% compared with 28% transmission of the square lattice array.

Figure 2.15. (a,b) Transmission of a square and hexagonal arrays (d : hole diameter) as a function of the period a_0 (Ref. [89]), c) Peak positions of different metals with the change of period. Dotted line: light on a glass substrate (Ref. [88]).

Hue Cao [90] and Koerkamp et al. [91] have shown that the extraordinary transmission is significantly affected by the hole shape. The square holes are considerably better than the round holes while rectangular holes are better than square ones [92]. Kim & Moyer [93] fabricated the triangular holes arrays which shown more transmission than circles or squares.

Figure 2.16. The transmission spectra for different hole shape. a,b) Ref. [90], c) Ref. [91], d) Ref. [93].

With respect to the hole size, in circle hole, the maxima and minima occur wavelength positions do not change too much [89], but the transmission increases when the hole diameter d increases (Fig. 2.17a). In square hole (Fig. 2.17b), the broader width causes a stronger transmission and broader peaks. The peaks position change as well [94].

Figure 2.17. a) Transmission spectra for different hole diameter d (Ref. [89]), b) Transmission spectra for different square hole width (Ref. [94]).

From Ref [95] when film thickness increases until it equals the depth of the skin, the enhancement also increases. If metal film is thicker than a skin depth, a slight improvement at the resonant frequencies is added (Fig. 2.18a). Ref. [96] strongly confirm this dependence, as shown in Fig. 2.18 b, c. Furthermore, if the holes was filled with the dielectric material, the better transmission could be obtained [97]. Gordon et al. [98] used elliptical holes which their direction are different from the hole array to separate the role of the hole shape and the period on light polarization.

Figure 2.18. a) The transmission spectra from bottom to top correspond to a metal film thickness of 10, 25, 50, 100, 150, and 300 nm respectively (Ref. [95]), b, c) Measured amplitude transmission of various thickness (Ref. [96]).

2.2.3. Application

Besides finding the mechanism behind the EOT phenomenon and the dependence of EOT on the geometrical parameter, applications are also attracted more attention. With the advances in fabrication of subwavelength hole-arrays, it can create easily an array of hole at the nanoscale on a large substrate with high transparent and low-cost techniques, such as soft interference lithography [99], template stripping [100], nano sphere lithography [101], nanoimprinting [102], nanoimprinting lithography [103] and laser interference lithography [104]. It helps many groups integrate hole array into devices for a larger number of applications including filtering, polarization control, nonlinear optics, sensing, and spectroscopy.

Filtering and switching. for filter design purposes, the nanoholes array was used as ultracompact optical filter, in which its spectrum properties are adjustable and scaled easily [105]. For optically-triggered switching, the properties (refractive index, the absorption) of materials can be applied to change the resonances, [106] (Fig. 2.19).

Figure 2.19. Differential transmission of an array of nanoholes (Ref. [106]).

Polarization control. The elliptical and rectangular holes can be used to create a nano polarizers to the resonant transmission [91, 107]. The polarization of the transmitted beam is also affected by the array arrangement because the SPs, at the hole, are scattered in the electric field direction of the incident light [98] (Fig. 2.20).

Figure 2.20. The transmitted polarization is controlled by the lattice arrangement (Ref. [108]).

Nonlinear optics. materials classically have weak nonlinear optical properties. To have the nonlinear conversion, high local fields and phase-matching are needed. Subwavelength hole arrays can provide resonant enhancement in subwavelength dimensions, below the diffraction limit and opportunity for phase-matching [3]. Some studies have been executed for SHG (Second Harmonic Generation) with triangular holes [109], double-holes [110], and also for THG (Third Harmonic Generation) [111].

Surface plasmon resonance (SPR) sensing. In Ref. [81], this was the first demonstration of the dependence of transmission resonance to the refractive index (RI) that the transmission resonance wavelength was shifted when the RI of the solution surrounding the arrays change. Standard SPR bio sensing from a planar gold film is proposed by Kretschmann and Raether [112], based on the total internal reflection phenomenon. However, the reflection setup generated the distortions to the imaging and this structure is really difficult to miniaturize or integrate into lab-on-chip devices. With nanohole arrays, we can use the transmittance mode of the SPR [113, 114] (Fig. 2.21).

Figure 2.21. a) The transmission mode configuration, b) Transmission spectrum of the different solutions of known refractive index, c) The relative red-shift for three SPR peak as a function of refractive index (Ref. [114]).

Surface-enhanced fluorescence. the fluorescence output which is normalized to the aperture fill fraction can be enhanced by nearly 40 times [115]. By changing the geometric parameters of the arrays, the transmission and localization of laser excitation can be tuned. Therefore, a large amount of fluorescence relative can be achieved compared to the identical films coated on glass slides [116]. The dependence of the measured enhancement factor (EF) with the holes period is shown in Fig. 2.22.

Figure 2.22. The measured enhancement factor (EF) with different the holes period (Ref. [116]).

Surface-enhanced Raman scattering. It is normally a weak signal. However, in surface enhanced Raman scattering (SERS), when the plasmonic structures adsorbed the molecules, the Raman signal can be notably enhanced [117]. Nanohole arrays resonantly enhanced the local fields at the surface, so it is useful for the dense bio-chips fabrication in the Raman detection with high sensitivity and selectivity. The dependence of the SERS responses on the hole period was shown in Fig. 2.23. When the laser wavelength is near to the SP resonance (red spectra), a strong enhancement is obtained [118].

Figure 2.23. Nanohole-enhanced Raman scattering with different hole period (p). The inset shows the transmission spectra of the array: (a) $p = 560$ nm; (b) $p = 590$ nm; (c) $p = 620$ nm (Ref. [118]).

Absorption spectroscopy. The metallic nanohole arrays can be applied to enhance absorption in visible absorption [106] and infrared absorption spectroscopy [119-121].

2.3. Remark

Most of the available studies focused more on the transmittance of the light after transmitting through subwavelength holes array so it motivates this study to investigate the phase information when the frequency comb laser interacts with the metallic subwavelength hole array. The successful of the study can propose a lot of applications in the future such as plasmonic ruler, bio-chemical sensing. Where the results could be measured with high speed, high resolution, and traceability to a time standard.

In Ref. [122] they demonstrated using Terahertz time-domain spectroscopy (THz-TDS) as a method for characterizing the transmission and the phase change of terahertz pulses, which pass over a metallic films perforated with a nanohole arrays on silicon wafers substrate. THz-TDS also was applied in Ref. [90] and [95]. But this method only works in the far-IR regime with the frequency range 0.1 THz to 10 THz correspond from 3 mm to 30 μm of wavelength. In this thesis, two different methods were used to analyze the phase information in the visible spectrum: spectrally resolved interferometry and heterodyne interferometry.

Figure 2.24. a) THz time-domain spectrometer experimental schematic (Ref. [123]). b) The phase spectrum from bottom to top correspond to a metal film thickness of 10, 25, 50, 100, 150, and 300 nm respectively (Ref. [95]); c,d) The phase spectrum for different hole shape (Ref. [90]).

Chapter 3. Plasmonic phase measurement using spectrally resolved interferometry

3.1. Introduction

Surface plasmons (SPs) are coherent oscillations of the free charges at the interface of the metallic surface and dielectric excited by the incident light [124-126]. Their resultant optical fields are strongly confined at the metal surface, which makes them highly sensitive to nanoscale structural shapes and local refractive index changes induced by biomolecular surface binding [127, 128], molecular composition changes [129, 130], and the spectral resonance of atomic vapours [131]. Therefore, surface plasmon resonance (SPR) has been widely used in the fields of chemical, biological, and environmental sensing, and has enabled high-sensitivity, label-free, and real-time measurement in a small footprint. Recently, a fast and robust sub-nanometre-resolution plasmonic ruler attracts higher attention [132-135]. Quantum mechanical effects in plasmonics, such as electron tunnelling and non-local screening, become important as the gap between plasmonic particles approaches the sub-nanometre scale, which is beyond the attainable resolution of state-of-the-art scanning electron microscopes (SEMs) [132]. Biomolecular rulers for detecting the hybridization dynamics of DNA oligonucleotides require real-time monitoring of the gap between two plasmonic particles attached to a DNA with sub-nanometre resolution [133-135]. However, picometre-precision plasmonic rulers for atomic scale sample dynamics measurement have remained unexplored to date.

1 Most SPR techniques are based on the monitoring of colorimetric spectral peaks,
2 intensity variations at a single wavelength of interest, or plasmon-enhanced
3 nonlinear/fluorescent emissions, all of which are based on intensity measurements [127,
4 128]. Meanwhile, in optical spectroscopy, broadband phase spectra are known to provide
5 richer, linear, and more direct sources of information on target samples compared to
6 traditional intensity spectra [75, 136]. However, despite their fundamental importance, the
7 direct acquisition of broadband phase spectra has proven difficult in plasmonics, owing to
8 the critical requirements for highly stabilized light sources, coherent optical
9 interferometers, and stable optical paths that are impervious to environmental changes.
10 There have also been attempts in plasmonics to develop broadband phase spectroscopy,
11 but these works leveraged phase spectra via traditional spectrometers designed for spectral
12 intensity measurement [41, 42, 137]. Therefore, because they still relied on intensity
13 measurements, the performance of these methods was limited by low-frequency noise.

14 A femtosecond frequency comb laser including millions of optical frequencies
15 which are phase-locked to an atomic clock of a time standard has a broad spectrum with
16 high phase stability [4, 5, 51]. Frequency combs made the realization of broadband phase
17 spectroscopy of gaseous constituents simpler and more precise [75, 136]. The
18 interrelationship between the frequency comb and surface plasmons was recently reported
19 [44], it was found that the performance of the frequency comb was maintained with
20 negligible degradations in absolute frequency position, stability and linewidth. However,

1 although the frequency comb was proved to be a promising light source for plasmonics, no
2 demonstrations have been provided to date.

3 Therefore, this research reported an interferometric approach to measure the
4 plasmonic EOT phase based on spectrally resolved interferometry using a frequency comb
5 as a light source. It converts the spectral phase distribution to spectral amplitude
6 distribution. A series of data processing, Fourier transform, data filtering, inverse Fourier
7 transform, and phase unwrapping, are used for the full reconstruction of amplitude and
8 phase spectrum over a wide spectral range.

9 **3.2. Method**

10 **3.2.1. Frequency comb**

11 A spectrally broadened visible frequency comb (FC-1500-250-WC, M-VIS, Menlo
12 Systems) was used as the light source. The master oscillator was an Er-doped fiber
13 femtosecond laser having a repetition rate of 250 MHz and carrier-envelope offset frequency
14 of 80 MHz, a center wavelength of 1560 nm, and a spectral bandwidth of ~25 nm. The
15 power was amplified at two Er-doped fiber amplifiers (EDFAs); one was used for
16 frequency stabilisation and the other for nonlinear spectral broadening. At the frequency
17 stabilisation part, the repetition frequency (f_r) and carrier-envelope offset frequency (f_0)
18 were referenced to Rb atomic clock (FS725, Stanford Research Systems) for establishing
19 a frequency comb [4, 5]. At the spectral broadening part, the infrared frequency comb
20 pulses were wavelength converted to a near-infrared range of ~780 nm by second harmonic

generation, and then coupled to a photonic crystal fiber to have a broad supercontinuum over 530 to 950 nm.

3.2.2. Design of the plasmonic EOT sample

The Finite-difference time-domain (FDTD, introduced by Kane Yee [138] in 1966) solution provided by Lumerical was used to solve Maxwell's equation for analysing the electromagnetic field distribution and the transmission spectrum. The electric field vector components in space are calculated at a certain time. Then, the magnetic components in that space are calculated at the next instant in time and the process is repeated until the electromagnetic field reaches a steady state. After a series of calculations, the optimal geometric parameters for our laser system were finalized as the diameter (d): 200 nm, pitch (l): 530 nm, and thickness (t): 100 nm. The array was made using electron-beam lithography onto 25 nm-thick ITO-coated 500 μm -thick quartz substrates (Fig. 3.1).

Figure 3.1. **a**, Plasmonic sample structure and its geometric parameters. **b**, The spectral intensity changes with different EOT pitch. **c**, The spectral phase changes with different EOT pitch.

3.2.3. Focusing on the plasmonic sample.

The frequency comb was focused on the sample surface by 4 $\times$ objective lens of 40 mm focal length. The focused power was adjusted to be less than 0.1 MW/cm² not to exceed

the thermal damage threshold ($\sim 1 \text{ TW/cm}^2$ for Au). Input polarization state was set to linear and parallel to the x -axis of periodic holes on the plasmonic sample. When the incident power to the plasmonic sample was 60 mW (beam diameter of 3 mm), the measured transmission power through the sample was 1.3 mW. At each nano-hole, the incident power is 0.60 nW and the transmitted power is 0.35 nW, which makes the transmittance of 58.3%. Based on the Bethe's theory [1], the transmittance of 780 nm light through a 100 nm radius nano-hole is 0.0065%. Therefore, the plasmonic EOT enhanced the light transmittance by $\sim 9,000$ times ($58.3/0.0065$) in this investigation.

3.2.4. Measurement principle

Spectrally resolved interferometry converts the spectral phase distribution to spectral amplitude distribution so that conventional colorimetric spectrometers can measure the phase. The simplest form of the electrical wave is $E = E_0 e^{i(kx - \omega t)}$. In the intensity measurement, the optical intensity, $I = |E|^2 = E_0^2$, is converted to the electrical signal; therefore, only E_0^2 is measured at the photodetector without an interferometer. In the case of phase measurement, the phase cannot be obtained directly by the photodetector. When two waves with the same frequency combine in the interferometer, the resulting intensity pattern $I = 2E_0^2[1 + \cos(k\alpha)]$ (α is the optical path difference) is determined by the phase difference between the two waves. Namely, the intensity measured by the photodetector now include the phase information. By using the signal analysis based on Fourier transform, the phase can be extracted out from these intensity data.

In Fig. 3.2, the experimental system to measure phase change by surface plasmon (SP) is illustrated. The generated frequency comb was divided into reference and measurement beams by 50/50 beam splitter, the measurement beam is transmitted through the EOT sample, after that is recombined with the reference by the second beam splitter. The combined beam was coupled to an optical spectrum analyser (OSA, Yokogawa AQ6370D) with a 0.05 nm wavelength resolution to spectrally analyse the interference between two beams. Since the transmittance of the plasmonic sample is relatively low (2-3% of the input), an optical attenuator was placed in the reference beam path to balance the power of two beams before the recombination, which improved the visibility of the interferogram. To balance the optical path lengths of the reference and measurement beams, optical delay lines with retro-reflectors were installed.

Figure 3.2. Mach-Zehnder interferometer optical setup. CLK: atomic frequency standard; SHG: second harmonic generation; PCF: photonic crystal fiber; HWP: half-wave plate; P: polarizer; BS: beam splitter; M: mirror; L: lens; S: plasmonic sample; RRs: right angle mirror; SMF: single-mode fiber; OSA: optical spectrum analyzer.

General spectrometers including OSA obtain spectral intensity information, not a spectral phase. A series of data processing is therefore required to reconstruct the phase

spectrum in spectrally resolved interferometry (Fig. 3.3a). The raw spectral interferogram (Fig. 3.3b) obtained by OSA was Fourier-transformed to Fourier domain (Fig. 3.3c). In the Fourier domain, the DC peak at zero frequency contains the power spectral density without phase information whereas the AC peak corresponding to the spectral carrier contains both the intensity and phase information. Therefore, the AC peak is band-pass filtered and then taken inverse Fourier transforms to the wavelength domain. Since the band-pass filter functions as the rectangular window that may distort the reconstructed signal, a Hanning window was utilized to restore the signal spectrum better around the edge region. After inverse Fourier transforms, the spectral intensity is directly obtained as shown in Fig. 3.3d, but the spectral phase requires one more step, phase unwrapping due to 2π phase ambiguity. Fig. 3.3e shows the final unwrapped spectral phase in spectrally resolved interferometry.

Figure 3.3. Spectral phase analysis in spectrally resolved interferometry. **a**, Data processing in spectrally resolved interferometry. **b**, A sample spectral interferogram with a coherent carrier. **c**, FFT spectrum. The coherent carrier is extracted out using a bandpass filter, shifted to the DC, and inverse Fourier transformed. The resulting spectral intensity and phase distributions are shown in **d** and **e**.

3.3. Simulation analysis

Fig. 3.4a shows a scanning electron microscope (SEM) image of the fabricated sub-wavelength nano-hole array. After fabrication by electron beam lithography, small pitch deviations on the order of 5.0 nm could not be resolved by the SEM images as shown in Fig. 3.4b. Fig. 3.4c, d, and e show the simulated spectral phase changes during the plasmonic EOT with different pitches, hole diameters, and thicknesses. The phase sensitivity of each parameter at a wavelength of 765 nm was 6.3 deg/nm, 0.18 deg/nm, and 0.014 deg/nm, respectively. The spectral phase was 36 times more sensitive to the pitch than the hole diameter, and 500 times more than the film thickness. Therefore, under an isotropic thermal expansion of the plasmonic sample, the phase change will be approximately 97.1% dominated by the hole pitch.

Figure 3.4. Subwavelength hole array design. **a**, Scanning electron microscope image of a sample for our experiments, the diameter (d): 200 nm, pitch (l): 530 nm, and thickness (t): 100 nm on a 25-nm thick ITO-coated Quartz substrate. **b**, Magnified views of the samples with different pitches. The pitch, the distance between two sampled holes in EOT, cannot be resolved due to the high pitch-to-deviation ratio ($\sim 0.95\%$). **c**, Spectral phase changes with different EOT **c**, pitches (l), **d**, hole diameters (d), and **e**, Au thin film thicknesses (t) by XFDTD simulation.

3.4. Plasmonic phase measurement using spectrally resolved interferometry

Figure 3.5. Phase measurement of plasmonic EOT by spectrally resolved interferometry. a) and c) Spectral interference with and without EOT, respectively. Insets show the magnification view of the interferogram. b) and d) Reconstructed intensity and phase spectrum by means of Fourier transform. Insets show the Fourier transform of the interference, which an AC peak was filtered out.

In Fig. 3.5, the pink interference (Fig. 3.5a) was obtained when the EOT sample was put in the measurement arm. Whereas the blue one (Fig. 3.5c) was in the case we removed the sample. The non-uniform spectral structures of the interferograms are caused by spectral broadening process. The frequency comb is made of femtosecond laser pulses whose original spectral bandwidth is tens of nm; the high peak power of femtosecond pulses enables the coherent nonlinear spectral broadening to over an octave spectrum. However, the spectral broadening is based on the nonlinear optical process including self-phase modulation and four-wave mixings, which are known to generate the non-uniform spike spectral distribution [139, 140].

The OSA only recorded the intensity of the interferogram, to get the phase information the Fourier filter was applied. The analysis of the process is shown in Fig. 3.3. The data obtained by the OSA was Fourier transformed. One of the AC peaks was extracted

by the band-pass filter, then it was analysed by inverse Fourier transform. Consequently, the reconstructed intensity and phase spectra are shown in Fig. 3.5b and d. By dividing the pink by the blue intensity and subtracting the pink by the blue, we derived the intensity and the phase change caused by the plasmonic sample (Fig 3.6a).

Because of the narrow wavelength range, the intensity ratio does not show clearly trend following the well-known EOT intensity transmittance in Ref. [2] but in a broader wavelength shown in the inset of the Fig. 3.6a we could see a series of transmission peaks and dips. As shown in figure Fig. 3.6a, the phase change of the light by the plasmonic sample was centered at 782 nm, comparable with the 775 nm in the simulation (Fig 3.4c). The depth of the experimental phase was 43.8 degrees.

Figure 3.6. The phase change when the frequency comb laser transmits through a metallic subwavelength hole array. a) The upper graph shows the ratio between intensity profiles in Fig 3.8b-3.8d. The inset shows the intensity ratio in a broadband wavelength range. The lower graph is the phase difference between the phases in Fig 3.8b-3.8d. b) Allan deviation of the phase fluctuation which is shown in the inset at three different wavelength positions.

To estimate the phase stability at different wavelength positions, the experiment was performed for one hour which results represented by the Allan deviation in Fig. 3.6b. The

760 and 820 nm spectra are outside of phase change position by the plasmonic sample (off-resonance). In those cases, the Allan deviations of each spectrum are the almost same level which is 10^{-2} at 10s averaging time. But near the 780 nm that is the position of phase change by the plasmonic sample (on-resonance), the Allan deviation has increased at the long averaging time. This long-term drift can be occurred by the geometrical parameter change of the plasmonic sample. Since the experimental environment is not perfectly controlled, the change in the phase of the light by plasmonic sample fluctuated with the time that makes the degradation on the frequency stability. It shows that the plasmonic phase is very sensitive to the sample geometrical parameter change caused by temperature. To demonstrate this hypothesis more convincing, a new setup was designed which helps control the temperature of the EOT sample (Fig. 3.7). Temperature change makes the geometrical parameters of the sample change such as pitch length, hole size, and thickness. Which pitch length has more effect on the phase than the others (Fig. 3.4).

Figure 3.7. The hardware configuration used for controlling the EOT sample's temperature.

A thermo-electric heating element (TEC1.4-6, Thorlabs) based on Peltier effect was used for modulating the temperature of the plasmonic sample. By modulating the injection current to the TEC sinusoidally, the temperature of the plasmonic sample mounted on the

TEC was modulated. The temperature of the plasmonic sample was monitored by a platinum resistance temperature detector (TH100PT, Thorlabs), which was glued on the sample surface. Since the heat capacity of the plasmonic sample is relatively low and the modulation frequency is low, the temperature distribution in the plasmonic sample is expected to be uniform.

The measured temperature is shown in Fig. 3.8 with the 0.005 Hz modulation frequency and $\sim 50^\circ\text{C}$ amplitude. In Fig. 3.8, the lower graph is the phase differences at three different wavelengths 760, 780 and 820 nm. At two off-resonance 760 nm and 820 nm, the phase was almost stable, no clear modulation can be observed. While at on-resonance 780 nm, the phase was modulated with the same frequency of the controlled temperature. The phase modulation amplitude was approximated 0.2 rad ~ 11.5 degrees. It strongly confirmed the sensitivity of the plasmonic EOT phase on the geometrical parameter of the plasmonic sample at the resonance.

Figure 3.8. The temperature of the plasmonic sample and the phase response to the temperature change in three different positions 760, 780, and 820 nm.

3.5. Conclusion

This chapter has demonstrated that the spectrally resolved interferometry can be used as a reliable method to study the phase behaviour of the interaction between the light and the subwavelength holes array. It also shows that the phase change by the EOT sample is sensitive to the change of the sample geometrical parameter.

Besides the advantage of measuring the phase of a broaden wavelength range in one shot, the spectrally resolved interferometry had shown some disadvantages. The spectral intensity measurements have hindered the ultimate resolution (a minimum resolution provided by optical spectrum analyzer is 0.05 nm), detection speed, dynamic range, and linearity of plasmonic measurements to date. In order to resolve broad plasmonic resonance peaks with high resolution, the scattered plasmonic field from the nano-structures should be averaged over a long period to suppress random background noise. However, even after averaging the data over a long period with a state-of-the-art spectrometer (in our case is 15 seconds), some residual low-frequency noise and inherent nonlinearity in resonant plasmonic peak shift remain. To overcome the limitation of the resolution and the measurement speed, we proposed a new technique called heterodyne interferometry which is explained in chapter 4.

Chapter 4. Plasmonic phase measurement using heterodyne interferometry

4.1. Introduction

To overcome the limitation of the spectrally resolved interferometry, a phase measurement using heterodyne interferometry was introduced, which is also based on Mach-Zehnder interferometer. Fig. 4.1a illustrates the fundamental concept of frequency-comb-referenced (FCR) plasmonic phase spectroscopy. A frequency comb that is phase-locked to a time standard passes through a plasmonic sample where the photon-plasmon-photon conversion is made. The plasmonic sample here consists of an array of sub-wavelength nano-holes on an Au thin-film. The incident photons of the frequency comb first couple to the surface plasmons at the Au surface, transmit through the nano-holes in the form of surface plasmons, and then coherently scatter back to photons. The other part of laser beam passes through an acousto-optic modulator (AOM) for an up-frequency shift, f_{AOM} , which works as the information carrier in the subsequent radio-frequency (RF) signal. This beam is considered a reference arm. Two beams from different paths interfere at two photo-detectors, one detects the signal at the plasmonic resonance wavelength and the other at the off-resonance wavelength, create a heterodyne beat frequency. Because a frequency comb can convert the plasmonic phase information from the optical domain to the RF domain (see Fig. 4.1b), clean phase information can be extracted from a heterodyne frequency by way of narrow-bandwidth RF filters and lock-in detection, to remove excess

Figure 4.1. Frequency-comb-referenced plasmonic phase spectroscopy. **a**, The principle of frequency-comb-referenced (FCR) phase spectroscopy. **b**, Spectral noise suppression and differential phase detection. CLK: atomic clock, M: mirror, L: lens, AOM: acousto-optic modulator, BC: beam combiner, APD: avalanche photodiode, BPF: band-pass filter, RF: radio-frequency, LFN: low-frequency noise.

11 avalanche photodiode, BPF: band-pass filter, RF: radio-frequency, LFN: low-frequency noise.

4.2. Measurement principle

When the light wave passes through the plasmonic nano-hole array, the transmitted electric fields of the measurement and reference waves, respectively denoted as E_{MEA} and E_{REF} , can be expressed as:

$$E_{MEA} = A \cdot \cos(2\pi f t + k_0 r_{MEA} + \Delta\varphi_{SP}) \quad (4.1)$$

$$E_{REF} = A \cdot \cos(2\pi(f + f_{AOM})t + k_0 r_{REF}) \quad (4.2)$$

where A is the field amplitude of the balanced measurement and reference waves, f is the optical frequency of a frequency comb mode corresponding to $n \cdot f_r + f_{CEO}$, f_r is the repetition rate, f_{CEO} is the carrier-envelope-offset frequency, n is the mode number, f_{AOM} is the frequency shift by AOM for the heterodyne detection, k_0 is the wave vector in free space, r_{MEA} and r_{REF} are the optical path lengths of the measurement and reference waves, and $\Delta\varphi_{SP}$ is the total phase retardation during the plasmonic coupling, plasmonic field propagation, and scattering back to photon at the plasmonic structure. In the Mach-Zehnder interferometer, the heterodyne optical beat converts the optical phase to the RF phase which can be expressed as

$$I_{SP_MEA}(t) = I_{DC} + I_0 \cdot \cos(2\pi f_{AOM} t - k_0(r_{MEA} - r_{REF}) - \Delta k_0 r_E(t) - \Delta\varphi_{SP}) \quad (4.3)$$

$$I_{SP_REF}(t) = I_{DC} + I_0 \cdot \cos(2\pi f_{AOM} t - k_0(r_{MEA} - r_{REF}) - \Delta k_0 r_E(t)) \quad (4.4)$$

where I_{SP_MEA} is the beat signal detected at the plasmonic resonant wavelength, I_{SP_MEA} is the beat signal at the off-resonant wavelength, I_{DC} is the background intensity including low-frequency noise contributions, I_0 the magnitude of the heterodyne beat at the RF frequency of f_{AOM} , the optical path difference of $r_{MEA} - r_{REF}$ is almost zero when the optical paths are well-matched, the environmental phase errors of $\Delta k_0 r_E(t)$ are cancelled

out by the differential phase measurement technique. Therefore, in ideal plasmonic phase spectroscopy, only the plasmonic phase change ($\Delta\phi_{SP}$) needs to be measured. The use of the RF lock-in detection at f_{AOM} results in the suppression of the low-frequency intensity noise and improves the noise floor of the spectral intensity measurement. However, as some of the phase noise is contributed by the frequency comb and interferometer unit, this phase noise must also be suppressed to enable higher-precision phase spectroscopy. This residual noise was far suppressed in this investigation by the differential phase measurement technique.

Figure 4.2. The scheme of plasmonic phase measurement in heterodyne Mach-Zehnder interferometry

In Ref. [44], the heterodyne Mach-Zehnder interferometry was also used to investigate the interrelation between the frequency comb and surface plasmon in the term of absolute frequency uncertainty, the stability and the linewidth.

Figure 4.3. RF beats generated by the interference between reference combs and plasmonic EOT combs (Ref. [44]).

4.3. Plasmonic phase measurement using heterodyne Mach-Zehnder interferometry

Figure 4.4. System configuration. CLK: clock, SHG: second-harmonic generator, PCF: photonic crystal fiber, HWP: half-wave plate, PBS: polarization beam splitter, BS: beam splitter, AOM: acousto-optic modulator, RR: retro-reflector, M: mirror, L: lens, G: grating, S: slit, and APD: avalanche photo-detector

An optical setup was configured as shown in Fig. 4.4 to detect the spectral phase response of the plasmonic specimen. The frequency comb was split into reference and

measurement beams, the reference part of the beam transmits through an acousto-optic modulator (AOM) for an up-frequency shift (f_{AOM}) of 53.2 MHz and the measurement part of the beam passes through the plasmonic sample. The optical path lengths of the two beams were matched within the short pulse envelope ($\sim 30 \mu\text{m}$) of the frequency comb using optical delay lines. Two beams were then combined by a beam combiner and directed to the phase detection part which was comprised of two gratings and two slits for optical band-pass filtering and two avalanche photodetectors (APDs) for heterodyne RF signal detection. The measurement APD detected the interference RF beat note at the side part of the plasmonic resonant wavelength, while the reference APD detected the beat note at the off-resonant wavelength. When the spectral phase distribution at the plasmonic sample changes, that phase change can be precisely quantified at a high update rate with low background noise.

Figure 4.5. RF beat spectrum with the plasmonic sample in heterodyne phase detection.

The interference beat signals were detected by high-speed avalanche photodetectors (APD210, Menlo Systems) at different wavelengths from 760 to 800 nm and analysed with a high-resolution RF spectrum analyser (DSA875, RIGOL). An RF spectrum is shown in Fig. 4.5; the repetition rate (f_r) is located at 250 MHz with a 70-dB signal-to-noise (S/N)

ratio; the beat frequency, $f_{AOM} - \Delta f_{SP}$ between the frequency-shifted reference frequency comb and the plasmonic frequency comb is at 53.2 MHz with an instrument-limited narrow linewidth of less than 10 Hz and a S/N ratio of ~ 55 dB; the beat frequency, $f_r - f_{AOM} + \Delta f_{SP}$ is at 196.8 MHz. Other minor spurious peaks are due to the imperfect sinusoidal modulation of AOM; their positions match with beat frequencies between the f_{AOM} -harmonics and the reference frequency comb of $2f_{AOM} - f_r$, $2f_r - 3f_{AOM}$, $3f_{AOM} - f_r$, and $2(f_r - f_{AOM})$.

Figure 4.6. Super-heterodyne scheme

The beat frequency at 53.2 MHz was filtered out by a low-pass filter and converted down to 1.2 MHz by mixing with the signal with a 52.0 MHz generated at the RF signal generator (DG4162, RIGOL) in the super-heterodyne unit (Fig. 4.6). Lastly, the phase of the down-converted frequency as 1.2 MHz could be measured with fine resolution in real time. While the reference APD detected the beat note at the fixed off-resonant wavelength, the measurement APD detected the interference RF beat note at the wavelength from 773 to 789 nm by scanning the grating tilt (Fig. 4.9e). The plasmonic phase spectra measured

by the phase difference between the reference and measurement frequency is shown in Fig 4.7.

Figure 4.7. The frequency-comb-referenced plasmonic phase spectrum

In Fig. 4.8, two schemes are illustrated for the plasmonic spectroscopy: FCR non-differential phase spectroscopy (Fig. 4.8a, using an RF signal generated by RF frequency generator as the reference) and FCR differential phase spectroscopy (Fig. 4.8b, the beat signal detected at the off-resonance wavelength was used as the reference signal). Because the frequency comb is tightly locked to a time standard, the phase noise caused by the light source is negligible in this investigation. However, the time-varying phase noise produced by the environmental effects in the interferometer was still relatively high at 71° over 3,600 seconds (see Fig. 4.8c). In the interferometer, two interferometric arms are exposed to different disturbances of temperature, pressure, humidity, and CO_2 concentration, which cause time-dependent slow variations in the optical path difference. When the estimated optical path length from the beam splitter to the beam combiner is about 0.85 m, the environmental changes in one interferometer arm, which include 1.0 mK in base temperature, 14 mK in air temperature, 4.9 Pa in air pressure, 1.5% in humidity, and 110

ppm in CO₂ concentration, cause a phase change of 5.0°, which is on the same order of magnitude as the plasmonic phase change made at the EOT sample. In order to suppress the environmental noise, a differential phase detection method was implemented, as shown in Fig. 4.8b. The wavelength-independent time-varying phase noise was efficiently cancelled, as shown in Fig. 4.8d. Because the reference signal traversed the same optical path as the measurement signal, the wavelength-independent common noise can be greatly suppressed. In addition, the concepts of common-path interferometry and balanced signal detection were implemented to provide higher noise immunity. For in-depth analysis, the phase stability of FCR plasmonic phase spectroscopy was evaluated in the form of the Allan deviation before and after the introduction of the differential phase detection as shown in Fig. 4.8e and 4.8f. A 48-fold improvement in phase stability was observed, with an average differential phase detection time of at 200 s.

Figure 4.8. **a**, FCR non-differential phase spectroscopy (using an RF reference signal). **c** and **e**, the phase fluctuation and the corresponding Allan deviation (dark yellow and orange are without and with EOT respectively). **b**, FCR differential phase spectroscopy. The heterodyne RF beat signal detected at the off-resonance wavelength is used as the reference signal for the differential phase detection. **d** and **f**, the phase fluctuation and the corresponding Allan deviation (blue and pink are without and with EOT respectively).

4.4. Plasmonic dynamics measured with FCR phase spectroscopy

To demonstrate the high-resolution dynamic plasmonic motion measurement by FCR differential phase spectroscopy, an angstrom-level thermodynamic modulation was applied to the plasmonic sample to change its physical dimensions, as shown in Fig. 4.9a. With the aid of a thermo-electric cooler (Fig. 3.7), the temperature of the plasmonic sample was modulated by 26.1 °C at 0.02 Hz, which translates to a pitch modulation of 1.94 Å around a nominal value of 530 nm considering the thermal linear expansion coefficient of gold ($\sim 1.42 \times 10^{-5} \text{ K}^{-1}$) [141]. The parametric effects of the temperature modulation to other than the pitch was evaluated to be less than 5.9% (see Table 4.1 and Fig. 4.10). The surface temperature was monitored by a platinum resistant thermistor, as shown in Fig. 4.9b, and the Fourier-transformed frequency spectrum clearly shows a distinct peak at the modulation frequency of 0.02 Hz (see a right-hand panel in Fig. 4.9b). The dynamic motion of the plasmonic sample was measured at three different wavelengths: one on-resonance at 780 nm and two off-resonances at 690 and 800 nm. At the resonance wavelength, the periodic dynamic motion at 0.02 Hz was resolved in the time and frequency domains with a peak-to-valley amplitude of 14.3° in (see Fig. 4.9d), whereas this periodic motion could not be seen at the off-resonance positions (see Fig. 4.9c and 4.9e). Here, the plasmonic resonance effect acts as an optical resonator like Fabry-Perot cavities, which increases the effective length of interaction between the photon and the plasmonic sample. This efficient interaction can also be observed in different plasmonic geometries, for example, a nano-gap antenna array (see Fig. 4.14), which implies that this phase spectroscopy is universally

applicable to various plasmonic structures. This demonstration shows that FCR differential phase spectroscopy can be used as a plasmonic ruler that not only provides high resolution but also high precision, thanks to its direct traceability to the atomic clock of the time standard.

Figure 4.9. Precision measurement of a sub-nanometre dynamic motion of a plasmonic EOT sample. **a**, Dynamic motion applied to a plasmonic EOT sample. **b**, Temperature variation at the sample surface. **c**, **d**, **e**, Dynamic motion measured by FCR differential phase spectroscopy at three different wavelengths, one at on-resonance (780 nm) and the other two at off-resonance ones (690 and 800 nm). **f**, Resolution analysis by Allan deviation. All three data were attained with the plasmonic sample at the on-resonance wavelength of 780 nm.

To quantitatively evaluate the measurement resolution and update rate, Allan deviations were derived at various averaging times for the following three principles: FCR

1 spectrally-resolved interferometry, FCR non-differential phase spectroscopy, and FCR
2 differential phase spectroscopy (see Fig. 4.9f). Compared to spectrally-resolved
3 interferometry, FCR non-differential phase spectroscopy provides a 20-fold improvement
4 in the phase stability of $2.4 \text{ \AA}$ at an average time of 40 s, and a 1000-fold improvement in
5 measurement speed of $200 \text{ samples} \cdot \text{s}^{-1}$ (the smallest averaging time). Meanwhile, in FCR
6 differential plasmonic phase spectroscopy, the long-term phase stability was improved by
7 an additional two orders of magnitude, and the measurement resolution was better than 5.3
8 pm for all averaging times longer than 100 ms. The resolution of the plasmonic ruler was
9 defined here to the measurement stability as an Allan deviation [142-144], which implies
10 that one can resolve a small motion with this amplitude. The best-attained resolution at 40
11 s corresponded to 1.67 pm in Allan deviation as shown in Fig. 4.9f, which is two orders of
12 magnitude better resolution than the previous report [134] even with a higher measurement
13 speed by three orders of magnitude. The dynamic plasmonic motion in Fig. 4.9d
14 corresponds to a modulation depth of $1.94 \text{ \AA}$ and a modulation frequency of 0.02 Hz, as
15 indicated by ‘M’ in Fig. 4.9f. From this figure, it can be seen that a motion of this magnitude
16 can be clearly resolved by FCR plasmonic phase spectroscopy. When considering the
17 wavelength uncertainty of the frequency comb, high-precision in RF heterodyne phase
18 detection, high-linearity in temperature-phase relationship (Fig. 4.13), and high phase
19 stability in a static plasmonic sample (Fig. 4.9f), the very high resolution and stability of
20 our plasmonic ruler is expected to be transferred to the measurement precision, which
21 should be certified by thorough uncertainty analysis in the future researches. This series of
22 experiments prove that the dynamic motions of plasmonic samples can be measured with

an unprecedented picometre resolution at a sampling rate of 200 Hz (corresponding to the smallest averaging time 0.005 s) with the proposed scheme, which will enable real-time monitoring of nanoscopic dimensional structural sample dynamics in physical, chemical, and biological sample sciences.

4.5. Discussion

4.5.1. Theoretical investigation the parametric effects under the temperature modulation

A small thermodynamic motion by applying the temperature modulation to the plasmonic sample could be associated with other side-effects than the pitch modulation, such as temperature change of the surrounding air, temperature change of the quartz substrate (causing the changes in thickness and refractive index), and other dimensional changes of the plasmonic sample (i.e. hole diameter and film thickness). Because the plasmonic resonance is known to be also sensitive to these parametric changes, all these effects have been carefully considered. The temperature-dependent refractive indices were calculated by NIST database and Sellmeier equation (Ref. [145-149]) as shown in Table 4.1; then, their effects on the plasmonic phase were analyzed by the FDTD simulation as shown in. Fig. 4.10. Under the air temperature modulation from 50 to 75 °C (the same amplitude with Fig. 4.9b), the plasmonic phase change made by the air refractive index change was evaluated to 0.0039% (Please See Fig. 4.10a). Under the temperature modulation of the substrate from 50 to 75 °C, the plasmonic phase change made by the quartz refractive index change was 0.0116% (Please See Fig. 4.10b). The thermal

expansion of the substrate additionally induces the phase change via the thickness change. Our differential plasmonic phase detection scheme measures the phase difference between two phases, one at the reference wavelength and the other at the measurement one; thus, the linear phase changes are subtracted out. Under the substrate's temperature modulation from 50 to 75 °C, the phase changes were 4.99° at the reference wavelength (700 nm) and 4.58° at the measurement wavelength (765 nm); thus, the residual phase difference after the subtraction was 0.41° which is 2.9% of the plasmonic phase change (See Figure 4.10c and 4.11c). Other parametric effects on the hole diameter and the film thickness were proved to be less than 2.8% and 0.2% of the pitch modulation as shown in Fig. 3.4d and 3.4e. These results imply that the plasmonic phase change is the most sensitive to the pitch modulation although it is also sensitive to the refractive indices of air and quartz substrate. Therefore, the thermodynamic motion of the plasmonic sample in this investigation is dominantly made at the pitch modulation; the overall side effects to air refractive index, substrate, hole diameter, and film thickness are proven to be less than 5.9%.

Table 4.1. Temperature dependence of the refractive indices of air and quartz substrate [145-149].

Temperature (°C)	n_{air}	n_{quartz}
25	1.000265910	1.449987180
50	1.000245296	1.449997576
75	1.000227647	1.450002088
Sensitivity (RIU/°C)	7.0596×10^{-7}	1.8048×10^{-7}

Figure 4.10. Spectral phase changes made by temperature changes in air and quartz substrate. **a**, Plasmonic phase change caused by the temperature-dependent air refractive index. **b**, Plasmonic phase change caused by the temperature-dependent refractive index of the quartz substrate. **c**, Phase change caused by the thickness change of the quartz substrate.

4.5.2. Experimental measurement of the substrate effect

To compensate for the phase change made by the substrate, a reference phase spectrum was acquired without the plasmonic structure at a standard environment and subtracted from the measurement phase spectrum attained with the plasmonic structure. The plasmonic structure was patterned at a certain part of the sample, so the sample was laterally shifted for acquiring the reference and measurement phase spectrum. In addition, when the temperature of the bare quartz substrate was modulated without the plasmonic structure on top, the phase modulation could not be detected as shown in Fig. 4.11, because the differential spectroscopic phase-detection cancels out the linear phase changes at the

- 1 two wavelengths, one on-resonance (measurement phase) and the other at off-resonance
 2 (reference phase) (See Fig. 4.11c).

Figure 4.11. Phase changes made by the temperature changes of quartz substrate without the plasmonic structure on top. **a**, Temperature modulation of the quartz substrate at 0.02 Hz. **b**, The phase modulation measured at three different wavelengths of 700, 780, and 860 nm. **c**, The phase changes made by the thickness variation of the quartz substrate using FDTD.

4.5.3. Phase drift and delay under the periodic temperature modulation

For generating a periodic structural change of the plasmonic sample, a sinusoidal temperature modulation was applied to the sample as shown in Fig. 4.9. Because the heat transfer has a slow dynamic response, there was unexpected slow temperature drift together with the target sinusoidal modulation (Fig. 4.9d). Meanwhile, in environmental phase stability tests shown in Fig. 4.8d, where the temperature modulation was not applied, no long-term phase change was observed. The temperature sensor was installed at the side part of the plasmonic metal sample which is a few millimeters apart from the plasmonic sample. Thus, the phase shift was made due to the slow heat transfer and the position of the temperature sensor, not due to the plasmonic ruler itself. Plasmonic propagation is

known to be ultrafast phenomena so plasmonic phase delay in metal nanostructure was measured to be less than tens of femtoseconds [150].

4.5.4. The depth and the bandwidth of the plasmonic phase dip

The depth of the spectral phase dip was different at two schemes, which was 43.8 degrees in the FCR spectrally resolved interferometry (Fig. 3.6a) and 212 degrees in the FCR differential phase spectroscopy (Fig. 4.7). The shallower phase dip in the spectrally resolved interferometry is expected to be caused by the accumulated environmental errors during the measurement; the environmental phase errors are accumulated during the acquisition time of ~ 4.0 seconds, resulting in lower the signal-to-noise ratio. On the contrary, the differential phase spectroscopy is immune to the low-frequency environmental noise, so it can provide better signal-to-noise ratio with high contrast. The spectral resolutions of both methods were better than 0.05 nm in wavelength, which is enough for the spectral dip detection.

Figure 4.12. EOT transmission and phase spectrum by simulation and experiment. **a**, (Simulation) Transmission spectrum. **b**, (Simulation) Phase spectrum. **c**, (Experiment) Transmission spectrum. **d**, (Experiment) Phase spectrum. The experimental phase dip shows a relatively narrower bandwidth.

The spectral bandwidths of the plasmonic phase dip in the simulation and two experiments were different while the transmissions matched with the others (Fig. 4.12). Basically, two experimental bandwidths, one attained by the spectrally resolved interferometry (5.2 nm as shown in Fig. 3.6a) and the other measured by the FCR differential phase spectroscopy (4.8 nm as shown in Fig. 4.7), agree well with each other, which is, however, different from the simulation result (42 nm as shown in Fig. 3.4c). There are three possible reasons which make the experimental results different from the simulation, surface quality of the sample, the incident angle of the light source to the

sample, and finite sample size. Surface plasmon propagation through rough surfaces can be deviated from the ideal plasmonic propagation. The total phase retardation, $\Delta\varphi$ during extra-ordinary transmission can be expressed by $\Delta\varphi = k_{sp}L + \varphi_0$, where k_{sp} represents the real part of the propagation constant of the surface plasmon, L is the propagation distance of surface plasmon and φ_0 is the intrinsic phase shift of the surface plasmon during the excitation and re-scattering process. The second term, φ_0 is not relevant to the bandwidth of the phase dip, because the intrinsic phase shift is known to be a linear function of the wavelength; therefore, the difference is expected to come from the first term related to the propagation effect [151-154]. Due to the imperfect manufacturing processes (including e-beam evaporation and focused-ion-beam drilling), the real plasmonic sample has the surface roughness and grain boundaries over several nanometers, which could not be considered in the simulation (the simulation is based on an ultra-flat perfect surface without surface roughness or grain boundary effects). These can result in longer electron relaxation time and additional delay in resonating plasmonic propagation, which induce much larger dispersion when coupled with the plasmonic resonance effect; as the result, a stronger phase change can be observed in the experiment. In order to couple the frequency comb into a small plasmonic sample, a loose focusing was done with a lens having a low numerical aperture of 0.1 in the experiment, whereas the incoming light was modelled as a single plane wave in the simulation. This incident angle could induce the different phase retardation and dispersion in the plasmonic propagation, which could average out the side parts of the spectral phase dip. Due to the fabrication issues of E-beam lithography, the plasmonic sample was manufactured over $500\text{ }\mu\text{m} \times 500\text{ }\mu\text{m}$ by printing the smaller sub-

sections ($20\ \mu\text{m} \times 20\ \mu\text{m}$ in size) by 625 times. Each sub-section could function as an unexpected boundary causing additional local reflections and resonances of the surface plasmons. The greater number of holes (or infinity holes) in simulation leads to stronger resonance which could make a broader phase dip in ideal cases. Due to the practical limitations, the perfect phase matching over a large (or infinity) area could not be realized in this experiment.

Regarding the oscillation in the experimental spectrum (Fig. 4.12), it could come from the light source. The frequency comb in this experiment has a center wavelength of 1560 nm, and a spectral bandwidth of ~ 25 nm, then it was wavelength converted to a near-infrared range of ~ 780 nm by second harmonic generation, and finally coupled to a photonic crystal fiber to have a broad supercontinuum over 530 to 950 nm. This process could make the spectrum not too smooth.

4.5.5. Sensing linearity

The sensing linearity between the input temperature and output plasmonic phase was evaluated and found to have an R^2 value of 0.9998 with a standard error of 0.0012 (see Fig. 4.13). The linear slope corresponded to $-73.3\ ^\circ\cdot\text{nm}^{-1}$. In the traditional Mach-Zehnder interferometry, the relation between the phase difference (φ) and the optical path difference (OPD) can be presented by the equation: $\varphi = \frac{2\pi}{\lambda} \text{OPD}$. In this case, with the $\lambda = 780$ nm, the calculated slope is $\frac{2 \times 180}{780} \approx 0.47\ ^\circ\cdot\text{nm}^{-1}$. It means the obtained slope is 155 times steeper than the slope of traditional optical interferometry. Comparing with the simulation

results (Fig. 3.4c), the simulated slope is 8.9 degree/nm. It is a 8-time difference from the experiment slope $-73.3^{\circ}\cdot\text{nm}^{-1}$. This number is comparable with the bandwidth difference ($42/4.8 = 8.75$, section 4.5.4). This high linearity between the phase and the effective plasmonic path proves that the phase multiplication factor at a plasmonic structure is consistent for a given shape and is not affected by geometric parametric modulation. Here, ‘deg °’ is for the angle, not temperature and ‘nm’ is the expanded length, not for wavelength. This shows the high-precision of the measurement with traceability to a time standard.

Figure 4.13. Linearity test between the temperature and phase in FCR differential phase spectroscopy.

4.5.6. Universality at plasmonic rods

To verify the universality of FCR plasmonic phase spectroscopy for other plasmonic structures, the plasmonic gap antenna structure was theoretically investigated. The

designed antenna consists of two Au nano-rods, having the width, thickness, and gap of 100 nm. The length (h) of rods was changed from 280 to 320 nm with a step size of 10 nm, as shown in Fig. 4.14. The scattered fields were monitored at the center of nano-gap and the phase change with different rod lengths was analysed. The consistent phase changes were observed around the specific wavelength region of plasmonic resonance. This implies that FCR plasmonic phase spectroscopy can also be applicable in other types of plasmonic geometry including the nano-antenna structure.

There are several plasmonic have been reported as a plasmonic ruler. For example, the gold sphere [155], a concentric square nanoring–disk and an outside nanorod [156], split-ring resonator structure [157], five gold nanorods for 3D ruler [134]. I believed that the FCR plasmonic phase spectroscopy can fully apply to these structures and these demonstrations will be my next research goal.

Figure 4.14. Plasmonic phase change at a pair of Au nanorods. **a**, Plasmonic phase distribution of a pair of plasmonic nanorods with different lengths. **b**, Magnified phase distribution around the resonance position. The phase gaps are in a linear relationship with the length of the structure.

4.5.7. The necessity of the frequency comb in plasmonic phase spectroscopy

Tunable single-wavelength lasers have long been used in the field of atomic and molecular spectroscopy due to the narrow linewidth of the atomic/molecular transition lines. Meanwhile, white-light sources have been utilized for broadband spectroscopy with a lower spectral resolution. Contrarily, in high-precision plasmonic phase spectroscopy intended in this investigation, the light source should satisfy three requirements: (1) broad wavelength range, (2) high wavelength stability, and (3) narrow modal linewidth, which cannot be fulfilled with a tunable single-wavelength laser or a white-light source but can be fulfilled with a frequency comb. Detailed explanation on these critical requirements and how a frequency comb satisfies those are summarized with Table 4.2 as follows.

(1) Broad wavelength range: Plasmonic resonance provides a broad resonance peak over 320 nm in full-width-half-maximum in the wavelength domain [134], which is about 1,600,000 times broader than those in atomic spectroscopy (typical linewidth is less than 100 MHz (0.2 pm at 780 nm central wavelength) [158]. Therefore, in order to confirm the multiple resonant peaks' wavelength positions and understand their resonance characteristics, a broadband light source is the prerequisite. In addition, the spectral resonance shift in a general plasmonic ruler is at least more than ~ 100 nm in wavelength. Even state-of-the-art tunable single-wavelength lasers can cover about 100 nm, which cannot fulfill this requirement; therefore, one cannot resolve even a single plasmonic peak with a tunable single-wavelength laser. Here, with the aid of the frequency comb, we could

1 carefully analyze the phase spectrum around the plasmonic resonant peaks over a broad
2 spectral range.

3 (2) High wavelength stability: Precision phase measurement in this investigation
4 provided a 1.67 pm position stability at an averaging time of 10 s for plasmonic motion
5 detection. To realize this high-level stability in phase measurement, a light source should
6 provide high wavelength stability, because the wavelength instability is amplified together
7 with target plasmonic motion. In this paper, we presented clear comparative data in Fig.
8 4.9f showing that a frequency comb provides superior phase stability than precedent
9 spectrally resolved interferometry. Our FCR plasmonic phase spectroscopy provides about
10 three orders of magnitudes better phase stability, so enabled to detect plasmonic motions
11 with a picometre position stability. In the cases without the repetition rate or carrier-
12 envelope-phase stabilization, the phase stability was significantly deteriorated especially
13 at longer averaging times in Allan deviation due to environmental disturbances; the phase
14 variation without the frequency comb stabilization was governed by environmental effects
15 so showed similar phase drift as shown in Fig. 4.8e. These exemplary cases prove that the
16 use of frequency comb is essential in precision plasmonic phase measurement intended in
17 this work; this phase measurement stability cannot be attained with traditional white-light
18 sources, super-continuum sources, picosecond lasers, or non-stabilized femtosecond lasers.

19 (3) Narrow linewidth: High-resolution in phase measurement in this investigation
20 was attained by high-resolution heterodyne phase detection using a radio-frequency (RF)
21 phase meter referenced to a well-defined time standard. This heterodyne phase detection

can be realized only with a narrow linewidth single-wavelength laser or a narrow linewidth frequency comb; white-light sources and supercontinuum sources cannot generate constant narrow-linewidth RF heterodyne beat notes with high signal-to-noise ratio which are the prerequisites for RF lock-in phase measurement, RF phase-locked loop, or optical frequency measurement; mode-locked picosecond lasers and non-stabilized femtosecond lasers suffer from severe phase noise and broader phase fluctuations, which limits the ultimate resolution and precision attainable in phase measurement.

Table 4.2. Comparison of different light sources for plasmonic phase spectroscopy [4, 5, 51, 75, 136, 159].

	Frequency comb	CW laser	White-light
Linewidth (for high phase resolution)	Narrow (<1 Hz)	Narrow (down to several Hz)	-
Phase noise suppression (by RF lock-in phase detection)	Possible	Possible	Impossible
Spectral bandwidth	Broad (420 of nm)	Narrow (same with linewidth)	Broad (over hundreds of nm)
Wavelength stability and accuracy	$10^{-12} \sim 10^{-17}$	$10^{-9} \sim 10^{-11}$	No
Traceability to time/frequency standards	Yes	No	No

Differential spectroscopic technique and common-path interferometric design were implemented so as to minimize the environmental phase noise. However, there are still residual optical path differences about a few tens of micrometers due to the high-order dispersion effects arisen by the plasmonic sample and acousto-optic modulator. Because these dispersive optical elements induce the wavelength-dependent phase delay, all the optical path differences cannot be exactly the same over the broad spectral range; therefore, a slight mismatch less than the pulse duration of 100 fs can still be there. Due to this

residual, a minor wavelength instability of $\sim 10^{-5}$ (3.85 GHz/385 THz) at 30 μm optical path difference could generate the measurement error of 300 pm. Therefore, high phase stability is still essential for the picometre-resolution plasmonic motion measurement.

4.5.8. Potential contributions

In the field of dimensional metrology, high-finesse Fabry-Perot interferometry and coherent X-ray interferometry have provided sub-atomic picometre resolution, which, however, cannot be easily implemented to plasmonic nanostructures due to their system complexity [1, 144, 160].

FCR differential plasmonic phase spectroscopy provides two orders of magnitude higher measurement resolution which could enable sub-molecular bio-chemical sensing [127, 128], and three orders of magnitude faster detection speed which enables real-time monitoring of dynamic chemical reactions, such as DNA hybridization or formation of molecular bonding [18, 124, 126, 129, 131, 142]. In addition, sub-nm gap plasmonic structures can be precisely characterized for understanding the tunnelling effect between the gap and local field distribution for strong-field physics [132, 161, 162].

Table 4.3. Comparison between molecular ruler techniques

Method	Resolution
Our method (Nanohole array)	1.67 pm
Fabry-Perot interferometry	14 pm [163], 2.8 Å [164]
X-ray interferometry [160]	7.62 pm
Glycosyltransferase PglH [165]	2.3 Å, 2.8 Å, 3.3 Å (different substrate)
Single pairs of gold and silver nanoparticles [135]	70 nm
Fluorescence resonance energy transfer (FRET) [166]	10–100 Å

4.6. Conclusion

In conclusion, this chapter have demonstrated that frequency-comb-referenced phase spectroscopy provides high speed, high resolution, and high linearity with respect to plasmonic rulers, with direct traceability to a time standard. As a demonstration, the 1.94 Å dynamic motion of a pair of nanoholes was measured with a resolution of 1.67 pm. The interaction through the propagation of the plasmonic field is enhanced by a factor of 155 compared to the physical sample length. The realization of a fast and robust plasmonic ruler with picometre resolution makes it possible to obtain high precision plasmonic phase spectroscopy for in-depth analysis of the dynamics of samples in nanoscopic volumes.

Chapter 5. Gas refractive index measurement using FCR plasmonic phase spectroscopy

5.1. Introduction

Refractive index (RI) is an important characteristic of all gases and solutions. Under proper conditions, its measurement can be done quickly and accurately. RI is the ratio between the speed of light in a vacuum to the speed of light in this environment. This velocity will decrease when the number of molecules in a volume unit increase. In the case of gas, its density will depend on pressure and temperature [167]. Therefore, the technique of determining the refractive index of a gas can be classified into two categories: direct measurement by gas refractometer and indirect calculation from measured values of gas parameters such as pressure and temperature. For example, in the case of air, most indirect measurements are based on Edlén's formula [146] with an air RI resolution of 5×10^{-8} RIU (refractive index unit) [168]. Surface-plasmon resonance (SPR), which are coherent oscillations of the free electrons at the metallic-dielectric interface excited by the incident light, has proven itself to be applicable in biological and chemical sensors [169]. Compared to other types of sensors, SP sensors can be easily scaled down, making them suitable for lab-on-a-chip systems [170].

The commercial SPR devices typically base on Kretschmann configuration using the total internal reflection mode [171]. The high sensitivity of the method is created by the dependence of SPR on the refractive index of the dielectric material on the metallic

surface [172], which shifting angular [169, 173], spectral position of the SPR dip [174] or phase information [175] of the reflected light beam. Recently, the SPR-based sensors work with transmission modes have been reported for ultrathin gold island films [176], immobilized nanoparticles on glass [177] and a periodic array of nanoholes on Au films [113]. This mode of the SPR allows the optical system to be simpler and provides a smaller probing area than the known Kretschmann configuration.

Table 5.1. The sensitivity and resolution of the reported gas refractive index methods

Method	The information parameter	The sensitivity	The resolution
Prism coupling SPR systems (Kretschmann)	Intensity [178]	3100 – 8000 nm/RIU	$\delta n = 10^{-6} - 10^{-5}$ RIU
	Phase [172]	8 400 000 degree/RIU	$\delta n = 4 \times 10^{-8}$ RIU
	Incident angle [179]	155 degree/RIU	$\delta n = 0.016$ RIU
Nanohole array	Intensity [113]	400 nm/RIU	$\delta n = 1.1 \times 10^{-3}$ RIU
2 slits SP	Intensity [170]	4547 nm/RIU	
Graphene plasmonic	Intensity [180]	2480 nm/RIU	
Photonic Crystal fiber [181]	Phase	634 500 degree/RIU	$\delta n < 10^{-6}$ RIU
	Intensity	1233 nm/RIU	

Most SPR techniques are based on the monitoring of colorimetric spectral peaks, intensity variations at a single wavelength of interest, or plasmon-enhanced nonlinear/fluorescent emissions, all of which are based on intensity measurements [127, 128]. The accuracy of this measurement method is limited by the noise level normally approximated to be $10^{-6} - 10^{-5}$ Refractive Index Units (RIU) [182]. Meanwhile, in optical spectroscopy, broadband phase spectra are known to provide richer, linear, and more direct sources of information on target samples compared to traditional intensity spectra [75, 136]. Namely, the detection limit can be at least 10^{-8} RIU [172], 100-fold better than the intensity-based measurement. However, despite their fundamental importance, the direct acquisition of broadband phase spectra has proven difficult in plasmonics, owing to the

critical requirements for highly stabilized light sources, coherent optical interferometers, and stable optical paths that are impervious to environmental changes. There have also been attempts in plasmonics to develop broadband phase spectroscopy, but these works leveraged phase spectra via traditional spectrometers designed for spectral intensity measurement [41, 42, 137]. Chapter 4 and 5 had demonstrated that the frequency comb referenced plasmonic phase spectroscopy can solve this problem [183].

Besides the resolution, the measurement speed is also an important parameter in gas sensing. However, all the reported study of SPR-based sensor used interferometric ellipsometer for the phase detection [172, 184, 185], this technique has limited detection speed similar to the spectrally resolved interferometry reported in chapter 3.

Therefore, this research wants to demonstrate the frequency-comb-referenced plasmonic phase spectroscopy can be used for high-resolution and high-speed gas refractive index detection.

5.2. Measurement principle

Typically, two groups of SP resonance can be distinguished in the transmitted spectrum because of the two surfaces of the metal layer in contact with the different dielectric medium, normally the glass substrate and air [81]. The properties of surface plasmon wave propagate on the interface of metal and air can be adjusted by changing the dielectric medium on the surface. At normal incidence, the excited SP wavelengths by holes array are calculated by:

$$\lambda_{max}(i, j) = \frac{a_0}{\sqrt{i^2 + j^2}} \sqrt{\frac{\epsilon_{S,L} \epsilon_M}{\epsilon_{S,L} + \epsilon_M}} \quad (5.1)$$

where a_0 is the period of the array, ϵ_M is the dielectric constant of the metal, $\epsilon_{S,L}$ is the dielectric constant of either the substrate (ϵ_S) or the medium (ϵ_L) on the metal surface. i, j are the scattering orders of the array. The dependence of SPPs on ϵ_L is allowed SPP to sense the changes of the medium refractive index and act as a refractive index sensor.

Figure 5.1. Gas sensing by FCR plasmonic phase spectroscopy. **a**, System configuration, the plasmonic sample was attached in a gas chamber. **b**, The illustration of the gas molecules on the Au surface. The frequency comb excites the surface plasmon wave propagates on the sample surface. **c**, Principle of gas sensing FCR plasmonic phase spectroscopy.

Figure 5.1 illustrates the fundamental concept of frequency-comb referenced (FCR) plasmonic phase spectroscopy for gas sensing. The measurement setup was based on Mach

1 – Zehnder interferometer (Fig 5.1a). The incident photons of the frequency comb first
2 couple to the SP on the Au surface, transmit through the nano-holes, and then coherently
3 scatter back to photons (Fig. 5.1b). This process is referred to as plasmonic extra-ordinary
4 transmission (EOT). When the gas flow on the Au surface, it effects to the characteristic
5 of the SP wave. The specific dependence of EOT resonances on the refractive index near-
6 surface suggests that nanohole arrays are good platforms for chemical sensing [80]. The
7 detail of the frequency comb and plasmonic phase spectroscopy was introduced in chapter
8 4. Because a frequency comb can convert the plasmonic phase information from the optical
9 domain to the RF domain (Fig. 5.1c). A frequency comb experiences photon–plasmon–
10 photon mode conversion when passing through a plasmonic sample. The measurement
11 frequency comb passing through the plasmonic structure experiences a plasmonic phase
12 change and interferes with the frequency-shifted reference frequency comb. The
13 interference beat signals are frequency down converted to RF signals, where state-of-the-
14 art RF electronics and time standards can be applied. The resulting RF electric field
15 oscillation (at the specific wavelength) detected by a photodetector. Its relative phase
16 difference, compared with the reference frequency, is measured with a precision phase
17 meter referenced to a time standard. When a small refractive index change is applied to the
18 gas, FCR phase spectroscopy can measure the change with high resolution at high update
19 rate (Fig. 5.1c).

5.3. Simulation analysis

Figure 5.2. Plasmonic sample design, development, and characterization by FDTD simulation. **a**, Plasmonic sample structure and its geometric parameters diameter (d) of 200 nm, a pitch (l) of 530 nm and a thickness (t) of 100 nm on a 25-nm-thick ITO-coated quartz substrate. **b**, Transmission intensity with the different gas refractive index. **c**, Spectral phase change with the different gas refractive index. **d**, 3D view of calculated intensity distribution $|E|^2$ around the sub-wavelength hole. **e**, The calculated intensity distribution of a plasmonic sample taken from 50 nm above the golden film at 613 nm wavelength. **f,g,h**, The calculated intensity distribution of a plasmonic sample taken from the side at 613, 690, 768 nm wavelength respectively.

The simulation model was built with the following parameters: the diameter (d): 200 nm, pitch (l): 530 nm, and thickness (t): 100 nm on a 25-nm thick ITO-coated Quartz substrate (Fig. 5.2a). By changing the refractive index of the gas layer, and the dependence of the transmitted intensity as well as the phase spectrum in the gas refractive index could be investigated.

We can see clearly the intensity peaks (Fig. 5.2b) as well as the phase difference (Fig. 5.2c) was changed strongest at the wavelength of 613 nm, when the other positions (2 and 3) were not shifted too much. This phenomenon matches well with the electric field distribution, where the intensity enhancement is strongest at the interface between the Au

surface and gas layer at 613 nm (Fig. 5.2f) and reduces significantly at 690 nm (Fig. 5.2g) and 768 nm (Fig. 5.2h). It also was predicted by equation 5.1, where two groups of resonance can be distinguished in the transmitted spectrum because of the two surfaces of the metal layer in contact with different dielectric medium [81]. From these results, the wavelength around 613 nm was chosen for the gas refractive index measurement. The enhancement field is confined in the area sizes of $300 \times 200 \times 150$ nm (length $\times$ width $\times$ height) (Fig. 5.2d and 5.2e), which has the strongest enhancement at the rear of the hole. This research will consider how small of the refractive index change the plasmonic phase spectroscopy could detect.

5.4. Changing the gas refractive index by controlling the gas pressure

In this experiment, Argon (Ar) was used for the measurement. There are several methods to change the refractive index of the gas: control temperature (T), change the pressure (P). In this case, the pressure was selected as the controlled variable. Using the Gladstone-Dale approximation of the Lorentz-Lorenz law, i.e., $(n - 1)/\rho = C$ (where ρ is the density of the gas and C a constant for the given wavelength) and the ideal gas equation $\rho = MP/RT$ (where R is the constant of the ideal gas and M the molar weight) [186], gives:

$$n - 1 = \mu \frac{P}{T} \quad (5.2)$$

Table 5.2. The values of the μ constant for $\lambda = 632.8$ nm ($288.15 \text{ K} \leq T \leq 322.15 \text{ K}$; $0 < P < 110 \text{ kPa}$) [186]

Gas	$\mu/10^9 \text{ K.Pa}^{-1}$
Ar	762.0 ± 1.2
N ₂	808.8 ± 1.2
CO ₂	1211.1 ± 1.2

5.5. Experimental result

5.5.1. Pressure control using flow controller

Figure 5.3. Gas refractive index control by changing the pressure. **a**, Pressure modulation applied to the gas flow. The gas from the cylinder goes through the flow controller, which controlled by the computer. Therefore, at the outlet, the pressure was modulated by 6.89 kPa at a frequency of 0.01 Hz. **b**, RF beat spectrum with the plasmonic sample in heterodyne phase detection. **c**, Pressure variation measured by a sensor inside the flow controller. The Fourier transformed frequency spectrum (right) shows a clear peak at 0.01 Hz. **d**, the periodic phase change was clearly observed in the case of the chamber has the EOT sample. **e**, the smaller amplitude of the phase modulation in the case of the chamber has no EOT sample.

The sample had attached in the transparent chamber. The top of the sample was covered by the slide glass, which shielded by the epoxy to make a chamber. The chamber gap is 0.3 mm. The gas would be pumped into the chamber via an inlet and release out through the outlet.

Figure 5.3a presents the gas supply setup. The gas from the cylinder was connected to the Flow controller, which controlled by the computer. The output port connected to the inlet of the chamber. The gas pressure go through the flow controller was monitored by the

1 sensor inside the controller. In this experiment, the pressure was modulated at 0.01 Hz with
 2 an amplitude of 6.89 kPa (Fig 5.3c), which can convert to the refractive index of
 3 1.7×10^{-5} (Table 5.3).

4 A broadband heterodyne Mach–Zehnder interferometer was configured to detect the
 5 spectral phase response of the plasmonic specimen. Figure 5.3b shows the detected RF
 6 spectra of the measurement signal. The repetition rate f_r was 250 MHz with a 50-dB signal-
 7 to-noise (S/N) ratio, while the target heterodyne beat f_{AOM} was at 36.2 MHz with an
 8 instrument-limited narrow linewidth of less than 10 Hz and a signal-to-noise ratio of ~40
 9 dB (Fig 5.3b). The beat f_{AOM} was filtered out and down-converted to 1.2 MHz by the
 10 heterodyne scheme (Fig 4.6). Finally, the phase difference between this frequency and the
 11 RF reference, generated by the frequency generator, was measured by the phase meter. In
 12 figure 5.3d, it clearly shows that the phase-modulated with an amplitude of 35 degrees at a
 13 frequency of 0.01 Hz, matching well with the pressure change. To confirm this phase
 14 modulation caused by EOT, the other experiment was conducted with the chamber without
 15 an EOT sample (the space gap: 0.3 mm = 300 μ m). The phase (Fig. 5.3e), in this case, was
 16 not perfectly sinusoidal modulation and the amplitude was significantly smaller than the
 17 first case. It was about 4 times of difference. In the case of chamber without an EOT
 18 sample, the phase modulation caused only by the physical optical path different (the
 19 refractive index of the 300 μ m thick gas layer was modulated). Consequently, the results
 20 were affected significantly by the environment noise, making the phase modulation curve
 21 not smooth (in the FFT domain (Fig. 5.3e), others stronger noise peak appeared beside the

peak at 0.01 Hz). Therefore, in 35 degrees measured in the first experiment, there were about 9 degrees caused by the gas thickness itself, the remain 26 degrees came from the enhancement of the EOT sample. If we has a chamber (without EOT sample) with the gap thickness of $0.15\ \mu\text{m}$ (the excited SP area above the Au surface, section 5.3) plus $0.1\ \mu\text{m}$ (the Au layer thickness), the phase caused by the gas inside this chamber was $(0.15+0.1)/300 \times 9 = 0.0075$ degree. It means the enhancement of the EOT is $26/0.0075 \approx 3466$. Which are comparable with the enhancement in Ref. [187] (500-fold) and Ref. [188] (1340-fold).

Table 5.3. The calculated refractive index and measured phase corresponding to the pressure change

Case	Pressure change (kPa)	Δn (RIU)	Phase change (degree)	The phase changed by EOT only (degree)	Sensitivity (degree/RIU)
Without sample	6.89	1.7×10^{-5}	9	26	$\approx 1.5 \times 10^6$
With sample	6.89	1.7×10^{-5}	35		

5.5.2. Pressure control using a speaker

In the experiment with the flow controller, the speed and the controlled pressure amplitude are limited by the component specification. To overcome this limitation, a speaker was used as a pressure modulation. Sound when it propagates through the gas, it compresses and stretches the gas molecule. Therefore, it generates a small pressure change in the level of Pa as well as modulates with the high frequency (Fig. 5.4).

Figure 5.4. The speaker structures. When the membrane moving up and down, it changes the gas pressure.

5.5.2.1. Pressure measurement

Figure 5.5. Pressure measurement. a, Measuring the depth of water. b, c, Measuring the bubble diameter based on Laplace pressure corresponding to pull and push stage of the 200 Hz vibration.

Before doing the phase measurement the pressure (P_2) generated by the speaker needs to be measured. Because P_2 was quite small, it could not go out of the chamber, therefore, a fixed pressure (P_1) was pumped through the chamber. P_1 acted as a carrier to bring the P_2 out. To measure P_2 , two different methods was used to compare mutual:

1. Measuring the depth of water: Firstly, the speaker was turned off, then the outlet was deep into water until the bubble did not go out. It means P_1 was balanced with the water pressure (P_w). After that, turn on the speaker (20 V – 5Hz), the bubble continuously went out, the tube was slowly dipped down until the bubble stop flow

out. From the distance (d) the tube moved, the P_2 was calculated as $P_2 = d \times \rho$ (ρ : the specific weight of water). The results were shown in Table 5.4 with different control voltages and the table 5.5 with different controlled frequencies.

Table 5.4. The measured and converted pressure [189] at 5Hz when the supplied voltage change.

Voltage (V)	Measured pressure (mm H ₂ O)	Converted pressure (Pa)	Refractive index ($\Delta n \times 10^{-8}$)
10	0.83	8.14	2.05
12	3.97	38.97	9.83
14	6.08	59.69	15.05
16	8.91	87.47	22.06
18	9.76	95.82	24.16
20	11.42	112.11	28.27

Table 5.5. The measured and converted pressure when changing the frequency (supplied voltage 20 V)

Frequency (Hz)	Measured pressure (mm H ₂ O)	Converted pressure (Pa)	Refractive index ($\Delta n \times 10^{-8}$)
5	11.42	112.11	28.27
10	11.63	114.18	28.80
100	3.90	38.29	9.66
200	4.00	39.27	9.90

Figure 5.6. The relation between the refractive index change and speaker-controlled voltage (a) and frequency (b).

2. Measuring bubble diameter based on Laplace pressure: the pressure difference between the inside and the outside of a curved surface that forms the boundary between a gas region and a liquid region [190]. The pressure difference is caused by the surface tension of the interface between liquid and gas [191]. ΔP is the pressure difference between inside and outside bubble.

$$\Delta P = \gamma \left(\frac{1}{R_i} + \frac{1}{R_i + d} \right) \approx \frac{2\gamma}{R} \quad (5.3)$$

In Fig. 5.5b and 5.5c, the captured bubble corresponded to the pull and push stage of the sound vibration (200 Hz). By measuring their radius, the pressure is calculated by equation 5.3. The reference line is the tube size of 4 mm matching to 261 pixels. The measured radius and calculated pressure are shown below (P_{Ar} : the pressure inside the bubble, P_W : pressure outside the bubble, $\gamma = 72$ mN/m at 25 °C):

- $R_1 = 1.088$ mm $\Rightarrow \Delta P_1 = P_{Ar1} - P_W = -132.32$ Pa
- $R_2 = 1.410$ mm $\Rightarrow \Delta P_2 = P_{Ar2} - P_W = -102.12$ Pa
- The sound pressure = $P_{Ar2} - P_{Ar1} = \Delta P_2 - \Delta P_1 = -102.12 + 132.32 = 30.2$ Pa.

This pressure is comparable with the value in table 5.5 (red color). The difference may be due to the camera's shooting speed (11 fps) lower than the sound frequency (200 Hz), therefore it could not capture exactly the minimum and maximum of the pressure vibration.

Because the values were comparable between the two methods, the measured P_2 (Table 5.4 and 5.4) was acceptable.

5.5.2.2. Phase measurement

Figure 5.7. The demonstration of the high-resolution refractive index measurement. **a**, The Pa level pressure modulation applied to a gas flow using a speaker. **b**, Response phase when the speaker was controlled by 5 Hz frequency, the red curve is the Gaussian fitting. **c**, Relation between the relative phase (peak intensity /noise level) and the refractive index (RI) when the controlled voltage change with the minimum step of 0.2 V (the inset). **d**, Resolution analysis by Allan deviation.

A setup using a speaker as a pressure modulation was shown in Fig. 5.7a. It generates a pressure of P_2 . The supplied voltage to the speaker was varied from 0 to 20 V with the smallest step was 0.2 V, and the frequency <500 Hz (this frequency is limited by the specification of the phase meter, not the speaker). A stable pressure (P_1) of 101 kPa controlled by the flow controller was pumped to the speaker chamber. P_1 acted as a carrier to bring the P_2 out. To isolate the vibration effect caused by the speaker to the interferometry setup, the speaker was placed inside a metallic box with a wall thickness of 6 mm.

To quantitatively evaluate the measurement resolution, the Allan deviations were derived at various averaging times (Fig. 5.7d). It found that the minimum stability can be

achieved at the sampling time 0.2 s, corresponding to the frequency of 5 Hz. Hence, to demonstrate the high-resolution ability of FCR plasmonic phase spectroscopy, the speaker was controlled with the frequency of 5 Hz. After experimenting, the 5 Hz modulation could not observe clearly in the measured phase (like the 0.01 Hz in Fig. 5.3d); therefore, the Fourier transform was performed to monitor the data in the frequency domain. The 5 Hz peak was resolved clearly in Fig. 5.7b. The maximum relative phase (peak intensity/noise level) was 5.6. The controlled voltage was gradually reduced with the minimum step of 0.2 V and associating with the data in table 5.4, the relation between the RI and the relative phase was shown in Fig. 5.7c. The slope is 5.4×10^{-8} RIU/Rel. Phase. The minimum voltage step was 0.2 V (the inset in Fig. 5.7c), it means the experiment successfully detected the minimum Δn of 4.6×10^{-9} RIU. If the performance of the system could be improved more (the isolation of the sample from environmental influences and the technique to control the gas pressure more precise), the result could be approach to the theoretical resolution $\delta n = 1.6 \times 10^{-11}$ RIU detected by the Allan deviation (Fig. 5.7d).

5.6. Conclusion

This chapter has successfully demonstrated the ability of the frequency-comb-referenced phase spectroscopy in the gas refractive index measurement. The frequency comb interacts with the target gas efficiently on a plasmonic sample surface, so provides higher speed and higher resolution. As a demonstration, the minimum refractive index change $\Delta n = 4.6 \times 10^{-9}$ RIU was measured with the resolution of $\delta n = 1.6 \times 10^{-11}$. Which are three order better than the reported references (table 5.1). Based on this result, the FCR-

- 1 plasmonic phase spectroscopy will be applied in chemical or biological sensors for more
- 2 application. In this experiment, the refractive index is derived from the density of the gas,
- 3 therefore it could not identify a gas species of differentiating gas species in a mixture

Chapter 6. Conclusion and future work

6.1. Conclusion

To date, most of the research works on the EOT have focused on the dependence of the intensity behaviour (the transmittance) on several sample parameters such as hole size, the period of the array, the thickness of the metallic film, metal type, and the shape of the hole. The phase behavior has, however, not been much explored although it is an important feature for plasmonic processes. This thesis has investigated the ability of the two interferometric approaches to measuring the plasmonic EOT phase, which are spectrally resolved interferometry and heterodyne interferometry using frequency comb as a light source. They are named as frequency comb referenced (FCR) plasmonic phase spectroscopy.

This is the first frequency-comb-referenced measurement of plasmonic phase spectroscopy. Frequency comb can transfer the phase information in the optical domain to the radio-frequency (RF) domain, thereby enable broadband plasmonic phase spectroscopy having a higher speed, higher precision, and direct traceability to time standards. Due to plasmonic field enhancement during the extraordinary transmission, the phase retardation is a hundred times stronger than the interaction of the frequency comb with the physical bulk material, which drastically increased the attainable resolution. As an example, a 1.94 Å dynamic motion of a pair of nanoholes was measured with a 1.67 pm resolution in the feasibility test experiment, which shows the ability of plasmonic phase spectroscopy to

function as a high-precision plasmonic ruler. In the refractive index measurement, the FCR-plasmonic phase spectroscopy successfully measured the gas refractive index change $\Delta n = 4.6 \times 10^{-9}$ RIU with the resolution of $\delta n = 1.6 \times 10^{-11}$ RIU.

The main contributions of this study are listed as follow:

- Numerical simulation for the plasmonic EOT phenomenon.
- Experimental demonstration the capability of spectrally resolved interferometry in measuring the broadband plasmonic phase spectrum.
- Experimental demonstration the capability of frequency comb-referenced plasmonic phase spectroscopy based on heterodyne interferometry for the high speed, high precision, and direct traceability to the time standards phase measurement.
- Evaluation of dynamic motion of a pair of nanoholes using frequency comb-referenced plasmonic phase spectroscopy.
- The experiment allows measurement of refractive index change only not the absolute refractive index of the gas with high resolution and high-speed using frequency comb-referenced plasmonic phase spectroscopy.

6.2. Future work

With superior performances obtained, the future work will focus on fundamental understanding the detailed physics behind these performances and theoretical investigation to verify the universality of FCR plasmonic phase spectroscopy for other plasmonic

structures: nanorods, two nano-slits, and sub-wavelength slit-groove. It is the basis for applying the FCR plasmonic phase spectroscopy into applications such as bio-molecular detection, plasmonic ruler.

6.2.1. 2D Plasmonic ruler

Theoretical physics behind this extraordinary optical transmission still being studied. Important influences on transmission include surface plasmon polaritons (SPPs), Rayleigh anomalies (RAs), evanescent waves, and localized waveguide [2, 81-83, 192-197]. Although an RA is a non-resonant spectral feature, the coupling between RAs and SPPs on opposite sides of the Au film of subwavelength hole arrays can create a sharp, strong RA-SPP resonance [195] and sometimes a higher EOT.

The SPP modes occur at the wavelengths satisfying[83]:

$$\lambda_{SPP} = \frac{P}{\sqrt{n_x^2 + n_y^2}} \sqrt{\frac{\epsilon_{Au}\epsilon}{\epsilon_{Au} + \epsilon}} \quad (6.1)$$

In addition, another optical phenomenon is the RA (also called Wood anomaly or Rayleigh-Wood anomaly), which is related to the diffraction light parallel to the surface [195, 196]:

$$\lambda_{RA} = \frac{P}{\sqrt{n_x^2 + n_y^2}} \sqrt{\epsilon} \quad (6.2)$$

Where P is periodic of the subwavelength hole array, ϵ the relative permittivity of the adjacent dielectric material, n_x and n_y integer numbers indicating the SPP mode order.

Applying these theoretical to my study, a very sharp peak at 768 nm, which appear in both simulation and experiment EOT transmission spectra (Fig. 6.1a and 6.1b), could be

related to the Rayleigh anomalies. It is quite weak compared to two broader adjacent peaks, which are associated with SPP. In figure 6.1c, the pitch of the array was changed from 530 nm to 450 nm. All the peaks shift to the left, but the sharp one moves faster and then coupled with one of the broader peaks to generate a stronger and narrower peak. From these phenomena and two equations 6.1, 6.2, We have a hypothesis: If the geometrical dimension of a nanoholes array varies independently in the X and Y direction, by monitoring the different change of the peaks position (SPP and RA) or the phase, the displacement in each direction could be measured separately. It is the concept of the 2D plasmonic ruler. We have succeeded to detect a 1.94 Å dynamic motion with an unprecedented 1.67 pm precision [183], therefore it is absolutely feasible to apply FCR plasmonic phase spectroscopy in the 2D plasmonic ruler. Several works are using SPP for 2D or 3D plasmon ruler [134, 156], they are valuable references that can evaluate the effectiveness of our method.

Figure 6.1. EOT transmission spectrum by simulation (a) and experiment (b) of the 530 nm pitch array. (c) EOT transmission spectrum by simulation of the 450 nm pitch array.

To demonstrate the feasibility of the hypothesis, a set of simulation was conducted with different pitch value (around 530 nm) in the X and Y-direction of the EOT sample (Fig. 6.2a). In the intensity and phase data (Fig. 6.2b and 6.2c), at the wavelength of 850 nm, three groups of spectra are monitored clearly correspond to l_x of 525, 530, and 535 nm,

they almost do not depend on l_y . At the position of the sharp peak (around 760 nm), the data looks more complicated, it means the data depends on both l_x and l_y . These results strongly support the hypothesis. Finally, if two dimensions X and Y could be measured separately by the experiment, the hypothesis could be confirmed. It will be our future work.

Figure 6.2. **a**, Circular hole array with the pitch l_x and l_y correspond to x and y-direction. **b**, Transmission intensity with the different pitch in x and y-axis ($l_x - l_y$). **c**, Spectral phase change with the different pitch in x and y-axis ($l_x - l_y$).

In the above chapter, the thermo-electric heating element (TEC) was introduced for the dynamic motion control. But this motion was the same in both directions of the sample. Therefore, to changing the pitch l_x and l_y differently, the sample was attached on two TEC, one at the horizontal side and the other at the vertical side. To verify this setup is working as expected, the thermal dynamic motion was simulated in Solidworks (Fig. 6.3a). The temperature of the TEC1 and TEC2 were controlled with the different frequencies (0.02 Hz and 0.013 Hz respectively) but a same amplitude of 25 degree Celsius. The monitored temperature at the nanohole array is shown in Fig. 6.3c, which profile is the combination of two profiles in Fig. 6.3b. The Fourier transformed frequency spectrum (right) shows clearly two peaks at 0.013 Hz and 0.02 Hz. The displacement at the center position (the nanohole array) was also analysed. In the horizontal, the motion strongly depended on the

frequency 0.02 Hz of the TEC1 (Fig. 6.3d), while in the vertical, the motion associated with the frequency 0.013 Hz of the TEC2 (Fig. 6.3e). These positive results have proven that l_x and l_y can change differently by 2D temperature control. The remaining work is applying the FCR plasmonic phase spectroscopy to measure these displacements independently.

Figure 6.3. The thermal dynamic motion simulated by Solidworks. **a**, The EOT sample is attached to two TECs, which transfer the heat to the center of the sample in two directions. **b**, The applied temperature on TEC 1 and TEC2 with the different frequencies. **c**, Measured temperature at the center of the sample (Nanoholes Array position). **d**, Displacement of the center caused by the heat in the horizontal direction. **e**, Displacement of the center caused by the heat in the horizontal direction.

6.2.2. Single-molecule detection

Any measurement method desires to accomplish the individual quantum level of sensitivity. For gas or biological sensors, quantum is an atom or molecule. Level of this resolution is beyond the capabilities of some available measurement method comprising solid-state gas sensors [198, 199] and nanotube-based sensor [200, 201]. The thermal

1 motion of the charge and disabilities, which increases the intrinsic noise signal, is the
 2 underlying cause of the resolution limit of these sensors [202]. To improve sensitivity, they
 3 have tried to study new methods as using graphene - low-noise material electronically
 4 [203], or using optical methods [172, 175, 184, 185, 204]. Optical methods are particularly
 5 prominent because of its advantages, such as higher sensitivity, electrical passiveness and
 6 robustness [205].

7 The ability to detect single molecules on a dry surface of the optical technique can
 8 be enhanced using nanostructures. Hundreds of such nanostructures, which help to enhance
 9 fluorescence or the weak signals from molecules with low quantum yields and change the
 10 direction of radiation [206, 207], can be fabricated on substrates with each nanostructure
 11 acting as an independent detector for the single-molecule detection improvement [83, 184].
 12 The surface plasmon resonance (SPR) on these nanostructures, which are coherent
 13 oscillations of the free electrons at the interface of the metallic surface and dielectric
 14 excited by the incident light [124-126], can focus light far beyond the diffraction limit [207-
 15 210].

16 To consider the ability of the method in single-molecule detection, we converted the
 17 known pressure in table 5.4 to the gas density information [211]. With the assumption that
 18 the gas in the sample chamber was uniform (Fig. 5.1 b), we can calculate the number of
 19 the Ar molecules within the area of the holes array of $1000 \times 1000 \times 0.15 \mu\text{m}$ (length $\times$
 20 width $\times$ height). Then, we divided this amount to the number of the hole (~ 4 million of
 21 holes) to derive the **No. Molecules/hole** (Table 6.1). From the result in chapter 5, we

detected the $\Delta n = 4.6 \times 10^{-9}$ RIU with the resolution of $\delta n = 1.6 \times 10^{-11}$, it corresponds to 18.9 No. Molecules/hole and the resolution of ~ 0.1 . These values are comparable to the reported studies (table 6.2), which proved the FCR plasmonic phase spectroscopy can be applied to single-molecule detection.

Table 6.1. The conversion between refractive index and No. Molecules/hole

Pressure (Pa)	Refractive index ($\Delta n \times 10^{-8}$)	No. Molecules/hole
8.14	2.05	84.33
38.97	9.83	403.34
59.69	15.05	617.72
87.47	22.06	905.24
95.82	24.16	991.60
112.11	28.27	1160.25

Table 6.2. Comparison between our method and current single molecule detection technique.

Method	The information parameter	The sensitivity	The resolution
Array of Au double-dots [184]	Graphene hydrogenation	44 degree/pg mm ⁻²	1 x 10 ⁻⁴ pg mm ⁻²
	Streptavidin–biotin affinity	25 degree/20–100 molecules per nanodot	<1 molecule/nanodot
Silver–Stibnite nanoporous [212]	GH shift interrogation	4.5x10 ⁻⁷ RIU/nm	
	Streptavidin–biotin affinity	1 fM	1180 molecules/mm ²
Our method (Nanohole array)	Number of the molecule per hole	18.9	~ 0.1

List of publications

- [1] Nguyen Duy Anh, Byung Jae Chun, Sungho Choi, Dong-Eon Kim, Seungchul Kim, and Young-Jin Kim, 'Plasmonic Dynamics Measured with Frequency-Comb-Referenced Phase Spectroscopy', *Nature Physics*, 15 (2019), 132-37.
- [2] D. A. Nguyen, B. J. Chun, and Y. Kim, 'Plasmonic Phase Change Measurement in Metal Nanostructures by Frequency-Comb-Based Spectrally Resolved Interferometry', in 2017 Conference on Lasers and Electro-Optics Pacific Rim (CLEO-PR) (2017), pp. 1-2.
- [3] Duy Anh Nguyen, Byung Jae Chun, and Young-Jin Kim, 'Frequency-Comb-Referenced Phase Spectroscopy Measures Plasmonic Dynamics with Picometre Resolution', in Conference on Lasers and Electro-Optics (San Jose, California: Optical Society of America, 2019), p. SM4F.2.

References

1. Bethe, H.A., *Theory of Diffraction by Small Holes*. Physical Review, 1944. **66**(7-8): p. 163-182.
 2. Ebbesen, T.W., et al., *Extraordinary optical transmission through sub-wavelength hole arrays*. Nature, 1998. **391**(6668): p. 667-669.
 3. Gordon, R., et al., *Resonant optical transmission through hole-arrays in metal films: physics and applications*. Laser & Photonics Reviews, 2010. **4**(2): p. 311-335.
 4. Hansch, T.W., *Nobel Lecture: Passion for precision*. Reviews of Modern Physics, 2006. **78**(4): p. 1297-1309.
 5. Hall, J.L., *Nobel Lecture: Defining and measuring optical frequencies*. Reviews of Modern Physics, 2006. **78**(4): p. 1279-1295.
 6. Diddams, S.A., et al., *An Optical Clock Based on a Single Trapped 199Hg^+ Ion*. Science, 2001. **293**(5531): p. 825.
 7. Oskay, W.H., et al., *Single-atom optical clock with high accuracy*. Phys Rev Lett, 2006. **97**(2): p. 020801.
 8. Udem, T., et al., *Absolute Optical Frequency Measurement of the Cesium D_1 Line with a Mode-Locked Laser*. Physical Review Letters, 1999. **82**(18): p. 3568-3571.
 9. Ye, J., H. Schnatz, and L.W. Hollberg, *Optical frequency combs: From frequency metrology to optical phase control*. Ieee Journal of Selected Topics in Quantum Electronics, 2003. **9**(4): p. 1041-1058.
 10. von Zanthier, J., et al., *Absolute frequency measurement of the In^+ clock transition with a mode-locked laser*. Optics Letters, 2000. **25**(23): p. 1729-1731.
 11. Reichert, J., et al., *Measuring the frequency of light with mode-locked lasers*. Optics Communications, 1999. **172**(1-6): p. 59-68.
 12. Coddington, I., et al., *Rapid and precise absolute distance measurements at long range*. Nat Photon, 2009. **3**(6): p. 351-356.
 13. Joo, K.-N. and S.-W. Kim, *Absolute distance measurement by dispersive interferometry using a femtosecond pulse laser*. Optics Express, 2006. **14**(13): p. 5954-5960.
 14. Hyun, S., et al., *Absolute distance measurement using the frequency comb of a femtosecond laser*. Cirp Annals-Manufacturing Technology, 2010. **59**(1): p. 555-558.
 15. Jang, Y.S., et al., *Absolute distance measurement with extension of nonambiguity range using the frequency comb of a femtosecond laser*. Optical Engineering, 2014. **53**(12).
 16. Steinmetz, T., et al., *Laser frequency combs for astronomical observations*. Science, 2008. **321**(5894): p. 1335-7.
 17. Fritz, R., *8th Symposium on Frequency Standards and Metrology 2015*. Journal of Physics: Conference Series, 2016. **723**(1): p. 011001.
 18. Ideguchi, T., et al., *Coherent Raman spectro-imaging with laser frequency combs*. Nature, 2013. **502**(7471): p. 355-+.
 19. Hlubina, P., *Dispersive white-light spectral interferometry to measure distances and displacements*. Optics Communications, 2002. **212**(1-3): p. 65-70.
 20. Schnell, U., E. Zimmermann, and R. Dandliker, *Absolute distance measurement with synchronously sampled white-light channelled spectrum interferometry*. Pure and Applied Optics: Journal of the European Optical Society Part A, 1995. **4**(5): p. 643.
 21. Smith, L.M. and C.C. Dobson, *Absolute displacement measurements using modulation of the spectrum of white light in a Michelson interferometer*. Applied Optics, 1989. **28**(16): p. 3339-3342.
 22. Calatroni, J.E., P. Sandoz, and G. Tribillon, *Surface profiling by means of double spectral modulation*. Appl Opt, 1993. **32**(1): p. 30-7.
 23. Schwider, J. and L. Zhou, *Dispersive interferometric profilometer*. Optics Letters, 1994. **19**(13): p. 995-997.
-

24. Zuluaga, A.F. and R. Richards-Kortum, *Spatially resolved spectral interferometry for determination of subsurface structure*. Optics Letters, 1999. **24**(8): p. 519-521.
25. Hlubina, P., T. Martynkien, and W. Urbanczyk, *Dispersion of group and phase modal birefringence in elliptical-core fiber measured by white-light spectral interferometry*. Optics Express, 2003. **11**(22): p. 2793-2798.
26. Lee, J.Y. and D.Y. Kim, *Versatile chromatic dispersion measurement of a single mode fiber using spectral white light interferometry*. Optics Express, 2006. **14**(24): p. 11608-11615.
27. Liang, Y. and C.P. Grover, *Modified white-light Mach-Zehnder interferometer for direct group-delay measurements*. Applied Optics, 1998. **37**(19): p. 4105-4111.
28. Sainz, C., et al., *Real-Time Interferometric Measurements of Dispersion-Curves*. Optics Communications, 1994. **110**(3-4): p. 381-390.
29. Joo, K.-N. and S.-W. Kim, *Refractive index measurement by spectrally resolved interferometry using a femtosecond pulse laser*. Optics Letters, 2007. **32**(6): p. 647-649.
30. Kim, J.-A., et al., *A digital signal processing module for real-time compensation of nonlinearity in a homodyne interferometer using a field-programmable gate array*. Measurement Science and Technology, 2008. **20**(1): p. 017003.
31. Cheng, Z.G., et al., *Study of a dual-frequency laser interferometer with unique optical subdivision techniques*. Applied Optics, 2006. **45**(10): p. 2246-2250.
32. Kochert, P., et al., *Phase measurement of various commercial heterodyne He-Ne-laser interferometers with stability in the picometer regime*. Measurement Science and Technology, 2012. **23**(7).
33. Choi, H., K. Park, and J. La, *Novel phase measurement technique of the heterodyne laser interferometer*. Review of Scientific Instruments, 2005. **76**(9).
34. Park, Y. and K. Cho, *Heterodyne interferometer scheme using a double pass in an acousto-optic modulator*. Optics Letters, 2011. **36**(3): p. 331-333.
35. Kimachi, A., *Real-time heterodyne imaging interferometry: focal-plane amplitude and phase demodulation using a three-phase correlation image sensor*. Applied Optics, 2007. **46**(1): p. 87-94.
36. Yang, S.M. and G.F. Zhang, *A review of interferometry for geometric measurement*. Measurement Science and Technology, 2018. **29**(10).
37. Meskers, A.J.H., J.W. Spronck, and R.H.M. Schmidt, *Heterodyne displacement interferometer, insensitive for input polarization*. Optics Letters, 2014. **39**(7): p. 1949-1952.
38. Giorgetta, F.R., et al., *Broadband Phase Spectroscopy over Turbulent Air Paths*. Physical Review Letters, 2015. **115**(10).
39. Diddams, S.A., L. Hollberg, and V. Mbele, *Molecular fingerprinting with the resolved modes of a femtosecond laser frequency comb*. Nature, 2007. **445**(7128): p. 627-630.
40. Thorpe, M.J., et al., *Broadband cavity ringdown spectroscopy for sensitive and rapid molecular detection*. Science, 2006. **311**(5767): p. 1595-1599.
41. Otto, L.M., et al., *Polarization interferometry for real-time spectroscopic plasmonic sensing*. Nanoscale, 2015. **7**(9): p. 4226-33.
42. Gao, Y., et al., *Plasmonic Mach-Zehnder interferometer for ultrasensitive on-chip biosensing*. ACS Nano, 2011. **5**(12): p. 9836-44.
43. Morrill, D., D.F. Li, and D. Pacifici, *Measuring subwavelength spatial coherence with plasmonic interferometry*. Nature Photonics, 2016. **10**(10): p. 681-687.
44. Geng, X.T., et al., *Frequency comb transferred by surface plasmon resonance*. Nature Communications, 2016. **7**.
45. Udem, T., R. Holzwarth, and T.W. Hansch, *Optical frequency metrology*. Nature, 2002. **416**(6877): p. 233-237.
46. <https://www.nist.gov/director/pao/optical-frequency-combs>.
47. Maddaloni, P., P. Cancio, and P. De Natale, *Optical comb generators for laser frequency measurement*. Measurement Science and Technology, 2009. **20**(5).

-
48. Takahata, K., et al., *Absolute frequency measurement of sub-Doppler molecular lines using a 3.4- μ m difference-frequency-generation spectrometer and a fiber-based frequency comb*. Physical Review A, 2009. **80**(3).
 49. Jin, J., et al., *Absolute length calibration of gauge blocks using optical comb of a femtosecond pulse laser*. Interferometry Xiii: Techniques and Analysis, 2006. **6292**.
 50. Kim, Y.J., et al., *A wide-range optical frequency generator based on the frequency comb of a femtosecond laser*. Optics Express, 2008. **16**(1): p. 258-264.
 51. Newbury, N.R., *Searching for applications with a fine-tooth comb*. Nat Photon, 2011. **5**(4): p. 186-188.
 52. Kim, S.W., *Combs rule*. Nature Photonics, 2009. **3**(6): p. 313-314.
 53. Jones, D.J., et al., *Carrier-envelope phase control of femtosecond mode-locked lasers and direct optical frequency synthesis*. Science, 2000. **288**(5466): p. 635-639.
 54. Holzwarth, R., et al., *Optical frequency synthesizer for precision spectroscopy*. Phys Rev Lett, 2000. **85**(11): p. 2264-7.
 55. Minoshima, K. and H. Matsumoto, *High-accuracy measurement of 240-m distance in an optical tunnel by use of a compact femtosecond laser*. Applied Optics, 2000. **39**(30): p. 5512-5517.
 56. Ye, J., *Absolute measurement of a long, arbitrary distance to less than an optical fringe*. Optics Letters, 2004. **29**(10): p. 1153-1155.
 57. Cui, M., et al., *High-accuracy long-distance measurements in air with a frequency comb laser*. Optics Letters, 2009. **34**(13): p. 1982-1984.
 58. Balling, P., et al., *Femtosecond frequency comb based distance measurement in air*. Optics Express, 2009. **17**(11): p. 9300-9313.
 59. Joo, K.N., Y. Kim, and S.W. Kim, *Distance measurements by combined method based on a femtosecond pulse laser*. Optics Express, 2008. **16**(24): p. 19799-19806.
 60. Cui, M., et al., *Long distance measurement with femtosecond pulses using a dispersive interferometer*. Optics Express, 2011. **19**(7): p. 6557-6570.
 61. Liu, T.A., N.R. Newbury, and I. Coddington, *Sub-micron absolute distance measurements in sub-millisecond times with dual free-running femtosecond Er fiber-lasers*. Optics Express, 2011. **19**(19): p. 18501-18509.
 62. Lee, J., et al., *Time-of-flight measurement with femtosecond light pulses*. Nature Photonics, 2010. **4**: p. 716.
 63. Morgner, U., et al., *Sub-two-cycle pulses from a Kerr-lens mode-locked Ti : sapphire laser (vol 24, pg 411, 1999)*. Optics Letters, 1999. **24**(13): p. 920-920.
 64. https://www.rp-photonics.com/mode_locking.html.
 65. Jones, R.J., *The Femtosecond Frequency Comb: From Seconds to Attoseconds*.
 66. Ferguson, A.I., J.N. Eckstein, and T.W. Hänsch, *A subpicosecond dye laser directly pumped by a mode-locked argon laser*. Journal of Applied Physics, 1978. **49**(11): p. 5389-5391.
 67. Ferguson, A.I., J.N. Eckstein, and T.W. Hänsch, *Polarization spectroscopy with ultrashort light pulses*. Applied physics, 1979. **18**(3): p. 257-260.
 68. Telle, H.R., et al., *Carrier-envelope offset phase control: A novel concept for absolute optical frequency measurement and ultrashort pulse generation*. Applied Physics B, 1999. **69**(4): p. 327-332.
 69. Margolis, H.S., *Spectroscopic applications of femtosecond optical frequency combs*. Chemical Society Reviews, 2012. **41**(15): p. 5174-5184.
 70. Cundiff, J.Y.a.S.T., *Femtosecond Optical Frequency Comb: Principle, Operation, and Applications*. Kluwer Academic Publishers / Springer, 2005.
 71. Apolonski, A., et al., *Controlling the phase evolution of few-cycle light pulses*. Physical Review Letters, 2000. **85**(4): p. 740-743.
 72. Teets, R., J. Eckstein, and T. Haensch, *Coherent Two-Photon Excitation by Multiple Light Pulses*. Physical Review Letters - PHYS REV LETT, 1977. **38**: p. 760-764.
-

-
73. Eckstein, J.N., A.I. Ferguson, and T.W. Hänsch, *High-resolution two-photon spectroscopy with picosecond light pulses*. Physical Review Letters, 1978. **40**(13): p. 847-850.
 74. Eckstein, J.N., *High resolution spectroscopy using multiple coherent interactions*. 1978.
 75. Mandon, J., G. Guelachvili, and N. Picqué, *Fourier transform spectroscopy with a laser frequency comb*. Nature Photonics, 2009. **3**: p. 99.
 76. Marian, A., et al., *United time-frequency spectroscopy for dynamics and global structure*. Science, 2004. **306**(5704): p. 2063-8.
 77. Picqué, N. and T.W. Hänsch, *Frequency comb spectroscopy*. Nature Photonics, 2019. **13**(3): p. 146-157.
 78. Ideguchi, T., *Dual-Comb Spectroscopy*. Optics and Photonics News, 2017. **28**(1): p. 32-39.
 79. Wood, R.W., *XLII. On a remarkable case of uneven distribution of light in a diffraction grating spectrum*. Philosophical Magazine, 1902. **4**(21): p. 396-402.
 80. Genet, C. and T.W. Ebbesen, *Light in tiny holes*. Nature, 2007. **445**(7123): p. 39-46.
 81. Krishnan, A., et al., *Evanescently coupled resonance in surface plasmon enhanced transmission*. Optics Communications, 2001. **200**(1-6): p. 1-7.
 82. Lezec, H.J. and T. Thio, *Diffraction evanescent wave model for enhanced and suppressed optical transmission through subwavelength hole arrays*. Optics Express, 2004. **12**(16): p. 3629-3651.
 83. Ghaemi, H.F., et al., *Surface plasmons enhance optical transmission through subwavelength holes*. Physical Review B, 1998. **58**(11): p. 6779-6782.
 84. Martin-Moreno, L. and F.J. Garcia-Vidal, *Optical transmission through circular hole arrays in optically thick metal films*. Optics Express, 2004. **12**(16): p. 3619-3628.
 85. Gao, H.W., J. Henzie, and T.W. Odom, *Direct evidence for surface plasmon-mediated enhanced light transmission through metallic nanohole arrays*. Nano Letters, 2006. **6**(9): p. 2104-2108.
 86. https://en.wikipedia.org/wiki/Surface_plasmon.
 87. Rodrigo, S.G., *Optical Properties of Nanostructured Metallic Systems*. Springer.
 88. Przybilla, F., et al., *Optical transmission in perforated noble and transition metal films*. Journal of Optics a-Pure and Applied Optics, 2006. **8**(5): p. 458-463.
 89. Thio, T., et al., *Surface-plasmon-enhanced transmission through hole arrays in Cr films*. Journal of the Optical Society of America B-Optical Physics, 1999. **16**(10): p. 1743-1748.
 90. Cao, H. and A. Nahata, *Influence of aperture shape on the transmission properties of a periodic array of subwavelength apertures*. Optics Express, 2004. **12**(16): p. 3664-3672.
 91. Koerkamp, K.J.K., et al., *Strong Influence of Hole Shape on Extraordinary Transmission through Periodic Arrays of Subwavelength Holes*. Physical Review Letters, 2004. **92**(18): p. 183901.
 92. van der Molen, K.L., et al., *Role of shape and localized resonances in extraordinary transmission through periodic arrays of subwavelength holes: Experiment and theory*. Physical Review B, 2005. **72**(4): p. 045421.
 93. Kim, J.H. and P.J. Moyer, *Transmission characteristics of metallic equilateral triangular nanohole arrays*. Applied Physics Letters, 2006. **89**(12).
 94. van der Molen, K.L., et al., *Influence of hole size on the extraordinary transmission through subwavelength hole arrays*. Applied Physics Letters, 2004. **85**(19): p. 4316-4318.
 95. Shou, X., A. Agrawal, and A. Nahata, *Role of metal film thickness on the enhanced transmission properties of a periodic array of subwavelength apertures*. Optics Express, 2005. **13**(24): p. 9834-9840.
 96. Azad, A.K. and W.L. Zhang, *Resonant terahertz transmission in subwavelength metallic hole arrays of sub-skin-depth thickness*. Optics Letters, 2005. **30**(21): p. 2945-2947.
 97. Chen, Y.G., et al., *Numerical investigation of the transmission enhancement through subwavelength hole array*. Optics Communications, 2007. **274**(1): p. 236-240.
 98. Gordon, R., et al., *Basis and lattice polarization mechanisms for light transmission through nanohole arrays in a metal film*. Nano Letters, 2005. **5**(7): p. 1243-1246.
 99. Henzie, J., M.H. Lee, and T.W. Odom, *Multiscale patterning of plasmonic metamaterials*. Nature Nanotechnology, 2007. **2**(9): p. 549-554.
-

100. Nagpal, P., et al., *Ultrasoother Patterned Metals for Plasmonics and Metamaterials*. Science, 2009. **325**(5940): p. 594-597.
101. Masson, J.F., M.P. Murray-Methot, and L.S. Live, *Nanohole arrays in chemical analysis: manufacturing methods and applications*. Analyst, 2010. **135**(7): p. 1483-1489.
102. Nakamoto, K., et al., *Development of a mass-producible on-chip plasmonic nanohole array biosensor*. Nanoscale, 2011. **3**(12): p. 5067-5075.
103. Wong, T.I., et al., *High throughput and high yield nanofabrication of precisely designed gold nanohole arrays for fluorescence enhanced detection of biomarkers*. Lab on a Chip, 2013. **13**(12): p. 2405-2413.
104. Yang, J., et al., *Design and fabrication of broadband ultralow reflectivity black Si surfaces by laser micro/nanoprocessing*. Light-Science & Applications, 2014. **3**.
105. Ortuno, R., et al., *Midinfrared filters based on extraordinary optical transmission through subwavelength structured gold films*. Journal of Applied Physics, 2009. **106**(12).
106. Dintinger, J., S. Klein, and T.W. Ebbesen, *Molecule-Surface Plasmon Interactions in Hole Arrays: Enhanced Absorption, Refractive Index Changes, and All-Optical Switching*. Advanced Materials, 2006. **18**(10): p. 1267-1270.
107. Sepulveda, B., et al., *Shape effects in the localized surface plasmon resonance of single nanoholes in thin metal films*. Optics Express, 2008. **16**(8): p. 5609-5616.
108. Onishi, T., et al., *Polarization control of vertical-cavity surface-emitting lasers by utilizing surface plasmon resonance*. Ieee Journal of Quantum Electronics, 2007. **43**(11-12): p. 1123-1128.
109. Airola, M., Y. Liu, and S. Blair, *Second-harmonic generation from an array of sub-wavelength metal apertures*. Journal of Optics a-Pure and Applied Optics, 2005. **7**(2): p. S118-S123.
110. Lesuffleur, A., L.K.S. Kumar, and R. Gordon, *Apex-enhanced second-harmonic generation by using double-hole arrays in a gold film*. Physical Review B, 2007. **75**(4).
111. Xu, T.J., X.J. Jiao, and S. Blair, *Third-harmonic generation from arrays of sub-wavelength metal apertures*. Optics Express, 2009. **17**(26): p. 23582-23588.
112. Kretschm.E and H. Raether, *Radiative Decay of Non Radiative Surface Plasmons Excited by Light*. Zeitschrift Fur Naturforschung Part a-Astrofysik Physik Und Physikalische Chemie, 1968. **A 23**(12): p. 2135-&.
113. Brolo, A.G., et al., *Surface plasmon sensor based on the enhanced light transmission through arrays of nanoholes in gold films*. Langmuir, 2004. **20**(12): p. 4813-4815.
114. De Leebeeck, A., et al., *On-chip surface-based detection with nanohole arrays*. Analytical Chemistry, 2007. **79**(11): p. 4094-4100.
115. Liu, Y.D. and S. Blair, *Fluorescence enhancement from an array of subwavelength metal apertures*. Optics Letters, 2003. **28**(7): p. 507-509.
116. Brolo, A.G., et al., *Enhanced fluorescence from arrays of nanoholes in a gold film*. Journal of the American Chemical Society, 2005. **127**(42): p. 14936-14941.
117. Moskovits, M., *Surface-Enhanced Spectroscopy*. Reviews of Modern Physics, 1985. **57**(3): p. 783-826.
118. Brolo, A.G., et al., *Nanohole-enhanced Raman scattering*. Nano Letters, 2004. **4**(10): p. 2015-2018.
119. Williams, S.M., et al., *Accessing surface plasmons with Ni microarrays for enhanced IR absorption by monolayers*. Journal of Physical Chemistry B, 2003. **107**(43): p. 11871-11879.
120. Rodriguez, K.R., et al., *Enhanced infrared absorption spectra of self-assembled alkanethiol monolayers using the extraordinary infrared transmission of metallic arrays of subwavelength apertures*. Journal of Chemical Physics, 2004. **121**(18): p. 8671-8675.
121. Coe, J.V., et al., *Extraordinary IR transmission with metallic arrays of subwavelength holes*. Analytical Chemistry, 2006. **78**(5): p. 1384-1390.
122. Qu, D.X., D. Grischkowsky, and W.L. Zhang, *Terahertz transmission properties of thin, subwavelength metallic hole arrays*. Optics Letters, 2004. **29**(8): p. 896-898.
123. http://photonicswiki.org/index.php?title=Terahertz_Radiation.

124. Kauranen, M. and A.V. Zayats, *Nonlinear plasmonics*. Nature Photonics, 2012. **6**: p. 737.
125. Mühlischlegel, P., et al., *Resonant Optical Antennas*. Science, 2005. **308**(5728): p. 1607.
126. Novotny, L. and N. van Hulst, *Antennas for light*. Nature Photonics, 2011. **5**: p. 83.
127. Anker, J.N., et al., *Biosensing with plasmonic nanosensors*. Nat Mater, 2008. **7**(6): p. 442-53.
128. Willets, K.A. and R.P. Van Duyne, *Localized surface plasmon resonance spectroscopy and sensing*. Annu Rev Phys Chem, 2007. **58**: p. 267-97.
129. Zhang, Y., et al., *Coherent anti-Stokes Raman scattering with single-molecule sensitivity using a plasmonic Fano resonance*. Nat Commun, 2014. **5**: p. 4424.
130. Zheng, J., et al., *From molecular to macroscopic via the rational design of a self-assembled 3D DNA crystal*. Nature, 2009. **461**(7260): p. 74-7.
131. Stern, L., M. Grajower, and U. Levy, *Fano resonances and all-optical switching in a resonantly coupled plasmonic-atomic system*. Nat Commun, 2014. **5**: p. 4865.
132. Savage, K.J., et al., *Revealing the quantum regime in tunnelling plasmonics*. Nature, 2012. **491**(7425): p. 574-7.
133. Liu, G.L., et al., *A nanoplasmonic molecular ruler for measuring nuclease activity and DNA footprinting*. Nat Nanotechnol, 2006. **1**(1): p. 47-52.
134. Liu, N., et al., *Three-dimensional plasmon rulers*. Science, 2011. **332**(6036): p. 1407-10.
135. Sonnichsen, C., et al., *A molecular ruler based on plasmon coupling of single gold and silver nanoparticles*. Nat Biotechnol, 2005. **23**(6): p. 741-5.
136. Giorgetta, F.R., et al., *Broadband Phase Spectroscopy over Turbulent Air Paths*. Phys Rev Lett, 2015. **115**(10): p. 103901.
137. Morrill, D., D. Li, and D. Pacifici, *Measuring subwavelength spatial coherence with plasmonic interferometry*. Nature Photonics, 2016. **10**: p. 681.
138. Kane, Y., *Numerical solution of initial boundary value problems involving maxwell's equations in isotropic media*. IEEE Transactions on Antennas and Propagation, 1966. **14**(3): p. 302-307.
139. Pronin, O., et al., *High-power multi-megahertz source of waveform-stabilized few-cycle light*. Nat Commun, 2015. **6**: p. 6988.
140. Reeves, W.H., et al., *Transformation and control of ultra-short pulses in dispersion-engineered photonic crystal fibres*. Nature, 2003. **424**(6948): p. 511-5.
141. Nix, F.C. and D. MacNair, *The Thermal Expansion of Pure Metals: Copper, Gold, Aluminum, Nickel, and Iron*. Physical Review, 1941. **60**(8): p. 597-605.
142. Abbott, B.P., et al., *Observation of Gravitational Waves from a Binary Black Hole Merger*. Phys Rev Lett, 2016. **116**(6): p. 061102.
143. Çelik, M., et al., *Picometre displacement measurements using a differential Fabry–Perot optical interferometer and an x-ray interferometer*. Measurement Science and Technology, 2012. **23**(8): p. 085901.
144. Han, D., et al., *DNA origami with complex curvatures in three-dimensional space*. Science, 2011. **332**(6027): p. 342-6.
145. Ciddor, P.E., *Refractive index of air: new equations for the visible and near infrared*. Applied Optics, 1996. **35**(9): p. 1566-1573.
146. Edlén, B., *The Refractive Index of Air*. Metrologia, 1966. **2**(2): p. 71-80.
147. Ghosh, G., M. Endo, and T. Iwasaki, *Temperature-dependent Sellmeier coefficients and chromatic dispersions for some optical fiber glasses*. Journal of Lightwave Technology, 1994. **12**(8): p. 1338-1342.
148. http://www.schott.com/d/advanced_optics/3794eded-edd2-461d-aec5-0a1d2dc9c523/1.0/schott_tie-19_temperature_coefficient_of_refractive_index_eng.pdf.
149. <https://emtoolbox.nist.gov/Wavelength/Ciddor.asp>.
150. Gong, Y., et al., *Ultrafast imaging of surface plasmons propagating on a gold surface*. Nano Lett, 2015. **15**(5): p. 3472-8.
151. Dombi, P., et al., *Observation of few-cycle, strong-field phenomena in surface plasmon fields*. Opt Express, 2010. **18**(23): p. 24206-12.

152. Lee, H.S., et al., *Loss mechanisms of surface plasmon polaritons propagating on a smooth polycrystalline Cu surface*. Opt Express, 2012. **20**(8): p. 8974-81.
153. Zeng, X., et al., *Phase change dispersion of plasmonic nano-objects*. Sci Rep, 2015. **5**: p. 12665.
154. Sardana, N., et al., *Surface plasmons on ordered and bi-continuous spongy nanoporous gold*. New Journal of Physics, 2014. **16**(6): p. 063053.
155. Zhang, W., Q. Li, and M. Qiu, *A plasmon ruler based on nanoscale photothermal effect*. Opt Express, 2013. **21**(1): p. 172-81.
156. Liu, X., et al., *A sensitive 2D plasmon ruler based on Fano resonance*. RSC Advances, 2016. **6**(85): p. 81757-81762.
157. Liu, N., et al., *Three-dimensional photonic metamaterials at optical frequencies*. Nature Materials, 2008. **7**(1): p. 31-37.
158. Kübler, H., et al., *Coherent excitation of Rydberg atoms in micrometre-sized atomic vapour cells*. Nature Photonics, 2010. **4**: p. 112.
159. Bjorklund, G.C., *Frequency-modulation spectroscopy: a new method for measuring weak absorptions and dispersions*. Optics Letters, 1980. **5**(1): p. 15-17.
160. Yacoot, A. and N. Cross, *Measurement of picometre non-linearity in an optical grating encoder using x-ray interferometry*. Measurement Science and Technology, 2002. **14**(1): p. 148-152.
161. Tame, M.S., et al., *Quantum plasmonics*. Nature Physics, 2013. **9**: p. 329.
162. Zhu, W., et al., *Quantum mechanical effects in plasmonic structures with subnanometre gaps*. Nature Communications, 2016. **7**: p. 11495.
163. Ushakov, N. and L. Liokumovich, *Resolution limits of extrinsic Fabry-Perot interferometric displacement sensors utilizing wavelength scanning interrogation*. Appl Opt, 2014. **53**(23): p. 5092-9.
164. Mathew-Fenn, R.S., et al., *A molecular ruler for measuring quantitative distance distributions*. PLoS One, 2008. **3**(10): p. e3229.
165. Ramirez, A.S., et al., *Structural basis of the molecular ruler mechanism of a bacterial glycosyltransferase*. Nature Communications, 2018. **9**.
166. Sekar, R.B. and A. Periasamy, *Fluorescence resonance energy transfer (FRET) microscopy imaging of live cell protein localizations*. J Cell Biol, 2003. **160**(5): p. 629-33.
167. Edmondson, W., *GAS ANALYSIS BY REFRACTIVE INDEX MEASUREMENT*. BJA: British Journal of Anaesthesia, 1957. **29**(12): p. 570-574.
168. Schellekens, P., et al., *Measurements of the Refractive Index of Air Using Interference Refractometers*. Metrologia, 1986. **22**(4): p. 279-287.
169. Liedberg, B., C. Nylander, and I. Lunström, *Surface plasmon resonance for gas detection and biosensing*. Sensors and Actuators, 1983. **4**: p. 299-304.
170. Wu, X., et al., *Refractive index sensor based on surface-plasmon interference*. Opt Lett, 2009. **34**(3): p. 392-4.
171. Kretschmann, E. and H. Z. Raether, *Notizen: Radiative Decay of Non Radiative Surface Plasmons Excited by Light*. Vol. 23. 1968.
172. Kabashin, A.V. and P.I. Nikitin, *Surface plasmon resonance interferometer for bio- and chemical-sensors*. Optics Communications, 1998. **150**(1): p. 5-8.
173. Melendez, J., et al., *A commercial solution for surface plasmon sensing*. Sensors and Actuators B: Chemical, 1996. **35**(1): p. 212-216.
174. Zhang, L.M. and D. Uttamchandani, *Optical chemical sensing employing surface plasmon resonance*. Electronics Letters, 1988. **24**(23): p. 1469-1470.
175. Kabashin, A.V., S. Patskovsky, and A.N. Grigorenko, *Phase and amplitude sensitivities in surface plasmon resonance bio and chemical sensing*. Opt Express, 2009. **17**(23): p. 21191-204.
176. Kalyuzhny, G., et al., *Transmission surface-plasmon resonance (T-SPR) measurements for monitoring adsorption on ultrathin gold island films*. Chemistry, 2002. **8**(17): p. 3849-57.

177. Malinsky, M.D., et al., *Chain Length Dependence and Sensing Capabilities of the Localized Surface Plasmon Resonance of Silver Nanoparticles Chemically Modified with Alkanethiol Self-Assembled Monolayers*. Journal of the American Chemical Society, 2001. **123**(7): p. 1471-1482.
178. Jung, L.S., et al., *Quantitative Interpretation of the Response of Surface Plasmon Resonance Sensors to Adsorbed Films*. Langmuir, 1998. **14**(19): p. 5636-5648.
179. <http://biosensingusa.com/technical-notes/technical-note-102-spr-sensitivity-detection-limit/>.
180. Wenger, T., et al., *High-sensitivity plasmonic refractive index sensing using graphene*. 2D Materials, 2017. **4**(2): p. 025103.
181. Andrews, N.L., et al., *In-fiber Mach-Zehnder interferometer for gas refractive index measurements based on a hollow-core photonic crystal fiber*. Opt Express, 2016. **24**(13): p. 14086-99.
182. Schasfoort, R. and A. Tudos, *Handbook Of Surface Plasmon Resonance*. 2007. 403.
183. Anh, N.D., et al., *Plasmonic dynamics measured with frequency-comb-referenced phase spectroscopy*. Nature Physics, 2019. **15**(2): p. 132-137.
184. Kravets, V.G., et al., *Singular phase nano-optics in plasmonic metamaterials for label-free single-molecule detection*. Nature Materials, 2013. **12**: p. 304.
185. Sreekanth, K.V., et al., *Biosensing with the singular phase of an ultrathin metal-dielectric nanophotonic cavity*. Nature Communications, 2018. **9**(1): p. 369.
186. Clergent, Y., C. Durou, and M. Laurens, *Refractive Index Variations for Argon, Nitrogen, and Carbon Dioxide at $\lambda = 632.8$ nm (He-Ne Laser Light) in the Range $288.15\text{ K} \leq T \leq 323.15\text{ K}$, $0 < p < 110\text{ kPa}$* . Journal of Chemical & Engineering Data, 1999. **44**(2): p. 197-199.
187. Wientjes, E., et al., *Strong antenna-enhanced fluorescence of a single light-harvesting complex shows photon antibunching*. Nature Communications, 2014. **5**: p. 4236.
188. Kinkhabwala, A., et al., *Large single-molecule fluorescence enhancements produced by a bowtie nanoantenna*. Nature Photonics, 2009. **3**: p. 654.
189. <https://www.convertunits.com/from/mmH2O/to/pascal>.
190. Butt, H.-J.G., Karlheinz; Kappl, Michael, *Physics and Chemistry of Interfaces*. 2006.
191. Gennes, P.-G.d.F.B.-W.D.Q., *Capillarity and Wetting Phenomena*. Springer, 2004.
192. Sarrazin, M., J.-P. Vigneron, and J.-M. Vigoureux, *Role of Wood anomalies in optical properties of thin metallic films with a bidimensional array of subwavelength holes*. Physical Review B, 2003. **67**(8): p. 085415.
193. Ruan, Z. and M. Qiu, *Enhanced Transmission through Periodic Arrays of Subwavelength Holes: The Role of Localized Waveguide Resonances*. Physical Review Letters, 2006. **96**(23): p. 233901.
194. Genet, C., M.P. van Exter, and J.P. Woerdman, *Fano-type interpretation of red shifts and red tails in hole array transmission spectra*. Optics Communications, 2003. **225**(4): p. 331-336.
195. McMahon, J.M., et al., *Tailoring the sensing capabilities of nanohole arrays in gold films with Rayleigh anomaly-surface plasmon polaritons*. Opt Express, 2007. **15**(26): p. 18119-29.
196. Gao, H., et al., *Rayleigh anomaly-surface plasmon polariton resonances in palladium and gold subwavelength hole arrays*. Opt Express, 2009. **17**(4): p. 2334-40.
197. Jiang, Y.-W., et al., *Effect of Wood's anomalies on the profile of extraordinary transmission spectra through metal periodic arrays of rectangular subwavelength holes with different aspect ratio*. Optics Express, 2009. **17**(4): p. 2631-2637.
198. Moseley, P.T., *Solid state gas sensors*. Measurement Science and Technology, 1997. **8**(3): p. 223-237.
199. Capone, S., et al., *Solid State Gas Sensors: State of the Art and Future Activities*. Vol. 35. 2004.
200. Kong, J., et al., *Nanotube Molecular Wires as Chemical Sensors*. Science, 2000. **287**(5453): p. 622.
201. Collins, P.G., et al., *Extreme Oxygen Sensitivity of Electronic Properties of Carbon Nanotubes*. Science, 2000. **287**(5459): p. 1801.
202. Dutta, P. and P.M. Horn, *Low-frequency fluctuations in solids: $\frac{1}{f}$ noise*. Reviews of Modern Physics, 1981. **53**(3): p. 497-516.

-
203. Schedin, F., et al., *Detection of individual gas molecules adsorbed on graphene*. Nat Mater, 2007. **6**(9): p. 652-5.
 204. Anker, J.N., et al., *Biosensing with plasmonic nanosensors*. Nature Materials, 2008. **7**: p. 442.
 205. Karim, F., T. B. Smith, and C. Zhao, *Review of optical detection of single molecules beyond the diffraction and diffusion limit using plasmonic nanostructures*. Vol. 12. 2017. 012504.
 206. Schuller, J.A., et al., *Plasmonics for extreme light concentration and manipulation*. Nature Materials, 2010. **9**: p. 193.
 207. Gramotnev, D.K. and S.I. Bozhevolnyi, *Plasmonics beyond the diffraction limit*. Nature Photonics, 2010. **4**: p. 83.
 208. Maier, S.A. and H.A. Atwater, *Plasmonics: Localization and guiding of electromagnetic energy in metal/dielectric structures*. Journal of Applied Physics, 2005. **98**(1): p. 011101.
 209. Zijlstra, P., P.M.R. Paulo, and M. Orrit, *Optical detection of single non-absorbing molecules using the surface plasmon resonance of a gold nanorod*. Nature Nanotechnology, 2012. **7**: p. 379.
 210. Barnes, W.L., A. Dereux, and T.W. Ebbesen, *Surface plasmon subwavelength optics*. Nature, 2003. **424**(6950): p. 824-830.
 211. https://www.ajdesigner.com/idealgas/ideal_gas_law_density.php.
 212. Sreekanth, K.V., et al., *Large-Area Silver–Stibnite Nanoporous Plasmonic Films for Label-Free Biosensing*. ACS Applied Materials & Interfaces, 2018. **10**(41): p. 34991-34999.