Study of visible light modulation based on magneto-optical thin films and dynamically tunable all dielectric metasurface embedded in nematic liquid crystal

Sun, Ming-Yu

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**NANYANG
TECHNOLOGICAL
UNIVERSITY**

SINGAPORE

**Study of visible light modulation based on
magneto-optical thin films and dynamically
tunable all dielectric metasurface embedded in
nematic liquid crystal**

Sun Ming-Yu

SCHOOL OF ELECTRICAL & ELECTRONIC ENGINEERING

2019

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magneto-optical thin films and dynamically tunable
all dielectric metasurface embedded in nematic
liquid crystal**

Sun Ming-Yu

School of Electrical & Electronic Engineering

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

2019

Statement of Originality

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

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Supervisor Declaration Statement

I have reviewed the content and presentation style of this thesis and declare it is free of plagiarism and of sufficient grammatical clarity to be examined. To the best of my knowledge, the research and writing are those of the candidate except as acknowledged in the Author Attribution Statement. I confirm that the investigations were conducted in accord with the ethics policies and integrity standards of Nanyang Technological University and that the research data are presented honestly and without prejudice.

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Zheng Yuanjin

.....
Date

.....
[Supervisor's Name Here]

Authorship Attribution Statement

This thesis contains material from 2 paper(s) published in the following peer-reviewed journal(s) where I was the first and/or corresponding author.

Chapter 3 is based on the results published as M. Y. Sun, X. W. Xu, X. A. Liang, X. W. Sun and Y. J. Zheng. Effect of oxidation on perpendicular magnetic behavior of MnBi thin films, *Journal of Alloys and Compounds* 672 59-63 (2016). DOI: 10.1016/j.jallcom.2016.01.240.

The contributions of the co-authors are as follows:

- A/Prof Zheng Yuanjin suggested the project direction and helped review the manuscript drafts.
- I prepared the manuscript drafts. The manuscript was also revised by Dr Xu Xuewu and Prof Sun Xiaowei.
- I co-work on the study with Dr Xu Xuewu and Dr Liang Xin'an, with all the laboratory work performed at the School of Electrical and electronic engineering and the Data Storage Institute of A*STAR. I also analyzed the data.
- For the details, including sample preparation, sample structure characterization, capture as well as physical properties measurement were conducted by me.

Besides, Chapter 5 to 7 are based on the results accepted by *Scientific Report* journal as M. Y. Sun, X. W. Xu, X. W. Sun, X. A. Liang, V. Valuckas, Y. J. Zheng, R. Paniagua-Domínguez and A. I. Kuznetsov, Efficient visible light modulation based on electrically tunable all dielectric metasurfaces embedded in thin-layer nematic liquid crystals, *Scientific Report* (2019). (Accepted)

The contributions of the co-authors are as follows:

- A/Prof Zheng Yuanjin and Dr A. I. Kuznetsov gave a supervision on the project's progress and helped review the manuscript.
- I wrote the drafts of the manuscript. The manuscript was revised together with Dr. Xu Xuewu, Dr Ramon J. Paniagua-Domínguez and Prof Sun Xiaowei.
- I performed the device preparation, including device fabrication, LC infiltration and alignment check, as well as the simulation and measurement, including the numerical analysis, transmission spectra testing and phase capture.
- Dr. Liang Xin'an helped to carry out the numerical analysis and built the phase measurement setup and the post-processing algorithms for phase retrieval.
- Dr Vytautas Valuckas fabricated the metasurfaces and did the SEM characterization for samples presented in Chapters 4,5 and 7.
- Besides, Dr. Mike Li Shiqiang (not included in the authorship of this journal manuscript) fabricated and did the SEM characterization of the metasurfaces presented in Chapter 6.

30-May-2018

.....
Date

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[Student's Name Here]

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Table of content

Statement of Originality	II
Supervisor Declaration Statement	III
Authorship Attribution Statement	III
Acknowledgements	V
Table of content.....	VII
Abstract.....	X
List of figures.....	XIII
List of tables.....	XXVIII
 Chapter 1: Introduction	 1
1.1 Background.....	1
1.2 Motivation and objectives.....	8
1.3 Issue statement.....	10
1.4 Major contribution.....	12
1.5 Organization of the thesis	13
Chapter 2: Literature review	14
2.1 Magneto-optical spatial light modulation	14
2.1.1 Basics of polarization rotation due to magneto-optical effect	14
2.1.2 Magneto-optical materials	17
2.2 Huygens' surface based on the Mie scattering.....	22
2.2.1 Light-dielectrics interaction	22
2.2.2 Mie-type resonant scattering.....	23
2.2.3 Huygens' surface	24
2.3 Basics of liquid crystal optics.....	29
2.3.1 Liquid crystal material	29
2.3.2 Optics of nematic liquid crystal.....	30
2.3.3 Liquid crystal with microstructures	34
Chapter 3: Magneto-optical spatial light modulation based on MnBi thin film ...	38
3.1 Introduction	38
3.2 Experimental results	39
3.2.1 Fabrication of MnBi thin films.....	40
3.2.2 Perpendicular magnetization of MnBi thin films	44
3.2.3 Magneto-optical performance of MnBi thin films.....	52
3.3 Discussion.....	54
3.3.1 Condition for LTP MnBi fabrication	54

3.3.2	Magnetic properties of MnBi	55
3.3.3	Enhanced MOKE of MnBi thin films with dielectrics	59
3.3	Summary	62
Chapter 4: Optical performance of TiO₂ nano disks metasurface		64
4.1	Introduction	64
4.2	Numerical design of TiO ₂ metasurface	65
4.2.1	Numerical setup for calculation	65
4.2.2	Numerical optical performance of TiO ₂ based on nano disk atoms ...	66
4.3	Experiments	73
4.3.1	Fabrication of TiO ₂ based metasurface	73
4.3.2	Measurement methods	75
4.3.3	Optical performance of TiO ₂ based metasurface	78
4.4	Discussion	80
4.5	Summary	82
Chapter 5: Optical performance of thin layer nematic LC infiltrated TiO₂ nano disks metasurface		84
5.1	Introduction	84
5.2	Numerical analysis of LC based TiO ₂ metasurface	85
5.2.1	Numerical analysis of optical response of TiO ₂ metasurface with liquid crystal for perfect alignment	85
5.2.2	Refined numerical analysis introducing the influence of nanoantennas' anchoring effect	91
5.2.3	Numerical analysis of optical response for the rotated nanoantenna's periodicity layout	94
5.2.4	Numerical phase modulation of TiO ₂ metasurface by LC	96
5.3	Experiments	99
5.3.1	Fabrication process of thin layer liquid crystal based TiO ₂ metasurface	99
5.3.2	Optical performance of LC based TiO ₂ metasurface	104
5.4	Discussion	107
5.4	Summary	111
Chapter 6: Alignment of LC infiltrated in the nano structure		113
6.1	Introduction	113
6.2	Experiments	114
6.2.1	Fabrication of LC based TiO ₂ metasurface of different atom geometries	114
6.2.2	LC alignment in vicinity of TiO ₂ nanoantennas	116
6.2.3	LC alignment influenced by TiO ₂ nanoantennas' geometry	118
6.3	Discussion	125

6.4	Summary	128
Chapter 7: Electric modulation of LC infiltrated TiO₂ metasurface device		
	performance	129
7.1	Introduction	129
7.2	Numerical analysis of LC switching process	130
7.3	Experiments and discussion	132
7.3.1	Electrical modulation of transmittance spectra.....	132
7.3.2	Electrical modulation of phase performance	134
7.4	Summary	136
Chapter 8: Summary and outlook.....		138
8.1	Summary	138
8.2	Outlook	140
Publication list.....		143
Bibliography		145

Abstract

The study of visible light modulators has been intensively focused for advanced applications like the light communication, imaging detection and reconstruction and next generation 3D display like the glass-free flat display and hologram, which calls for highly efficient phase and amplitude modulation available for integrated devices. Traditionally, some 2D spatial light modulators (SLM) have been developed, *e.g.* the liquid crystal display (LCD), digital micro-mirror devices (DMD) and LC on silicon (LCoS), which, however, are insufficient for the future requirement. Magneto-optical based SLM (MO-SLM) shows outstanding performance like fast signal detection as much as $\sim 10^6$ Hz with only a thin film structure. Besides, low conductive dielectrics based metasurface has been widely studied since the Mie scattering can be regulated by the geometry of the atoms and refractive index of the environment, thus leads to a lossless phase and amplitude modulation within the subwavelength periodicity of the nano structures as small as hundreds of nano-meters. Efficient dynamic visible light modulation can be expected in the tiny structures by combing the manually designable metasurface with the tunable medium.

However, for the reflective Kerr type magneto-optical devices, issues like the small polarization rotation angles ($\sim 0.1^\circ$), oxidation of the materials and reduced magnetization after pixilation process has proved the limitation of MOSLM development at the current stage. Here, to find potential solutions toward the highly efficient phase and amplitude modulation, two ideas are proposed: magneto-optical SLM (MO-SLM) based on the MnBi thin films with large perpendicular magnetic anisotropy as well as the dielectric TiO_2 metasurface which is tunable by LC with large birefringence. Device fabrication and optics analysis is carried out to verify the performance and feasibility of the technology for application.

In this paper, the background and motivation of the research work is given in Chapter 1; the literature review about the MO effect, Mie scattering, and LC optics is given in Chapter 2; the magneto-optical spatial light modulation based on the MnBi thin films is discussed in Chapter 3; the fabrication and optical response of TiO_2 metasurface before and after LC infiltration is discussed in

Chapter 4 and 5; the LC alignment performance within the nano antennas is introduced in Chapter 6; the electrical tuning of LC infiltrated TiO₂ metasurface is demonstrated in Chapter 7.

For study of MOSLM, the 60 nm thin layer low temperature phase (LTP) MnBi thin films were successfully fabricated with a large perpendicular magnetization anisotropy (PMA) of 480 emu/cm³ together with a magneto-optical Kerr effect (MOKE) as much as 0.5° polarization rotation which is much larger than other materials reported. Thin film MnBi samples were fabricated by magnetron sputtering deposition of the multilayer with a total thickness ratio of Mn/Bi=20/40 nm before a 2hrs thermal annealing at 350 °C. An increased number of the periods x of the multilayered stack structure as [Mn/Bi] _{x} can improve the inter-diffusion of Mn and Bi atoms during the thermal annealing thus leads to a better MnBi phase formation. The perpendicular magnetization anisotropy was measured by superconductive quantum interference device (SQUID) and the Micro-Magnetic Alternating Gradient Magnetometer (AGM), showing a large PMA about 500 emu/cm³. However, the sample is apt to be oxidized presented by magnetic measurements compared between a 14-day interval exposure in ambient environment. Ru and Ta layers were deposited on top of the MnBi film as the capping layer. Ta capping layer shows a better performance than Ru for protection of the MnBi magnetic properties. MO performance was tested, showing a consistent dependence with the PMA on the Mn/Bi contents. A dramatic enhancement of Kerr signal can be expected by introducing a layer of dielectric TiO₂ layer (0.86° to 9.5° at 633 nm) based on the numerical simulation. However, the large PMA and MOKE is normally received in cost of large coercivity, which would hinder the possible application of the high-speed switching of MO-SLM for display application.

In the meantime, the idea of electrically tunable metasurface was studied based on the LC infiltrated TiO₂ nano cylinders metasurface. A wide range shift in spectra (close to 20 nm around the resonance $\lambda \sim 670$ nm) can be obtained in the sample with a 1.5 μ m thin layer LC and drivable under a small voltage below 8 V. A dynamic phase shift in the range of 0~1.5 π is obtained in the LC infiltrated TiO₂ cylinders metasurface device. TiO₂ metasurface of nano cylinders was fabricated by a series of standard process of e-beam lithography. The comparable

magnitude of electric and magnetic dipole resonance was excited simultaneously within the TiO_2 and tunable by the atoms' geometry. The geometry of the atoms was designed with a periodicity about $P = 360$ nm and the resonances were excited within the visible range around $\lambda \sim 600$ nm before LC infiltration and $\lambda \sim 670$ nm after LC infiltration due to the increased refractive index of the environment. Strong surface anchoring effect is observed with a large in-plane LC alignment deviation above $\varphi = 30^\circ$ with respect to the preset LC photoalignment or rubbing alignment. Based on the measurement of optical observation and Raman spectrum, the LC alignment is detected and show sensitive response to the nano antennas' geometry which would produce surface energy to the LC surrounded. Based on the Frank-Oseen model analysis, the stronger surface anchoring effect of the nano structure is non-ignorable for balance with the rubbing/photoalignment influence.

Based on the results in this dissertation, the dynamically tunable metasurface device can be expected as a candidate for the development of the tunable efficient visible light modulator device in future. For the future work, the study of relations between the LC alignment and nano antennas' geometry and a smart control of the addressing will be valuable for better device performance.

List of figures

- Figure 1.1 Current developed SLM for display industry
- Figure 1.2 Example of current main technology of spatial light modulation for the display applications
- Figure 1.3 (a) The concept of MOSLM for light modulation; (b) the MOSLM driven by circuits current; (c) the MOSLM driven by spin transfer torque.
- Figure 1.4 Example of typical LC based metasurface applications reported: (i) the thermally tunable dipole resonance excitation with LC infiltrated within the silicon sample; (ii) the electrically tunable fano response with high efficiency tuning range about 80%; (iii) Surface acoustic wave performance tuned by polymer dispersed LC; (iv) tunable hologram by electrical switching of LC within the plasmonic metasurface; (v) the electrically tunable metasurface based on silicon cylinders' metasurface toward the Huygens condition with a high phase modulation performance.
- Figure 2.1 Sketched illustration of magneto-optical effect for transmissive Faraday effect and reflected Kerr effect. The arrows indicate the direction of the polarizations.
- Figure 2.2 Sketch of incident electric field (polarization) and magnetization alignment for polar, longitudinal and transversal MOKE. The yellow array at the reflection surface defines the direction of vector product of the E and M interaction momentum.
- Figure 2.3 Design of magneto-phonic crystal (PLZT was used to exert the mechanical stimulation to the magnetic layer.); (a) and (c) give the wavelength dependent Kerr rotation and reflectivity results; (b) and (d) show the Kerr rotation and reflectivity under the electrical driving.
- Figure 2.4 Illustration of magneto-optical effect and the three configurations; (b) The light distribution and MO activity in Au/Co/Au stack with SiO₂ inserted at different positions; (c) MO activity influenced by the surficial plasmon polariton and the dispersion relations.

- Figure 2.5 Illustration of Mie type light-matter scattering for particle sizes smaller, comparable and larger to the incident wavelength. The x defines the relation between particle size and effective unit optical distance as $x=2\pi nr/\lambda$.
- Figure 2.6 (a) Schematic representation of electric and magnetic field distribution inside the scattered resonator particles; (b) experimental and numerical results of transmissive spectra depending on the nano disk radii variation range. The black dashed circle represents the nano disk radius window for Huygens' condition; (c) Near-field map of the cross-section of the nanodisk with optimized geometry for Huygens' condition, indicating a normalized distribution of the electric (E) and magnetic (M) fields distribution with respect to the incident polarized plane wave.
- Figure 2.7 (a) Sketched nano antennas as the Huygens source unit with the electric and magnetic dipoles excited under the polarized incidence; (b) to (f) the calculated results of transmittance, E and H fields amplitude, and the phase shift for non-overlapped (top) and overlapped response (bottom) of the atoms.
- Figure 2.8 Performance of applicable Huygens' surface: (a) Huygens' surface within the range of optimized nano antennas geometry for high efficient passive Hologram display; (b) development of phase gradient Huygens' surface for light bending performance; (c) electrically tunable metasurface with the optical response (transmissive spectra and phase shift) varies across the Huygens' condition.
- Figure 2.9 (a) Molecule structure of the nematic liquid crystal; (b) Raman spectra of LC showing the peaks of the typical chemical bonds: $\sim 1200\text{ cm}^{-1}$ for C-C skeletal bond, $\sim 1600\text{ cm}^{-1}$ for C-C benzene ring and $\sim 2200\text{ cm}^{-1}$ for C-N cyan bond.
- Figure 2.10 (a) Schematic representation of three phases of LC; (b) Illustration of polarized light propagation through the biaxial birefringent media; (c) Temperature dependence of refractive index of LC.

- Figure 2.11 Calculated transmittance of 90° twisted LC. The abscissa gives the ratio between dielectric anisotropy ($d\Delta n$) with the wavelength (λ)
- Figure 2.12 Samples of LC based nanostructured devices: (a) the LC tunable hologram; (b) thermal tunable LC based Si metasurface; (c) electrically tunable fano resonance performance; (d) electrically tunable Si based Huygens surface
- Figure 2.13 Schematic illustration of LC alignment within the nano structured cells under the influence of both the surface anchoring effect and top alignment energy by either rubbing or photoalignment
- Figure 3.1 (a) Structure of low temperature phase MnBi lattice; (b) Mn and Bi thermal annealing process for MnBi fabrication
- Figure 3.2 Some equipment for MnBi thin film fabrication: (a) magnetron-sputtering system, (b) homemade vacuum oven for thermal annealing, (c) AES system, (d) AGM system (e) optical microscope
- Figure 3.3 (a) XRD pattern of 30 nm Bi as deposited; (b) XRD pattern of MnBi (Mn/Bi = 15/30 nm) thermally annealed; Step profilers of Bi layers deposited at (c) DC mode for 4.5 mTorr and RF mode for (d) 1.5 mTorr and (e) 1.15 mTorr
- Figure 3.4 XRD patterns of Bi single layers with (a) 20 nm, (b) 30 nm and (c) 40 nm thicknesses, and (d) 20/40 nm and (e) 10/20 nm Mn/Bi films after thermal annealing in vacuum at 350 °C for 2 hrs.
- Figure 3.5 XRD patterns of MnBi thin films with Mn/Bi thickness ratios as (a) 24/40 nm, (b) 22/40 nm, (c) 20/40 nm and (d) 16/40 nm after thermal annealing in vacuum. The black dots represent the peaks of wafer substrate. The peaks of MnBi and Mn oxides were marked in the patterns. (a) Microscopic images of MnBi surface morphology with Mn/Bi thickness ratios from 24/40 to 14/40 nm, (b) AES cross sectional depth profile of 20/40 and 22/40 nm MnBi film.
- Figure 3.6 (a) Microscopic images of MnBi surface morphology with Mn/Bi thickness ratios from 24/40 to 14/40 nm; The circle marks the

- MnBi phase. (b) AES cross sectional depth profile of 20/40 and 22/40 nm MnBi film for O, Bi, Mn and Si.
- Figure 3.7 XRD patterns of $[\text{Mn/Bi}]_x$ multilayer MnBi films for (a) $x = 10$, (b) $x = 4$, (c) $x = 2$ and (d) $x = 1$; the dots point out the diffractive peaks of the silicon wafer
- Figure 3.8 Magnetic hysteresis loop of MnBi thin film measured by SQUID and AGM under magnetic fields perpendicular and parallel to the sample's surface
- Figure 3.9 PMA magnetic performance of wafer substrate and the MnBi thin film with Mn/Bi thickness ration from 24/40 to 16/40 measured by the AGM system
- Figure 3.10 Training effect of PMA MnBi under repeat magnetic training measurement
- Figure 3.11 PMA magnetic performance of MnBi thin film exposed without the capping layer
- Figure 3.12 PMA magnetic performance of the MnBi thin film with Ta and Ru capping layer and compared with the capping layer free sample
- Figure 3.13 PMA comparison of MnBi with Ta capping layer before and after exposure
- Figure 3.14 AFM surface morphology of the pixilated MnBi microstructures of (a) and (c) D500/S1500 and (b) and (d) D1000/S1000
- Figure 3.15 (a) PMA of pixilated MnBi thin films with Fill Factors of 0.0625, 0.1225, 0.25 and 1; (b) FF dependence of coercivity (H_c) and saturated magnetization (M_s)
- Figure 3.16 (a) MOKE results of MnBi with different Mn/Bi thickness ratios; (b) Comparison of Kerr rotation and PMA magnitude depending on the Mn/Bi thickness ratios
- Figure 3.17 (a) Surface morphology characterized by the optical microscope with 100X magnification for $[\text{Mn/Bi}]_x$ with $x =$ (i) 10, (ii) 4, (iii) 2 and (iiii) 1; (b) Kerr rotation signal of the multi-layered MnBi thin films
- Figure 3.18 XRD patterns of (a) as-deposited Mn/Bi/SiO₂/Si, (b) Sample 1 and (c) Sample 2 when fabricated, (d) Sample 1 and (e) Sample 2

after the 14-day exposure to air, and (f) bare MnBi films with Mn thicknesses of (i) 20 nm (Sample 1), (ii) 22 nm (Sample 3) and (iii) 24 nm (Sample 4) after the 14-day exposure to air. The unmarked peaks represent the wafer substrate.

Figure 3.19 Depth profile of elemental distribution of (a) Sample 1 and (b) Sample 2. The dashed lines (orange) give the Mn/Bi atomic ratio.

Figure 3.20 AFM and MFM images of (a) Sample 1 when fabricated, (b) Sample 1 and (c) Sample 2 after the 14-day exposure to air

Figure 3.21 Illustration of magneto-crystal anisotropy and inter-grain exchange energy across the domain boundaries. The hexagons define the magnetic domain areas and the red dash squares represent the boundaries' areas.

Figure 3.22 Dependence of MO properties of MnBi-based stack structures #1-#4 on the TiO_2 thickness (t): (a–c) Kerr rotation ($2\theta_k$) at RGB wavelengths; (d-f) Reflectivity at RGB wavelengths

Figure 4.1 The model of numerical calculation for FDTD simulation

Figure 4.2 The transmittance and reflectance spectra of TiO_2 nano cylinder ($P = 360$ nm, $R = 160$ nm and $H = 188$ nm) for $\varphi = 0^\circ, 45^\circ$ and 90° incidences. The value of the plot represents the percentage of the output intensities normalized to the incidence.

Figure 4.3 The electric and magnetic dipole resonances detection for the $\varphi = 0^\circ, 45^\circ$ and 90° incidences: (a) the spectra of electric and magnetic resonant dipole; (b) electric dipole resonance along the x and y directions; (c) magnetic dipole resonance along the x and y directions. The values of the plots represent the excitation magnitude of the dipoles amplitude normalized to the incident field.

Figure 4.4 (a) Transmittance, (b) Electric and (c) magnetic dipoles resonances of TiO_2 metasurface for various incident polarizations from $\varphi = 0^\circ$ to 180° . The value in (a) represents the percentage of transmittance normalized to the incident intensity and value in (b) and (c) represents the excitation magnitude of the dipoles amplitude normalized to the incident field.

- Figure 4.5 The electric (E) and magnetic (H) field distribution (top view) for incident polarization of $\varphi = 0^\circ$, 45° and 90° . The radius of the cylinder is set $R = 160$ nm. The value of the plots represents the dipoles amplitude normalized to the incident field.
- Figure 4.6 (a) Transmittance, (b) reflectance, (c) E_x , (d) E_y , (e) H_x and (f) H_y of the TiO_2 metasurface for various nano disk height from 185 to 200 nm for $\varphi = 0^\circ$ incident polarization. The radius of the nano disks was set 160 nm. The value in (a) and (b) represents the percentage of transmittance and reflectance normalized to the incident intensity and value in (c) to (f) represents the excitation magnitude of the dipoles' amplitude normalized to the incident field.
- Figure 4.7 (a) Transmittance, (b) reflectance, (c) E_x , (d) E_y , (e) H_x and (f) H_y of the TiO_2 metasurface for various nano disk radius from 146 to 164 nm for $\varphi = 0^\circ$ incident polarization. The height of the nano disks was set 188 nm. The value in (a) and (b) represents the percentage of transmittance and reflectance normalized to the incident intensity and value in (c) to (f) represents the excitation magnitude of the dipoles amplitude normalized to the incident field.
- Figure 4.8 Simulated results of the transmittance spectra (red curve) for the TiO_2 nano disk with geometry parameters: array pitch of 360 nm, radius of 160 nm, disk height of 188 nm for $\varphi = 0^\circ$ incident polarization, together with the corresponding 1.5π phase shift response (blue curve) with two steps located at the resonances of $\lambda \sim 620$ nm and $\lambda \sim 640$ nm in spectra.
- Figure 4.9 Near-field maps of the (a) top view (xy plane) and (b) side view (yz plane) of the nano disk array with the optimized geometry ($P=360$ nm, $R=160$ nm and $H=184$ nm) for the wavelength $\lambda \sim 640$ nm, showing a perpendicular electric (blue arrays) and magnetic field (yellow arrays) distribution in the plane. The value of the plots (a) and (b) represents the dipoles amplitude normalized to the incident field.

- Figure 4.10 The simulated data of phase change response for the range of (a) H and (b) R parameters. The black dash lines indicate the evolution of the dipoles' resonances with the variance.
- Figure 4.11 (a) Side view of the SEM capture of the TiO_2 nano disks fabricated; Top view of the (b) 130, (c) 140, (d) 150 and (e) 160 nm radius nano disks etched under the 0.84 exposure dosage.
- Figure 4.12 Capture of arrays fabricated under 0.84 exposure dosage for atoms with designed radius of 160, 150 and 140 nm.
- Figure 4.13 Measurement setup for the spectral and phase signal detection. The spectrometer consists of the microscope, spectrometer detector and CCD camera.
- Figure 4.14 Sketch of phase measurement optical setup (left) and logical chart for phase calculation based on the 5-frame algorithm phase-shift method (right). The 5 steps intensities were obtained via the movement of the mirror on the piezo nano stage.
- Figure 4.15 The calculated (a) unwrapped and (b) wrapped phase map of TiO_2 nano cylinders array (the square inside the map) by five-step algorithm program.
- Figure 4.16 Comparison of calculated ($P=360$ nm, $R=160$ nm and $H=188$ nm) (black curve) and measured (red and blue curves) transmittance spectra of the TiO_2 nanodisks metasurface before the LC infiltration. The inset gives the scanning electron microscope (SEM) image of the fabricated TiO_2 metasurface.
- Figure 4.17 Transmittance spectra of TiO_2 nano disk ($P=360$ nm and $H=188$ nm) metasurface with the radius varies in the range from 140 to 160 nm for both the 0° (blue curves) and 45° (red curves) array layout measured by $\varphi = 0^\circ$ incident polarization. The value of the curves represents the percentage of the transmission intensity normalized to the incidence.
- Figure 4.18 Phase shift spectra of TiO_2 nano disk ($P=360$ nm and $H=188$ nm) metasurface with the radius varies in the range from 140 to 160 nm for both the 0° (blue curves) and 45° (red curves) array layout for $\varphi = 0^\circ$ incident polarization. The value of the curves represents the unwrapped phase shift data.

Figure 4.19 (a) Transmittance and phase shift response of TiO_2 nano disk metasurface with ambient refractive index ranging from 1.0 to 2.2; (b) the decomposition of electric and magnetic dipole response of the metasurface with ambient refractive index ranging from 1.2 to 2.2. The label of the dipole resonances map represents the intensity of the resonance.

Figure 5.1 Sketch of electrically tunable transmission type TiO_2 metasurface with LC infiltration sandwiched by ITO-coated glass substrates. The LC, in the absence of any applied voltage, is aligned by the photoalignment layer defined as x -axis coated onto the top ITO glass surface (the photoalignment direction is given by the white arrow). LC alignment near the nanostructures can be altered by its presence influenced by both the photoalignment layer and the anchoring effect of nanostructures.

Figure 5.2 (a) Numerically calculated transmission spectra of LC infiltrated TiO_2 metasurface for nano-disks' height ranging from 180 to 204 nm, with a fixed radius of 160 nm. The dashed lines indicate the evolution of electric and magnetic dipole resonances. (b) The resonance amplitude of both electric (E) and magnetic (H) dipoles. The value in (a) represents the percentage of transmittance normalized to the incident intensity and value in (b) represents the excitation magnitude of the dipoles' amplitude normalized to the incidence field.

Figure 5.3 (a) Numerically calculated transmission spectra of LC infiltrated TiO_2 metasurface for nano-disks' radii ranging from 140 to 170 nm, with a fixed height of 188 nm. The dashed lines indicate the evolution of electric and magnetic dipole resonances. (b) The resonance amplitude of both electric (E) and magnetic (H) dipoles. The value in (a) represents the percentage of transmittance normalized to the incident intensity and value in (b) represents the excitation magnitude of the dipoles amplitude normalized to the incidence field.

Figure 5.4 Numerically calculated transmission spectra of LC infiltrated TiO_2 metasurface (Periodicity 360 nm, Height 188 nm, Radius XX

160 nm) for the $\varphi = 0^\circ$, 45° and 90° polarized incidence. The LC is set aligned along with the $\varphi = 0^\circ$ parallel to x -axis direction.

Figure 5.5 (a) Numerically calculated evolution of electric and magnetic dipole excitation under incidence from $\varphi = 0^\circ$ to 90° ; (b) Evolution of electric dipole components along x and y directions. The value of the plot in (a) and (c) represents the excitation magnitude of the dipoles amplitude normalized to the incidence field.

Figure 5.6 (a) The coordinates of LC alignment with TiO_2 nano cylinder metasurface; (b) illustration of LC infiltrated TiO_2 metasurface models of (i) parallel (*pa.*) and (ii) twist (*tw.*) alignment for simulation. The in-plane angle φ defines the influence due to the surface nanoantennas' anchoring effect on the LC molecules.

Figure 5.7 Calculated transmittance percentage for the (a-c) parallel (*pa.*) and (d-f) twisted (*tw.*) model of LC alignment for incident polarization along $\varphi = 0^\circ$, $\varphi = 45^\circ$ and $\varphi = 90^\circ$ directions. The alignment angles are defined by the LC molecules orientation angles near the nanostructures from 0 to 45 degrees representing the influence of the anchoring effect. The data is given in percentage of the transmission normalized to the incident intensity.

Figure 5.8 (a) Calculated transmittance spectra of TiO_2 nano disks metasurface after LC infiltration for variation of in-plane LC alignment angles ranging from 0° to 90° with respect to the photoalignment direction (x -axis) using the parallel (*pa.*) alignment model. The incident light is polarized along the x -axis (0° pol.); (b) Electric and (c) magnetic dipole resonances and the excited electric dipole components along (e) x and (f) y directions for the incident polarization parallel to $\varphi = 0^\circ$ with LC in-plane alignment directions varied from $\varphi = 0^\circ$ to 90° to the x -axis corresponding to (a).

Figure 5.9 Calculated transmittance spectra of LC infiltrated TiO_2 metasurface for incident polarization from $\varphi = 0^\circ$ to 180° for (a) 0° array with LC along 45° direction (x -axis) and (b) 45° array with LC along 0° direction. The value of the plots represents the

percentage of the transmission normalized to the incident intensities.

- Figure 5.10 Comparison of numerically simulated transmittance (red curve) and phase shift (blue curve) results of optimized geometry nanoantennas ($P = 360$ nm, $H = 196$ nm and $R = 160$ nm) for LC aligned along the x -axis and $\varphi = 0^\circ$ incidence polarization. The black dash line marked the resonant position for both the transmittance and phase shift in spectrum.
- Figure 5.11 Numerically calculated phase shift of LC infiltrated TiO_2 metasurface for nano cylinders' (a) height from 180 to 204 nm, with a fixed radius of 160 nm, and (b) radii from 140 to 170 nm, with a fixed height of 188 nm. The dashed lines indicate the evolution of electric and magnetic dipole resonances.
- Figure 5.12 Numerically calculated phase shift of LC infiltrated TiO_2 metasurface ($H = 188$, $R = 160$ nm) for incident polarizations from $\varphi = 0^\circ$ to 180° with arrays of (a) 0° periodic layout infiltrated with 45° LC and (b) 45° periodic layout infiltrated with 0° LC
- Figure 5.13 Numerically calculated phase shift of LC infiltrated TiO_2 metasurface ($H = 188$, $R = 160$ nm) with a coherent in-plane LC alignment from 0° to 45° shown in (a) the stacks of phase shift spectra for 0° , 15° , 30° and 45° LC alignment and (b) the mapping of the continuous evolution for $\varphi = 0^\circ$ incident polarization.
- Figure 5.14 Fabrication process of LC cell for the transmissive type TiO_2 metasurface on ITO glass substrates
- Figure 5.15 The equipment for LC fabrication process: (a) glass cleaning tank, (b) heater oven, (c) sealant drawer, (d) rubbing stage, (e) spacers sprayer, (f) hot-press stage, (g) vacuum LC infiltrator
- Figure 5.16 (a) The CCD capture of LC background aligned with (i) & (iii) photoalignment and (ii) & (iv) rubbing alignment before and after applying voltages. The alignment direction was marked with the white arrows. (b) The micro-optical images captured by optical microscope for aso-dye solvent coated ITO glass under (v) 3000, (vi) 4000 and (vii) 5000 rpm.

Figure 5.17 (a) SEM images of the cross-section of the sealed ITO cell with 1.5 and 6 μm gaps for LC infiltration. The inset gives the image of ITO glass sprayed with 1.5 μm silica sphere spacers via the optical microscope. (b) The interference spectra of sealed ITO cell with gaps nominally of (i) 1.5, (ii) 5 and (iii) 10 μm .

Figure 5.18 Measured transmission of the fabricated LC cell. (a) Transmission of the bare LC cell without metasurface for incidence polarization varied from $\varphi = 0^\circ$ to 90° with respect to the photo-alignment direction (x -axis). The spectra are detected through a polarizer oriented perpendicular to the incident polarization. This configuration allows measuring a cross-polarized transmission induced by LC birefringence. The transmission signal is maximized for 45° and is almost zero for 0° and 90° polarization incidence indicating a well aligned LC orientation along the photo-alignment direction. (b) Captured LC cell image under 0, 0.5, 1, 2, 3 and 4 V with transmission passed through polarizers and analyzer before and after the cell set perpendicular to each other (cross-polarized light detection). The incident polarization is rotated 45° with respect to the LC photo-alignment direction (white arrow). The transmission can be almost blocked above 3 V indicating a complete switching of LC molecules to the vertical orientation (along the z -axis). (c) Transmittance percentage of the bare LC cell under electrical voltages from 0 to 8 V with the photoalignment direction 45° to the polarizer. The measurement setup is the same as in (b).

Figure 5.19 Transmittance of LC infiltrated TiO_2 nano cylinders with the designed radius varying from 120 to 160 nm fabricated with 0.8 exposure dosage. The figures show the results of 0° layout for $\varphi =$ (a) 0° , (b) 45° , (c) 90° polarizations and (d) 45° layout for $\varphi = 0^\circ$. The dash lines show the evolution of E and M resonances.

Figure 5.20 (a) Measured transmittance spectra of 0° array after LC infiltration for the $\varphi = 0^\circ$ (black curve), 45° (red curve) and 90° (blue curve) incidences; (b) Comparison between the simulated (red curve) and measured (blue curve) results for $\varphi = 0^\circ$ polarization incidence.

The green dash line gives the measured transmittance of the pure ITO soda lime glass substrates.

Figure 5.21 Transmittance of LC infiltrated arrays of (a) 0° and 45° periodic layout with incident polarization rotated from $\varphi = 0^\circ$ to 180° and compared against the numerical simulations. The dash lines show the evolution of the resonances in the transmittance spectra. The value of the plots represents the percentage of the transmission normalized to the incident intensities.

Figure 5.22 Illustration of birefringence within LC infiltrated 0° and 45° layout arrays for $\varphi = 0^\circ$ polarization incidence. The blue line across the atoms indicates the assumed LC's extraordinary direction with n_e . The angle φ defines the rotated LC alignment with respect to the x -axis.

Figure 5.23 Calculated results of transmittance of LC infiltrated TiO_2 cylinders with the $\varphi = 30^\circ$ LC in-plane alignment for incident polarizations varied from 0° to 180° . The value of the plot represents the percentage of the transmission normalized to the incident intensities.

Figure 5.24 Calculated electric and magnetic dipole resonances in the parallel model for the varied incident light polarizations with LC alignment set at 30° with respect to x -axis. (a) Electric dipole response for the incidence polarization varied from $\varphi = 0^\circ$ to 180° with respect to x -axis; (b) Comparison between the excited electric dipole components along x and y directions; (c) magnetic dipole response for the incidence polarization varied from $\varphi = 0^\circ$ to 180° with respect to x -axis. The intensity of the dipole resonance was normalized by the incident fields.

Figure 6.1 Sample of micro-structure of TiO_2 nanoantennas with different geometric parameters for (a) to (d) rectangular and (e) to (h) cylindroid shapes captured by scanning electron microscope (SEM)

- Figure 6.2 Measured Raman spectra of pure LC aligned along x -axis ($\varphi = 0^\circ$) illuminated by the 488 nm blue light. The peaks of the typical LC chemical bonds have been marked by symbols.
- Figure 6.3 (a) Measured Raman spectral curve of pure LC with different incident polarizations. The inset sketches the relations between incident polarization and LC alignment. (b) The measured Raman signal intensities for incident polarizations from -90° to 150° with respect to x -axis. All the Raman signals were normalized with the 0° signal (I_0)
- Figure 6.4 (a) Measured Raman spectrum of A6 array. The inserts show the capture of the array for the $\varphi = 0^\circ$ incident polarization. (b) The Raman spectra measured at different points of the array as indicated in the insert of (a) and the LC background for $\varphi = 0^\circ$ and 90° incidences.
- Figure 6.5 Capture of 1:1 aspect ratio's array of squares and cylinders with dimension from 160 to 320 nm with LC. The dimension is defined by the length of the side for square and the diameter for cylinder. The setup of polarizer (P) and analyzer (A) is given by the arrows at the lower right corner.
- Figure 6.6 (a) Measured Raman spectra for arrays of different length from 160 nm to 320 nm for the $\varphi = 0^\circ$ incident polarization. (b) The intensity of 1600 cm^{-1} peak for different geometry length normalized to the LC background of 0° alignment.
- Figure 6.7 Capture of rectangular and cylindroid arrays of aspect ratios from 1:4 to 1:1 with dimension from 120/320 to 320/320 nm with LC. The dimension is defined by the length of the side for the rectangular (a/b) and the axis for the cylindroid (D_1/D_2). The setup of polarizer (P) and analyzer (A) is given by the arrows at the lower right corner.
- Figure 6.8 (a) Measured Raman spectra for arrays of different aspect ratios from 1:4 to 1:1 with dimension from 120/320 to 320/320 nm with LC infiltrated for the $\varphi = 0^\circ$ incident polarization. (b) The intensity of 1600 cm^{-1} peak for different geometry length normalized to the LC background of 0° alignment.

- Figure 6.9 Capture of rotated square arrays with LC of 1:1 aspect ratios with dimension from 160 (A3) to 280 nm (A6) defined by the side length of the square. The rotation is set $\varphi = 30^\circ, 45^\circ, 60^\circ$ and 90° with respect to the x-axis. The setup of polarizer (P) and analyzer (A) is given by the arrows at the lower right corner. Mapping of the LC alignment is derived from the Raman spectra. The angles are calculated for the 1600 cm^{-1} peak for each position.
- Figure 6.10 The calculated LC alignment angles with respect to the x axis reflected by the Raman spectral mapping of A6 (280 nm square) array with LC infiltrated after (a) one and (b) two repeats of rubbing process. The angles are calculated based on 1600 cm^{-1} peak of spectra scanned for the 8×8 points along X and Y directions. The dash line frames the array area.
- Figure 6.11 Images of arrays captured for A6 array with (a) two and (b) one repeats of rubbing process, and (c) A11 array with one time rubbing process
- Figure 6.12 The calculated LC alignment angles with respect to the x axis reflected by the Raman spectral mapping of the arrays with LC infiltrated after one time rubbing process for (a) A4 (200 nm square), (b) A11 (200/320 nm rectangular), (c) B6 (280 nm cylinder) arrays; (d) sketched illustration of the LC alignment in vicinity of nano antennas. The dash line frames the array area.
- Figure 6.13 Images of one-time rubbed array captured $0^\circ, 30^\circ, 45^\circ$ and 60° with respect to the rubbing direction
- Figure 6.14 Sketch of the LC infiltrated nano antennas and the relations of the specific interaction for LC alignment including the LC elastic energy (F_{elas}), surface energy of rubbing/photoalignment (W_1) and the surface anchoring energy of the nano antennas (W_2).
- Figure 7.1 Numerical calculation of LC based TiO_2 metasurface with vertical LC rotation from $\theta = 0^\circ$ to 90° for $\varphi = 0^\circ$ incidence, mimicking the electrical switching process: (a) transmittance results, (b) comparison in spectra between transmittance and phase shift and (c) phase change results. The LC is set with $\varphi = 0^\circ$ in-plane

alignment and the TiO_2 is patterned with the geometry: $H = 188$ nm, $R = 160$ nm.

Figure 7.2 Calculated dipole components along x and y-axis directions: (a) E_x , (b) H_y for the incident polarization parallel to $\varphi = 0^\circ$ with zenith LC alignment varied from $\theta = 0^\circ$ to 90° . The value of the plots represents the excitation magnitude of the dipoles amplitude normalized to the incidence field.

Figure 7.3 Experimental results of electrical tuning of the liquid crystal infiltrated TiO_2 metasurface for the incident light polarization directions aligned at the 0° layout array with (a) $\varphi = 0^\circ$, (b) $\varphi = 45^\circ$ and (c) $\varphi = 90^\circ$ incident polarizations, together with (d) the 45° layout array for $\varphi = 0^\circ$ polarization under the increased DC voltages from 0 to 12 V. The symbol-line curves mark out the movement of electric (red) and magnetic (yellow) resonance positions under the applied voltage.

Figure 7.4 The evolution of resonances in transmittance spectra of LC infiltrated nano cylinders under the electrical driving from 0 to 16 V. The sample was measured with a $\varphi = 0^\circ$ incident polarization

Figure 7.5 Measured phase shift of the LC infiltrated nano cylinders of the new sample's geometry under the electrical voltages from 0 to 16 V: (a) comparison of the phase spectra for both $\varphi = 0^\circ$ (blue square curve) and 45° (red dot curve) incidence; (b) The phase shift response for $\varphi = 45^\circ$ at $\lambda \sim 670$ nm wavelength.

List of tables

Table 1.1	List of performance for current spatial light modulator devices
Table 2.1	List of the MO effect performance in typical material systems (summarized based on the reference in contents)
Table 3.1	Parameters for Mn/Bi thin films fabrication
Table 3.2	Design of the MnBi thin film pixilation scale and fill factor
Table 3.3	(n, k) and (Q_1, Q_2) parameters setting of the reported MnBi film at RGB wavelengths in simulation.
Table 3.4	MnBi-based stacks designed for the simulation of MO properties.
Table 3.5	Simulated MO properties of four different MnBi-based stacks
Table 4.1	Measured radius of the TiO ₂ nano disks fabricated under different exposure dosages from 1.0 to 0.8 (Radii unit: nm)
Table 5.1	Thickness and roughness of alignment layer by rubbing and photoalignment for different coating conditions
Table 6.1	List of designed TiO ₂ antennas geometries
Table 6.2	List of the surface energy ratio for arrays of varied geometries

Chapter 1: Introduction

1.1 Background

Spatial light modulation (SLM) technology is essential for the light manipulation for applications like beam steering, optical communication, 3D display and image processing *etc.* Based on the Huygens' principle, the light can be regarded as the combination of wave-fronts propagation. Therefore, the light can be manually controlled by modulating the amplitude and phase. To date, high concern has been concentrated on the development of new SLM devices with efficient performance (both in modulation of amplitude and phase under high frame rate) and available for the minimization and integration with the electronic devices. For example, the concept of hologram display has been proposed as early as 1947 and has been intensively studied during the past tens of years [1]. However, due to lack of high transmission/reflection phase modulation under high frame rate, the hologram display is difficult to be introduced to the personal terminal sets. Conventionally, kinds of SLM products have been developed for display industry (see Figure 1.1). The cathode ray tube (CRT, 1922) was the pioneer of vision to present the dynamic display via the spatial steering of the electrons' beam before bombing the florescent materials, followed with some similar improved applications like electroluminescent (ELD), plasma-display panel (PDP) and field-emission display (FED). However, such process will

Figure 1.1 Current developed SLM for display industry

unavoidably produce high power consumption, unshrinkable into smaller pixilation, and cannot realize the phase control of the output. Later, some SLM devices have been developed like the liquid crystal display (LCD), digital micro-mirror devices (DMD), liquid crystal on silicon (LCoS) *etc.* which can produce the light steering, amplitude and phase modulation. However, those devices can be hardly minimized with well-preserved modulation performance due to some basic limitations like the Mauguin condition of twisted LC and complicated piezo-stage structures of digital mirrors. Projector display has shown a good performance in the color vision display. However, the high-power consumption of emissive display and complicated structure of current SLM devices also prevent its further minimization in application. Therefore, study and development of novel SLM devices available for efficient amplitude and phase modulation even under high process frequency and small scales are essential for future applications [2].

Spatial light modulator (SLM) is a kind of device applied to modulate the light field information like intensity, brightness, beam direction *etc.*, as a response of other signal stimulation, based on kinds of light-matter interaction effects like the electro-optical (EO) [3], thermal-optical (TO) [4], magneto-optical (MO) [5], elastic-optical [6] and acoustic-optical effects [7].

Figure 1.2 Example of current main technology of spatial light modulation for the display applications [5, 8-11]

Table 1.1 List of performance for current spatial light modulator devices

	LC modulator [8]	DMD [9]	MOSLM [5, 11]	Metasurface [10]
Pixilation size	5~20 μm	5~15 μm	1~10 μm	<1 μm
Response time	10~1 kHz	32 kHz	>1 MHz	NA
Efficiency	~90%	~50%	<10%	>80%
Strength	Mature industry	Fast speed	Fast speed	Designable &minimizable
Weakness	Non-competitive response time and pixel size	Difficulty in pixel miniaturization	Limited MO rotation	Passive control

For display, SLM should be an important competent and capable for high refreshing rate, high conversion efficiency, low power consumption and stability. Some newly developed SLM devices have been given in Figure 1.2. The scannable parallel electric planes in CRT can be thought as the early version SLM for display. Later liquid crystal (LC) valve, LCoS (liquid crystal on silicon) and even the DMD (digital micro-mirror device) scannable projector came to market successively. The LC is currently the most popular technology, which shows typical advantages like low power consumption (2~3 V addressing voltages, micro-ampere driving current), small size ($\sim 5 \mu\text{m}$), high contrast ratio ($>1500:1$) *etc.* Normally humans experience vision staying for about 0.1~0.4 s refreshing frequency above 10 Hz is necessary to realize a consecutive display of the video. The mainstream of today's LCD products shows refreshing rate of 144 Hz. However, for 3d display, the data transferred will be multiplexed, which requires modulators with much higher the refreshing rate. Comparison of the performance of different SLMs is given in Table 1.1.

Considering the optical anisotropic response of the magnetic alignments, the magneto-optical effect shows nonreciprocity properties, *i.e.* the double increment of polarization plane rotation after switching of the magnetization. Based on that, magneto-optical devices like the light isolator and modulator have been developed. For example, by using the non-reciprocal devices, the reflection cannot influence the incidence, which confirms the reliability of the signal. Due

Figure 1.3 (a) The concept of MOSLM for light modulation [5]; (b) MOSLM driven by circuit current [12]; (c) MOSLM driven by spin transfer torque [11].

to the geometric restriction, only *ED* or *MD* wave can freely propagate in the thin films. In MO thin films, the *ED* and *MD* modes can be exchanged to each other. Almost only the magnetic component can pass through orthogonally to the surface of MO thin film wave guide [13]. All the effects can be tuned by the magnetic field. Recently, the MO effect has been focused on the spatial light modulation application [12, 14-19] (see Figure 1.3). The light propagated can be guided or blocked by changing the polarization states. Since the polarization rotated at the response of magnetic stimulation, which is thought as much as femtosecond, the MOSLM could show advantages over the current mainstream LC, DMD modulators in switching speed, pixel size and life-time. Besides, by introducing kinds of coupling effects, the MO materials can be applied to detect the light-matter interactions. Spintronics type MOSLM was also studied with the help of spin-transfer-torque, which combines both the fast switching and small pixilation ($\sim 1 \mu\text{m}$) [20-22]. However, the dream of MOSLM is still illusory due to the limited MO performance, especially for the nano-size situations due to the small polarization rotation usually around $0.1^\circ \sim 1^\circ$ is limited for signal detection. Besides, the magnetization would be quite weak for small size magnets particles. The MOSLM is more often developed based on the transmissive Faraday type (magneto-optical Faraday effect, MOFE) and reflected Kerr type (magneto-optical Kerr effect, MOKE) via the magneto-optical crystals or thin films like LiNbO_3 , YIG and some magnetic alloys like CoFeB. The YIG shows the largest transmissive Faraday effect with $\sim 1^\circ/\mu\text{m}$, while the alloys may show reflected Kerr effect with $\sim 0.1^\circ$ for thin films as thin as 100 nm (see Table 2.1 in Chapter 2). To try enhancing the MO rotation angles, people try assistance of SPP type surface structures to manually produce some additional phase for the excitation,

or the composited magneto-dielectric multilayers to concentrate the light for higher MO performance [23-29]. However, to realize the highly efficient MO effect is still a challenge. Details about the MO effect principle and the applications will be introduced in Chapter 2.

Some novel methods have been explored for the visible light modulation in hologram *e.g.* linking the surface plasmonic effect (SPP) with the optical phase-change responses, the CGH can be simulated into a surface with arrays of nano-sized particles, or the metasurface [30-32]. The enhanced Surface Plasmon Polariton (SPP) is regulated by the surface periodic structures, which can be used as the reference wave for the hologram. As the response of light-matter interaction between the incident light and nano-particles, the phase of the light would be modulated [33]. Therefore, the metasurface with different nano-pattern configurations can mimic the object response in the traditional hologram capturing, making it possible of the manual designed hologram and even the dynamic holographic display in the nanoscale devices. The emergency of nano-metamaterial has brought a new approach toward micro-sized reconstruction of CGH. For metasurface based spatial light modulators, it has been thought to be a manually designable structure for enhanced light manipulation within a subwavelength distance via microcosmic light-matter resonant excitation like surface plasmon [34-38] or Mie scattering [39-43]. The manipulation is realized by coupling the far-field output with the near-field emission from surface shaped antennas. Normally, the antennas of the metasurface are arranged in a 2D arrays for functions based on the principle of light-matter excitation, thus made to perform curious optical parameters in effective permittivity, permeability, refractive index, impedance which is hard to be observed in natural world, further leads to a modulation of light intensity, phase, polarization status [44, 45]. Consideration of working wavelength range is critical for design of metasurface, which defines the spectral position of resonance excitations. In early stage, idea of metasurface is more focused on the surface plasmonic effect in noble metal systems. However, a trade-off between the localization resonances and optical loss is unavoidable in such system and would become significant in short wavelength range like the near-IR and visible light with a rise of the interaction between photons and conductive electrons [46]. Dielectric embeddings attached with metal structures are considered to make up the low efficiency in high

frequencies modulation [47]. However, the enhancement is still insufficient. Later, people find high output efficiency averagely above 80% can be obtained in the high dielectric all dielectric systems based on the Mie-type light matter scattering [47]. In plasmonic systems, the modulation is realized via the superimposition of free electrons excitation on surface near metal antennas, and only the electric mode resonance can be generated [48]. In all dielectric antennas, the mode is excited via the displacement current in dielectrics and both electric and magnetic resonances can be simultaneously generated with close enhancement ratio [40, 43]. Therefore, simultaneous efficient transmission and phase control can be obtained when the two resonances are tailored to be spectrally overlapped. Details of Mie-scattering effects in plasmonic and dielectric nanostructures will be introduced in Chapter 2.

For a long time, the study of metasurface devices is only constrained in the passive type design. Dynamically tunable metasurface has been proposed to better integrate the nano-photonics with dynamic spatial light modulators [49]. Normally, the light-matter interaction for certain microstructures are regulated by whether the geometry of the micro-structures or the refractive index of the optical environment. Therefore, the idea to develop the tunable metasurface can be considered via two approaches: to change the geometry of the micro-atoms, including the shape and size of the antennas; to adjust the refractive index of the environment in vicinity of the atoms, thus shift the resonant excitations of the optical responses [50-52]. So far, the idea for the first approach, the tunable geometry of the atoms, has been generally implemented in the long wavelength range like microwave and THz wave since complicated structures are necessary for the excitation of the geometry tunable elements [48, 53-55]. The development of tunable metasurface for devices for short wavelength range is still challengeable due to lack of efficient tunable components. For example, excitation of magnetic resonance in the plasmonic metasurfaces is always negligible comparing to the enhanced electric mode due to the negative dielectric constant of noble metals. Therefore, complicated structures like split ring resonator [48] are necessary for plasmonic metasurface to manually produce the magnetic components, which would be an obstacle to shrink the structures' size for short wavelengths. Therefore, it is still difficult to realize dynamical tuning at

Figure 1.4 Example of the typical reported LC based metasurface: (i) the thermally tunable dipole resonance excitation with LC infiltrated within the silicon sample [4]; (ii) the electrically tunable fano response with high efficiency tuning range about 80% [42]; (iii) Surface acoustic wave performance tuned by polymer dispersed LC [63]; (iv) tunable hologram by electrical switching of LC within the plasmonic metasurface [64]; (v) the electrically tunable metasurface based on silicon cylinders' metasurface toward the Huygens condition with a high phase modulation performance [65].

visible range via the geometry adjustment like MEMS elements [56, 57]. Another way towards the tunable metamaterial is to change the refractive index surround the micro-structures. The refractive index has been proven to change by thermal, acoustic and electrical effect via certain choice of the materials [58]. For example, the birefringent crystals like LC [59, 60], the electro-optical (EO) materials like KDP and LiNbO₃, and charge injectable semiconductors like ITO [61] and graphene [62] via the charge density modulation, which more often follows a relation between the incident frequency (ω) and permittivity as:

$$\varepsilon = \varepsilon' + i\varepsilon'' = \varepsilon_\infty \left[1 - \frac{\omega_p^2}{\omega(\omega + i\gamma)}\right], \quad (1)$$

Some examples of the tunable metasurface for the light modulation was given in Figure 1.4. However, the approaches via electrical tunable or charge injectable semiconductor, or the phase change materials, always suffer from a limited tuning range of refractive index within $\Delta n \sim 10^{-2}$ at higher frequencies for the attempts [36, 66]. Therefore, metasurface embedded into the materials with high birefringence, for example the liquid crystal, will be an effective approach. When the LC experiences phase transition from isotropic to anisotropic crystal after thermal cooling across the critical temperature ($\sim 85^\circ\text{C}$), realizing a change of n from 1.5 to 1.6. Besides, by introducing the electro-optical birefringence effect, the switching of LC molecules would rotate the n axis along the main optical axis from 1.5 (n_o) to 1.7 (n_e). This is one of the best performances has been found for the candidates. Based on that, LC base metasurface has been explored or developed in both the plasmonic surface or the all dielectric metasurfaces by electrical, thermal and even acoustic approaches (see Figure 1.4). Details of the LC based metasurface studies will be extended in Chapter 2.

1.2 Motivation and objectives

As discussed above, the next generation 3D display like the glass-free flat display and hologram calls for advanced spatial light modulation of devices with high density and efficiency for optical processing, for which the lossless optical modulation with high processing speed and submicron pixilation would be appreciated. Traditional spatial light modulators (SLM) for 2D display like the LCD and DMD are insufficient for spatial light modulation of such advanced display technology. Magneto-optical based SLM can be expected due to the magnetic switching faster than $\sim 10^{-6}$ s with only a thin film structure, thus results in the sensitive detection of the output of optical polarization rotation. Mie scattering based all dielectric metasurface show novelty in lossless subwavelength light tailoring with the typical periodicity of the nano structures as small as hundreds of nano-meters. Development of tunable all dielectric metasurface can be an effective approach for the designable spatial light modulation with high efficiency, like the Huygens' surface. Either of them can

be expected a good candidate for the development of SLM for the 3D display application in future. Based on that, two approaches can be proposed for solution of the idea: the magneto-optical SLM (MO-SLM) and liquid crystal (LC) based all dielectric tunable metasurface. Study of fabrication and optics analysis was carried out to verify the performance and feasibility of the MO-SLM and tunable metasurface device for application.

The scope of this dissertation includes: the introduction of basics of magneto-optical effect, Mie scattering effect and the principles of liquid crystal, the magnetic and magneto-optical performance of the magnetic thin films for spatial light modulator development, the fabrication process, characterization, and both numerical and experimental analysis of the all dielectric metasurface before and after the LC infiltration, the analysis and discussion of LC alignment performance within the nanostructures and finally the electrical tuning of the LC based metasurface. Details of the objectives are listed below:

1. To collect comprehensive knowledge of magneto-optical effect, Mie scattering effect and liquid crystal physics and the current technology of spatial light modulation based on them.
2. To fabricate the magnetic thin films based on low-temperature-phase MnBi with strong perpendicular magnetic anisotropy and magneto-optical effect for both continuous and pixilated structures and find the effective method for maintaining in ambient environment.
3. To design and fabricate the all dielectric metasurface for visible light range based on TiO_2 nano disks surface on ITO glass with desired optical performance based on numerical and experimental analysis.
4. To design and fabricate the LC infiltrated TiO_2 all dielectric metasurface based on numerical and experimental analysis.
5. To unfold the story of optical performance of LC infiltrated nano structures with different geometry.
6. To realize the electrical tunable LC based TiO_2 metasurface device, thus verify the feasibility of the LC based metasurface device for spatial light modulation.

1.3 Issue statement

As discussed above, the magneto-optical effect and the metasurface platform are worthy to be studied for development of the advanced spatial light modulations, and some groups, so far, have achieved progress in those areas. However, the progress on those two approaches are still insufficient for practical implementation in many aspects.

For magneto-optical based spatial light modulation:

So far, most of the transmissive type MOSLM based on MO crystals calls for larger size of the components due to the limited Faraday rotation efficiency below $1^\circ/\mu\text{m}$. although it's a larger value rarely seen in the candidate MO materials' family, it is still far insufficient for the highly efficient modulation of the display output. Besides, the large size above several microns will also restrict the miniaturization of the pixilation due to the increased pixel aspect ratio as the pixel pitch over height. Reflected devices based on the magnetic thin films with MOKE could be a candidate for integration with the minimized devices of small pixilation for the thin layer thickness around several hundred nanometers. Normally the larger MOKE rotation signal happens on polar Kerr case with perpendicular magnetization alignment which is normal to the incident electric field plane, and lead to the maximum moment of the electric and magnetic interactions. (Details for explanation can be referred to the Chapter 2.) However, the candidates of magnetic thin films with intrinsic larger perpendicular magnetization anisotropy (PMA) are not plenty. Sometimes, to realize the perpendicular magnetization often calls for special interfacial process to induce, which more often only has a thin layer thickness below 30 nm. For example, the PMA of CoFeB, although has a large value of several hundred emu/cm^3 , only happens for thin layer of several nanometers, for which interfacial inducement layer, like the Ta, will be needed. However, as is commonly seen in the magnetic materials, the magnetization is hard to preserve in the smaller particles especially as small as tens of nanometers, which would lead to the soft para-magnetism, namely say, difficult to maintain the magnetization in the ambient states without external fields. In the meantime, the larger magneto-optical effect always happens in the cost of lower efficiency output. Attachment of a layer of the

dielectrics of larger refractive index can a method to relieve the weakness. But details of the feasibility are still in study. Furthermore, the magnetic thin films are more often the metal materials, which tends to be oxidized or damaged under the long-term exposure of ambient environment. Therefore, to find a material with large intrinsic perpendicular magnetization together with exploration of process to realize an enhancement of output efficiency and long-term protection will be necessary.

For tunable metasurface based spatial light modulation:

Metasurface, as introduced above, can be an effective platform for development of the minimized spatial light modulation devices. To develop the highly efficient tunable metasurface, two issues needs to be solved beforehand: the materials with highly efficient excitation of the optical resonance in visible light range and the large tuning range of the optical response upon the external adjustment. For the visible light modulation with high incident light frequency, the plasmonic effect, normally happens on the metal based micro-structures, will bring serious ohmic loss due to the high frequent electrons' oscillation, thus lead to high loss of the optical output and power consumption. Comparatively, the all-dielectric materials like the silicon and titanium dioxide can be the qualified candidates. Second, for the effective tuning mechanism, as introduced in the background Section 1.2, it may be possible a way to embed the tiny metasurface atoms designed for visible light modulation with the tunable dielectrics. Liquid crystals show the ever-found largest birefringence and has been chosen as the tuning component with the metasurface. However, the development of LC based metasurface spatial light modulator is still challengeable for three reasons: 1. The complicated LC fabrication process especially the super thin LC layers below 2 μm , which would unavoidably bring the inhomogeneity of the response which is uncontrollable by current design and fabrication approaches; 2. The unpredicted LC alignment in vicinity of the nano structures due to the anchoring effect induced by the nano-antennas' geometry, thus to receive the response out of design; 3. The effective dynamic control of the optical response with lower power consumption since most of the LC based metasurface developed so far normally calls for driving voltages above 30 V, which is unacceptable for the current electrical devices' addressing and driving. Therefore, to realize an effective LC

based metasurface for highly efficient visible light modulation with lower external driving would be valuable together with a systematical study of the LC alignment within the nano structures of different geometries.

1.4 Major contribution

The advanced display for the next generation calls for new technology for spatial light modulation. Here, in this dissertation, two approaches based on the magneto-optical effect and tunable metasurface has been explored. Strong perpendicular magnetic anisotropy and obvious magneto-optical Kerr effect have been observed in the fabricated MnBi thin films. Electrically tunable TiO_2 metasurface based on thin layer LC is realized with a low driving threshold from 3~5 V. The results show the possible performance of the idea of spatial light modulation based on MOKE and tunable all dielectric metasurface, including the potential and the obstacle.

For the study of MOKE based spatial light modulation, the perpendicular magnetization is essential to the Kerr signal response. Normally the perpendicular magnetization is obtained via a magnetic orbit interaction normal to the surface, which calls for the high quality of the lattice, however, is difficult to obtain. In this work, the low temperature phase (LTP) MnBi thin film is fabricated by a series of the standard process of magnetron sputtering deposition of interlaced Mn and Bi layers followed by a thermal annealing, in which a strong magnetization can be obtained. In the meantime, the magnetic alloys are easy to be oxidized, which would hinder the devices' operation in ambient environment. In this work, the capping layers with different materials were discussed and a well protection of perpendicular magnetization can be realized by the tantalum layer even after long time exposure in air. For verification of the capability in pixilation structures, the thin films were consequently patterned by the focused ion beam method. The details of the magnetic performance of pixilated thin films are systematically discussed in Chapter 3.

The all dielectric metasurface approach is explored based on the LC infiltrated TiO_2 nano disk metasurfaces, which was fabricated via a standard electron beam lithography method, followed by a series of LC infiltration process. For the LC based tunable metasurface, challenges normally exist in three areas:

1. the fabrication of LC cell with metasurface; 2. the unexpectable LC alignment in the nano antennas; 3. the uniform control of optical output under electrical driving of low power consumption. In this dissertation, by introducing the standard LC packaging process, the LC based metasurface can be successfully fabricated even for thin layer cells close to 1 μm . The electric driving is consequently reduced to less than 10 V, which is much smaller than other groups results, and would be suitable for further spatial light modulator development. Besides, the idea of the LC based TiO_2 nano disks metasurface would be an effective approach for dynamic Huygens's surface devices in future.

1.5 Organization of the thesis

This dissertation is organized with 7 chapters: the background introduction and motivation of the research work is given in Chapter 1; The detailed literature survey about magneto-optical effect, Mie scattering effect and the liquid crystal properties is presented in Chapter 2 together with the basic principles guiding the analysis of the following chapters; The fabrication and magnetic performance of magnetization and MOKE is discussed in Chapter 3 based on the MnBi thin films with strong perpendicular magnetic anisotropy; The fabrication and optical performance of the TiO_2 metasurface is discussed in calculation and experiments in Chapter 4; The fabrication and optical performance of the LC infiltrated TiO_2 metasurface is discussed in calculation and experiments in Chapter 5; The optical performance of LC alignment regulated by the nano antennas' geometry is discussed in calculation and experiments in Chapter 6; the electrical tuning of the transmission and phased output is discussed in Chapter 7 based on the LC infiltrated TiO_2 metasurface device; the summary and outlook of the research work is given in Chapter 8.

Chapter 2: Literature review

2.1 Magneto-optical spatial light modulation

2.1.1 Basics of polarization rotation due to magneto-optical effect

When the electromagnetic wave propagates through a magnetic medium, the light-matter interaction would lead to a moment along a certain direction, which splits the speeds of left and right circular polarization components, leading to the rotation of the output polarization (see Figure 2.1). For transmission output, the results can be called Faraday effect, while the reflection type corresponds to the Kerr effect. When an EM wave with certain frequency propagates along z -axis, the motion of electrons stimulated by EM field is in the form:

$$m_e \frac{dv}{dt} = -e(\mathbf{E} + B_0 \mathbf{v} \times \mathbf{z}). \quad (1)$$

We define $E_{\pm} = E_x \pm iE_y$, in which $E_{\pm}$ corresponds to right (left) hand circular polarization. For linearly polarized light, the electric vector can be written as:

$$\begin{aligned} E &= E_0 [e^{i(k+z-wt)} \mathbf{e}^+ + e^{i(k-z-wt)} \mathbf{e}^-] = E_0 [\mathbf{x}, \mathbf{y}, \mathbf{z}] \\ &= E_0 [\cos(kz - \omega t) \cos(\Delta kz), \cos(kz - \omega t) \sin(\Delta kz), 0] \end{aligned} \quad (2)$$

Therefore, the polarization angle $\varphi = \tan^{-1}(E_y/E_x) = \Delta kz$, namely say, the polarization angle would be changed in the presence of the equilibrium magnetic field. This is the magneto-optical rotation, which also depends on the distance the light interacts with the matters.

The Faraday effect, or the magnetic circular birefringence effect, is linearly proportional to the magnetic induction (B), contingent to the field (H) component in the propagation direction, and the length of the light-matter interaction (l), which can be expressed as:

$$\Psi = VBl, \quad (3)$$

in which V is the verdet constant, tabulated for various materials, temperature and wavelength conditions. V is positive when the rotation and the magnetization

Figure 2.1 Sketched illustration of magneto-optical effect for transmissive Faraday effect and reflected Kerr effect. The arrows indicate the direction of the polarizations.

are in right-hand spiral relation, and so is the Faraday rotation. Faraday effect closely connects with the Zeeman effect. The splitting of energy levels could lead to different rotation situations. For orbits with $\Delta m=1$, the photon has an angle moment $\hbar$ parallel to the magnetic field, which is in right spiral with the electric rotation, which is called the $\sigma+$ polarization. When $\Delta m= -1$, the photon angle moment is antiparallel to H , leading to the $\sigma-$ polarization.

Magneto-optical Kerr effect (MOKE) has been referred to the reflection type of light incident onto the magnetic surface. According to the magnetization configures within the thin film samples, the MOKE can be defined as polar, longitude and transversal Kerr effect (see Figure 2.2), of which can be distinguished with the different E and M vectors alignment relations: in polar MOKE, the magnetization aligned perpendicular to the reflection surface and while parallel to the incidence plane (dashed square in Figure 2.2), with the maximized interaction happens for 0° incidence with a perfect perpendicular intersectional angle between E and M components, thus will lead to a maximum unparalleled vector product with the incident direction and a large polarization rotation; in longitudinal MOKE, the magnetization simultaneously aligns parallelly to the reflection surface and the incidence plane, which is normally one

Figure 2.2 Sketch of incident electric field (polarization) and magnetization alignment for polar, longitudinal and transversal MOKE. The yellow arrow at the reflection surface defines the direction of vector product of the E and M interaction momentum.

order of magnitude smaller than the polar MOKE and approaching 0 with a 0° incidence angle due to the smaller momentum between incident E components and the surface magnetization; in transversal MOKE, the magnetization is parallel to the reflection surface and perpendicular to the incidence plane, in which the vector product between E and M is always parallel to the incidence plane, which would lead to negligible polarization of the propagations. When the object is put under the magnetic field, the dielectric tensor:

$$\varepsilon = \begin{pmatrix} \varepsilon & a\pi_z & a\pi_y \\ -a\pi_z & \varepsilon & -a\pi_x \\ -a\pi_y & a\pi_x & \varepsilon \end{pmatrix}, \quad (4)$$

in which the off-diagonal components will be influenced by the magnetic factor (magnetic field in paramagnets and magnetization in ferrimagnets). Normally, the initial polarization is supposed to start at p -polarization. In polar and longitudinal cases, the s -polarization can be tuned by the magnetic vectors, which leads to the rotation of polarization plane. We use r_{ij} as the coefficients probing the polarization conversion (i and j are the directional suffixes). Therefore, the reflectivity conversion matrix can be defined as:

$$R = \begin{pmatrix} r_{pp} & r_{ps}(H) \\ r_{sp}(H) & r_{ss} \end{pmatrix}. \quad (5)$$

For transversal model, the magnetic field aligns parallel to the s - polarization,

bringing negligible variation in the s -component. Therefore, the transversal configuration only affects the reflection efficiency. However, to realize a better performance via MO effects, both the polarization rotation and reflectance are important for consideration [67-69].

2.1.2 Magneto-optical materials

Magnetic thin films

As introduced above, the Kerr effect can be categorized as polar, longitudinal and transversal types. Generally, the polar MOKE prototype may lead to the maximum Kerr rotation. The magnetic thin films with the perpendicular magnetic anisotropy (PMA) normal to the surface may be the candidates to realize the polar MOKE. Although there are kinds of magnetic materials discovered. However, the typical magnetic materials with intrinsic PMA are limited to the doped magnetic oxides, and alloys. Some of them are summarized and listed accordingly below in Table 2.1. For the monomer elements like the Fe, Co and Ni, the PMA is always limited due to a small magneto-crystal anisotropy (comparatively, Co has the largest magneto-crystal anisotropy), which will restrict the MO effect with the same intensity of the

Table 2.1 List of the MO effect performance in typical material systems
(summarized based on the reference cited in this section)

	Rotation angle	MO effect type
Co	0.1°/100 nm	Kerr
CoPt	0.1°~0.4°/100 nm	Kerr
MnBi	0.5°~2°/100 nm	Kerr
Bi: YIG	<1°/μm	Faraday
Ag/Co/Ag	0.1°~0.2°/100 nm	Kerr with SPP
Ag/SiO ₂ /Co/Ag	0.4°/100 nm	Kerr with SPP
Ag (grating)/Bi: YIG	4°/μm	Faraday with SPP
[SiO ₂ /TiO ₂] _m /YIG/[TiO ₂ /SiO ₂] _n	8°/μm	Faraday of MPC

incidence [70-73]. Magnetic alloys like Permalloy (NiFe), CoFe, CoPt or CoFeB *etc.* may show a larger Kerr rotation due to an enhanced intrinsic magneto-crystal anisotropy from the stronger exchange interactions between elements [74-77]. Comparatively, low temperature phase MnBi shows a largest PMA observed in all the magnetic thin films due to its typical hexagonal interlayer lattice [78-81]. Doped YIG (Yttrium Iron Garnet composites) is a typical MO crystal with large Faraday Verdet parameters [82]. However, the large size crystal over several microns defines its limited application in integration with the minimized thin layer chips or devices. To be noted, almost all the MO rotations of minimized structures are below 2° , which is quite weak for the larger efficiency modulation application requirement ($>50\%$) like the display. Nano-photonics process like the surface plasmon polariton (SPP) or magneto photonic crystal (MPC) assisted structures has been introduced to the magnetic thin layers (see Table 2.1) [83-86]. Details of the nano-photonics assisted magneto-optical effect will be introduced in the next sections below.

Magneto-optical photonic crystal

Photonic crystal (PC), the periodic dielectric medium, controls the light propagation, originating from the photonic bandgap decided by the periodic structure itself and localization of light in the vicinity of defects [83]. When the PC constitutes with the magnetic component, for example, the defect layer, the unique magneto-optical interaction would be exhibited in the magneto-photonic

Figure 2.3 Design of magneto-photonic crystal (PLZT was used to exert the mechanical stimulation to the magnetic layer.); (a) and (c) give the wavelength dependent Kerr rotation and reflectivity results; (b) and (d) show the Kerr rotation and reflectivity under the electrical driving [84].

crystal (MPC) (see Figure 2.3) [84]. Due to the strong confinement of light in the MPC, large enhancement of the magneto-optical performance can be demonstrated in such systems, like the (Bi: YIG/SiO₂)_n multilayer stacks [85]. For example, in the (Bi: YIG/SiO₂)_n 1D MPC, the multilayer film was designed by $n_M d_M = n_S d_S = \lambda/4$, which confirms the equal optical distance for each section [86]. Due to the multiple interference between the dielectric layers, the light is weakly localized in the stacks while back scattering at the magnetic defected layers was enhanced. By designing the thickness of the defected layer, the PC provides a resonant transmission with a large MO rotation at the certain wavelength. Due to the “selection” of the PC, the light of the wavelength can only localize in the defect layer, fulfilling the localization mode within the photonic bandgap from the *Fabry-Perot* resonance. With the integration of limited light diffusion and enhanced light confinement in magnetic defect layer, the high transmission and large MO rotation can be simultaneously obtained at the resonant wavelength decided by the MPC.

So far, series of MPC with high transmittance and large magneto-optic rotation have been worked out, like (SiO₂/Ta₂O₅)₉/Bi: YIG/(Ta₂O₅/SiO₂)₁₉ for reflection type ($R \sim 99.91\%$, $\theta \sim 44.23^\circ$ with 1.3 μm YIG film) and transmission type ($T \sim 99.99\%$, $\theta \sim 44.33^\circ$) [86]. In the meantime, the cascade MPC structures may help to widen the spectra with better magneto-optical performance.

Magneto-optical plasmonic metasurface

Magneto-optical plasmonic metasurface is thought to another approach showing mutual-promotion performance.

i) Surface plasmon polariton

When the electromagnetic wave (EM wave) propagates onto the interface of hetero-materials with opposite permittivity like metal-air or metal dielectric interface, the frequency could match the oscillation of surface free charges, exciting additional EM wave, *i.e.* the Surface Plasmon Polariton (SPP) phenomenon. Normally the SPP includes both the polariton, the evanescent wave excited into the thinner medium, and the plasmon, the charge motion in the metal. Usually the surface plasmon exists in kinds of structures like single entity surface, continuous thin films, periodic patterns, *etc.* Localized surface plasmon (LSP) is

caused by the entity surface with dimensions of the wavelength order or smaller, while the surface plasmon polariton (SPP) propagating along the interface is regulated by the surface structure. The SPP wavelength is usually shorter than the wavelength of incident light, therefore the surface plasmon is able to confine the EM wave into the sub-wavelength area, which is critical for developing the nano-photonic devices. Normally the SPP is sensitive to the optical atmosphere (refractive index n). So far kinds of approaches towards the tunable plasmonic effect have been studied based on the thermal-optical, electro-optical and acoustic-optical effect. Magnetism intrinsically has the super-fast property, which is available for the femtosecond level switching. In the meantime, the magnetic field can be used to tune the optical anisotropy of the material, which provides us another perspective to the study of tunable plasmon effect [87, 88].

ii) *SPP effect on the MO activity*

The MO activity can be defined as a combination of polarization plane rotation and ellipticity:

$$\Phi = \theta + i\varphi = r_{ps}/r_{pp}, \quad (6)$$

in which r_{ps} is the reflectance in the orthogonal direction from the polarization conversion due to the MO contribution. r_{pp} the reflectance along the original direction, only results from the pure optical reflection. Evidently, both the increased r_{ps} or reduced r_{pp} can enhance the MO activity. It was reported that the polarization conversion efficiency r_{ps} is determined by both the field concentration and propagation distance (d) as:

$$r_{ps} \propto \varepsilon_{mo} d(\mathbf{E}_p \cdot \mathbf{E}_s). \quad (7)$$

ε_{mo} is the MO constant of the materials. Since the SPP confines the field, the enhanced intensity will increase the MO activity. What's more, when the magnetic layer contacts with the metal layers, multiple reflection would happen within the magnetic layer, which effectively increased the propagation distance to obtain the higher MO performance.

To date, enhancement of magneto-optical effect has been found from both the LSP and SPP systems (see Figure 2.4). In 1980s, larger faraday coefficient

Figure 2.4 Illustration of magneto-optical effect and the three configurations; (b) The light distribution and MO activity in Au/Co/Au stack with SiO₂ inserted at different positions; (c) MO activity influenced by the surficial plasmon polariton and the dispersion relations [87, 89].

was predicted and experimentally verified in the suspension with MO Fe₃O₄ particles embedded, which was attributed to the increased local field at the surface area of MO particles [88].

Similar enhancement effect was also found in dielectric/MO metal systems, like Co and Co-Fe, which depended on the fraction of ferromagnetic metals [89]. Later, the magnitude of MO activity almost kept the same at the LSP resonance energy of 3.2 eV for Ni array nanowires with only 17% the volume of the continuous film. The resonance was red-shifted for a larger diameter fraction of MO metal pillars. In the meantime, the MO changed sign when the wavelength varies across the LSP resonance, which also exists in the noble metal/MO metal systems. However, the MO activity needs to face the trade-off between light efficiency and absorption for electron excitation. Recently, Banthi *et al* reported a simultaneous large MO effect and low optical loss by insertion of 20 nm SiO₂ in the Au/Co/Au multilayers, which produced the splitting the single mode (Au/Co interface) into two modes (Au/SiO₂ and SiO₂/Co) [90]. The MO rotation was almost unchanged while the extinction spectrum strongly depends on the

position of the dielectric insertion (in the front or at the back of Co layer). When SiO₂ was put in the front of Co, light concentrated less in metal layer while keeping larger MO activity, which improved the figure of merit of MO vs optical loss. LSP induced enhanced MO activity also happens in the dielectric MO material systems like YIG embedded with Au particles. When the particles are well defined after high temperature annealing, the LSP resonance and the enhanced Faraday effect show blue-shift correlation.

2.2 Huygens' surface based on the Mie scattering

2.2.1 Light-dielectrics interaction

The spatial electromagnetic field distribution generated by the dielectric media can be expressed by the Maxwell equations, and further simply expressed by the Helmholtz equations for the harmonic field oscillations as:

$$\begin{cases} \nabla^2 E + k^2 E = 0 \\ \nabla^2 H + k^2 H = 0 \end{cases} \quad (8)$$

For dielectrics with zero conductivity $\sigma=0$, $k^2 = \omega^2 \varepsilon \mu$, then we can obtain the one-dimensional solution:

$$\begin{cases} E = E_0 e^{[i(kx - \omega t)]} \\ H = H_0 e^{[i(kx - \omega t)]} \end{cases}$$

when ε is considered infinite with no loss of light intensity. The energy flux $S = E \times H$ propagates along the k vector. For conductive dielectrics ($\sigma \neq 0$), $k^2 = \omega^2 \left(\varepsilon + \frac{i\sigma}{\omega} \right) \mu = k_r^2 + ik_i^2$, in which k_r represents the reflection vector while k_i is for the incidence. Then we can obtain the one-dimensional solution as:

$$\begin{cases} E = E_0 e^{(ik_r x - i\omega t - k_i x)} \\ H = H_0 e^{(ik_r x - i\omega t - k_i x)} \end{cases}$$

Thus, the loss can be expressed as:

$$\frac{e^{(ik_r x - i\omega t - k_i x)}}{e^{(i\sqrt{\omega^2 \varepsilon \mu x - i\omega t})}} = e^{[-k_i + i(k_r - \sqrt{\omega^2 \varepsilon \mu})]x} \quad (9)$$

Therefore, when the light illuminates onto the dielectric media, absorption and scattering will simultaneously happen.

2.2.2 Mie-type resonant scattering

Normally, based on the particle sizes, three types of scattering may happen during the light-matter interaction process: the elastic Mie scattering and Rayleigh scattering, as well as the inelastic Raman scattering (see Figure 2.5). Rayleigh scattering, in some way, can be regarded as the special case of Mie scattering happens when light is scattered by particles much smaller than the incident wavelength, *e.g.* the gas molecule, with the scattering intensity inversely proportional to the bi-quadratic wavelength. Therefore, the Rayleigh Scattering shows obvious wavelength dependence and the scattering for shorter wavelength would be dramatically stronger than the longer wavelength. For Raman scattering, it shows a shifted spectral response when being characterized for the Raman molecules like silicon (Si), polymers *etc.*, however, is weak in the signal output. Comparatively speaking, the Raman scattering is roughly six orders magnitude smaller than the Mie scattering and about four orders less than the Rayleigh scattering.

Mie scattering, named after the German physicist Gustav Mie, describe the elastic light scattering by the dielectric particles, *e.g.* smoke, aerosol, fog *etc.*, which is governed by both the refractive indices (both the particle and the

Figure 2.5 Illustration of Mie type light-matter scattering for particle sizes smaller, comparable and larger to the incident wavelength. The x defines the relation between particle size and effective unit optical distance as $x = \frac{2\pi nr}{\lambda}$.

environment) as well as the particle size compared with the incident wavelength.

Besides, Mie scattering shows strong angular dependency of the scattered intensity especially for smaller particles, which prefers to distribute along the incident propagations. When the scattering particles are in size comparable with the incident wavelength, the internal geometry and electronic distribution of the particles need to be considered. Multipolar mode will be excited upon the EM wave incidence and further to reconstruct the scattered wave. For inhomogeneity of the geometry and refractive index of the particle, phase delay of the output will be produced in time and space.

Since the scattering mode is sensitive to the particle size compared with the effective unit optical incident distance ($x = \frac{2\pi nr}{\lambda}$, r is the particles' radii) (see Figure 2.5), the relations of the electric and magnetic dipole scattering can be tuned by special geometric design along certain excitation directions [91]. Based on the principle, the Mie scattering so far has been applied to kinds of the applications like tissue detection [92], manual magnetic particle formation [93], Huygens' surface with highly efficient phase shift and the optical devices minimization *etc.* [94]

2.2.3 Huygens' surface

According to the Huygens' principle, the wavefront can be regarded as the secondary source of the outgoing wave, which also sustains the phase and frequency as the primary. The emerging wavefront, thereafter, may be shaped in the way decided by the position dependent phase delay during the propagation. Recently, the Huygens surface, the manually designed surface with many particles arranged in the 2D subwavelength periods, has been developed for kinds of high efficient optical modulation. Based on the Huygens principle, the pure-forward wave calls for the elementary source radiation with crossed electric and magnetic dipole resonances in far-field, thus realize an overlapped electric dipole (ED) and magnetic dipole (MD) modes of output in phase. Therefore, the design of elements with comparable crossed E and M dipole resonances is critical for the realization of Huygens' surface, the less reflective platform for electromagnetic wave manipulation.

So far, some groups have tried studying the Huygens' surface in experiments is developed based on the metallic elements for the wavelength from microwave to mid-infra (mid-IR) range, within which the dissipative loss is negligible [95, 96]. Normally, the effect by surface plasmonic polariton (SPP) is dominant for the light scattering with the metals. Due to the low permittivity of the metallic materials, the electrons inside the materials are nearly free to move under external excitations. When under the illumination of the polarized light (electric fields), the electrons will be easily to be excited corresponding to the incident frequency, then generate certain secondary electric mode along the periods of the surface

Figure 2.6 (a) Schematic representation of electric and magnetic field distribution inside the scattered resonator particles; (b) experimental and numerical results of transmissive spectra depending on the nano disk radii variation range. The black dashed circle represents the nano disk radius window for Huygens' condition; (c) Near-field map of the cross-section of the nanodisk with optimized geometry for Huygens' condition, indicating a normalized distribution of the electric (E) and magnetic (M) fields distribution with respect to the incident polarized plane wave. [40]

geometry. However, for higher frequencies like near-IR and vis. light, the excitation would be dramatic, thus lead to a larger ohmic loss. Besides, the equivalent magnetic permeability by SPP is way insufficient to excite the magnetic dipole resonances of close strength with the electric mode in spectra. People have developed structures like the resonant rings or squares to manually excite two electric modes together crossly overlapped [93]. However, it would be more difficult to build the elements when scaling down to shorter wavelengths.

Mie scattering can be an alternative approach for simultaneous E and M modes excitation. As discussed above, the Mie scattering in all dielectric media can be obviously influenced by the geometry of the media particles. In metasurface, the individual nano antenna can be represented by a Huygens source, namely a combined set of electrical and magnetic mode along the x and y -axis directions (see Figure 2.6). So far, the idea of the all-dielectric Huygens' surface has been explored based on the silicon (Si) and titanium dioxide (TiO_2). Due to the large permittivity of the dielectric, the strong resonant responses can be excited even for the shorter wavelengths, which would be easier for the realization of Huygens condition. When the polarized light, circular electric

Figure 2.7 (a) sketched nano antennas as the Huygens source unit with the electric and magnetic dipoles excited under the polarized incidence; (b) to (f) the calculated results of transmittance, E and H fields amplitude, and the phase shift for non-overlapped (top) and overlapped response (bottom) of the atoms [98].

Figure 2.8 Performance of applicable Huygens' surface: (a) Huygens' surface within the range of optimized nano antennas geometry for highly efficient passive Hologram display [98, 100]; (b) development of phase gradient Huygens' surface for light bending performance [101]; (c) electrically tunable metasurface with the optical response (transmissive spectra and phase shift) varies across the Huygens' condition [65].

current can be generated around the surface of the elements with the surface displacement current along the incident polarization. Magnetic dipoles taking place inside the nano structure via Mie scattering effect abide by the relation among incident wavelength (λ), refractive index (n_{sp}) and particle radius (R_{sp}) as $\lambda/n_{sp} \approx 2R_{sp}$ [93] (see Figure 2.6). Therefore, significant electric and magnetic resonances can be simultaneously excited in all dielectric metasurfaces of high refractive index nano structures. The magnetic excitation $\mathbf{m}$ is defined perpendicularly to the electric dipole $\mathbf{p}$ by antiparallel electric displacement current near the opposite surface of the nano particles as $\mathbf{m}_j = \omega/(2i) \cdot (\mathbf{r}_j - \mathbf{r}_0) \times \mathbf{p}_j$ [37, 48], hence distributes perpendicularly to the incidence polarization direction. The Mie scattering for electric and magnetic resonances occurs at different frequencies. Due to the different responses in spectra, coupling between electric and magnetic resonances can be tailored by either designing the nano structure geometry parameters or adjusting the optical environment [48, 97].

Some methods have been developed for Mie-scattering approximation in the small elements. Staude *et al* has proposed the discrete dipole approximation

(DDA) analysis to simulate the transmission and reflection with combined contribution of the electric and magnetic modes:

$$t = 1 + \frac{2i\gamma_e\omega}{\omega_{e,0}^2 - \omega^2 - 2i\gamma_e\omega} + \frac{2i\gamma_m\omega}{\omega_{m,0}^2 - \omega^2 - 2i\gamma_m\omega} \quad [98, 99], \quad (10)$$

The polarizability of each mode is expressed under the influence of both the Lorentzian frequency dependence $\omega_{e,0}$ and $\omega_{m,0}$ and the damping parameters γ_e and γ_m . According to their calculated results in Figure 2.7b to f, the two dips with comparable strength correspond to the electric and magnetic dipole resonances, and accordingly π phase shift can be induced by each mode at the same position in spectra. For overlapped E and M modes, the comparable ED and MD strength will form a perfect Huygens' source, thus to realize a nearly pure-forward transmission. As the result, a doubled 2π phase shift is realized around the resonance areas, which corresponds to the combined influence of two resonances at the same spectral position.

So far, kinds of Huygens' surface have been studied for kinds of applications. For example, the visible light hologram captured based on the silicon based metasurface (see Figure 2.8a) [98, 101], beam manipulation from the high efficient phase gradient metasurface [102] and tunable metasurface for efficient light modulation under electrical or thermal driving [4, 65, 103]. More than that, enhanced capability has been explored by introducing the pure Huygens' surface with some optical components: LC infiltrated Huygens surface (see Figure 2.8c) [65], charge injective semiconductors *etc* [104].

Most of the study in metasurface area still focuses on the passive device level. Some groups have considered to improve the capability of the Huygens' surface toward the tunable device with high efficiency. However, the progress is still limited due to the difficulty of fabrication and optical control. In this dissertation, the tunable Huygens' surface based on TiO_2 atoms and liquid crystal will be comprehensively discussed. Details can be seen in Chapter 4 to 7.

2.3 Basics of liquid crystal optics

2.3.1 Liquid crystal material

Liquid crystal (LC) materials are referred to the state of matter show properties between the liquid (amorphous state) and crystal. Normally, the LC molecules can be oriented under the external influence like the mechanic force, temperature or electric field. The LC was first discovered by an Austrian botanist Friedrich Reinitzer in 1888. The LC molecules are normally polymers consisted of C-H alkyl bond, C-C Benzene rings, C-N cyan bond and C-C skeletal bond (see Figure 2.9), which is normally in the size of $2\sim 5\text{ nm} \times 0.5\text{ nm}$. For direction along the LC molecules, it shows the extraordinary refractive index of n_e , while the ordinary index n_o for the perpendicular direction, thus shows an anisotropy of the dielectric index depending on the orientation of the LC molecules. The values of n_e and n_o depend on the molecular composition. The LC can be workable only in the range between the melting point and clearing point with the LC phase in order, normally from $-20\text{ }^{\circ}\text{C}$ to $80\text{ }^{\circ}\text{C}$.

As shown in Figure 2.10a, there are three kinds of phase for the thermotropic LC: nematic (N), Smectic (Sm) and Cholesteric (Ch). For N phase, all the

Figure 2.9 (a) Molecule structure of the nematic liquid crystal; (b) Raman spectra of LC showing the peaks of the typical chemical bonds: $\sim 1200\text{ cm}^{-1}$ for C-C skeletal bond, $\sim 1600\text{ cm}^{-1}$ for C-C benzene ring and $\sim 2200\text{ cm}^{-1}$ for C-N cyan bond [105, 106].

molecules oriented along the long-range order, while randomly in spatial position, which is widely applied in the LC display technology. For Sm phase, it's similar to the N phase with molecules aligned along the same direction, while distributed in the layered structure with some degree deviated in each layer. For Ch phase, the molecules form a spiral structure with a fixed angle between the adjacent molecules. Normally the phases are basically defined by the LC molecule rod with alignment mode of splay, twist and bend, which are also the primary configuration for the LC system [107].

2.3.2 Optics of nematic liquid crystal

The properties of the LC materials are determined by the LC molecule alignment, which can be defined by the polar coordinates aligned with the LC directors. (see Figure 2.10b) [107]. For LC near the surface of the alignment layer, the molecules are fixed along the direction of the alignment. When there are no voltages driving applied, the LC molecules inside the cell is continuously twisted with the boundary alignment while keep parallel in-plane.

Normally the LC material has the resistivity of ρ in the range of $10^{10}\sim 10^{14}$ Ω/cm and relative permittivity ϵ_r in the range of 2 to 20, thus may induce a decay

Figure 2.10 (a) Schematic representation of three phases of LC; (b) Illustration of polarized light propagation through the biaxial birefringent media; (c) Temperature dependence of refractive index of LC [107].

time constant $\tau = \rho\varepsilon$ around the order of ~ 10 ms. In the LC, the anisotropic dielectric constant can be expressed as:

$$\varepsilon = \begin{pmatrix} \varepsilon_{\perp} & 0 & 0 \\ 0 & \varepsilon_{\perp} & 0 \\ 0 & 0 & \varepsilon_{//} \end{pmatrix}, \quad (11)$$

And the dielectric anisotropy is $\Delta\varepsilon = \varepsilon_{//} - \varepsilon_{\perp}$. Mostly the $5 < \Delta\varepsilon < 50$, or $0.05 < \Delta n < 0.22$ for LC. Consider an external electric field applied to the LC, the electric displacement vector $\mathbf{D} = \varepsilon_{\perp}\mathbf{E} + \Delta\varepsilon(\mathbf{n} \cdot \mathbf{E}) \cdot \mathbf{n}$, thus we receive the electric work:

$$W = - \int \mathbf{D} \cdot d\mathbf{E} = -\varepsilon_{\perp} \frac{E^2}{2} - \Delta\varepsilon \frac{(\mathbf{n} \cdot \mathbf{E})^2}{2}, \quad (12)$$

Therefore, for liquid crystal with $\Delta\varepsilon > 0$, W can be minimized when $\mathbf{n} // \mathbf{E}$, namely say the molecules are aligned parallel to the external fields.

As discussed above, for the biaxial LC material, the effective refractive index can be expressed based on the refractive index ellipsoid:

$$\frac{1}{n_e^2(\theta)} = \frac{\cos^2 \theta}{n_o^2} + \frac{\sin^2 \theta}{n_e^2}, \quad (13)$$

When the light comes through, only the e-wave (extraordinary) and o-wave (ordinary) can propagate. Therefore, for a random incident polarization, one has to decompose it into the e and o-wave components. When the light passes through the birefringent materials with dielectric anisotropy Δn , the e and o-wave will accumulate different phase delay, which is called the phase retardation:

$$\delta = \frac{\pi d \Delta n}{\lambda}, \quad (14)$$

where the d stands for the LC film thickness and λ is the incident wavelength. Thus, the incident polarization states can be adjusted, *e.g.* tuning the linear polarization to circular polarization, or rotation of linear polarization directions. Due to the larger refractive index, the extraordinary axis is often called the fast axis, namely the faster shift of phase change. For the phase retarded plate, the incident electric polarization can be decomposed into e and o-wave components as:

$$\mathbf{E} = iE_x e^{-jk_{xz}} + jE_y e^{-jk_{yz}}, \quad (15)$$

which can be further rearranged as:

$$\mathbf{E} = (iE_x e^{j\delta} + jE_y e^{j\delta}) e^{-jk_z + j\omega t - j\frac{\pi\Delta n d}{\lambda}}, \quad (16)$$

with the wave vector k expressed as $k = k_0 - \left(\omega t + \delta - \frac{\pi\Delta n d}{\lambda}\right)$. Therefore, for the quarter-wave plate ($\delta = \pi/4$, or $d\Delta n = \lambda/4$), with 45° incidence, the output can be expressed as $\mathbf{E} = iE_0 \cos(\omega t - kz) + jE_0 \sin(\omega t - kz)$, which turns the 45° linear polarization into the left-circular polarization. For the half-wave plate ($\delta = \pi/2$, or $d\Delta n = \lambda/2$), the output can be calculated with a rotation by 2θ with respect to the incident polarization. The transmittance through the retarded films between input and output can be simplified as:

$$T = \sin^2 \frac{\pi d\Delta n}{\lambda} = \sin^2 \delta, \quad (17)$$

Normally, the transmission of the LC cell with the director parallel to x -axis can be expressed as:

$$T = T(\alpha, \gamma, \phi, \delta) = \left| (\cos \gamma \quad \sin \gamma) \cdot M_{LC} \cdot \begin{pmatrix} \cos \alpha \\ \sin \alpha \end{pmatrix} \right|^2, \quad (18)$$

where α is the input polarizer angle to the x -axis, γ is the output polarizer angle to the x -axis, ϕ stands for the twist angle of LC and δ is the phase retardation. For the cross-polarizer geometry ($\alpha \perp \gamma$) and parallel LC molecule alignment ($\phi = 0^\circ$), the transmittance can be approximated as the integration of the birefringent optical accumulation:

$$T = \sin^2 \int_0^d \frac{\pi \Delta n}{\lambda} dz, \quad (19)$$

The transmission will show a uniformly periodic oscillation in intensity with the birefringence ($d\Delta n$). Normally the birefringence ($d\Delta n$) is spectral dependent, thus will lead to an intrinsic dispersion of transmission. For the vertically homogeneous liquid crystal (Δn is independent with z), the transmittance can be tuned between ON (100%) and OFF (0%) states by switching the Δn between M and $M \pm \frac{1}{2}$, $M=0, 1, 2, \dots$ (see Figure 2.11). For 90° nematic twist configuration,

Figure 2.11 Calculated transmittance of 90° twisted LC. The abscissa gives the ratio between dielectric anisotropy ($d\Delta n$) with the wavelength (λ)

which is widely applied in LCD technology, the transmittance can be expressed as:

$$T = 1 - \frac{\phi^2}{\beta^2} \sin^2 \beta, \quad (20)$$

where $\beta = \sqrt{\left(\frac{\pi}{2}\right)^2 + \left(\frac{\pi d \Delta n}{\lambda}\right)^2}$, thus shows reduced periods with the increment of the thickness. For larger thickness (Mauguin condition: $\Delta n \gg \frac{\sqrt{3}\lambda}{2d}$), the

Figure 2.12 Samples of LC based nanostructured devices: (a) the LC tunable hologram [64]; (b) thermal tunable LC based Si metasurface [4]; (c) electrically tunable fano resonance performance [65]; (d) electrically tunable Si based Huygens surface [42]

transmittance almost keeps stable close to 100%, showing an independence with the wavelength and thickness.

2.3.3 Liquid crystal with microstructures

Liquid crystal (LC) has a large birefringence as much as $\Delta n \sim 0.2$ at room temperatures throughout the wavelength ranges from UV to microwave. As shown in Figure 2.12, it can be an effective tunable media excited via the electrical, optical, magnetic and thermal approaches [58] with outstanding optical performances: electric drivable Au based plasmonic dynamic gratings [59], 85% modulation depth in Fano-resonance based all-dielectric silicon nanoholes [108], 40 nm wide tuning range in IR of the thermal drivable silicon metasurface [4], light drivable plasmonic color filter based on *trans-cis* reversible isomerization dynamics of *azo dye* doped LC upon UV and vis. light [109], and the surface acoustic waves (SAW) driven light shutters based on the polymer-dispersed liquid crystals [110] *etc.* Considering the mature LC technology in industry, the LC based tunable metasurface would be valuable for new concept SLM devices by integrating such designable nanophononics with the conventional technology.

LC based all dielectric tunable metasurface has been reported in high refractive index silicon ($n_{\text{Si}} \approx 3.84$ at 650 nm) with significant tuning range of electric and magnetic resonances in near-IR frequencies under the external thermal [4] and electrical control [101]. However, considering the lower band gap ($E_g \approx 1.1$ eV) of Si, significant loss would be unavoidable in the visible light frequencies ($h\nu > 1.6$ eV). TiO_2 has a wider band gap ($E_g \sim 3.2$ eV) and is lossless in visible light frequencies, which can be a good candidate designed for visible ranges metasurface [111]. Assisted by the tunable birefringence of LC, the resonant scattering of TiO_2 metasurface can be dynamically controlled. A challenge of the LC based tunable metasurface is the influence of anchoring effect of nano structures, which would lead to a deviation of LC alignment from preset direction by either rubbing or photoalignment process [112]. Comparatively, the refractive index of TiO_2 ($n_{\text{TiO}_2} \approx 2.57$ at 650 nm) is lower than Si, which would lead to a larger aspect ratio than Si ($AR = \text{Height}/\text{Radius}$, $AR_{\text{TiO}_2}/AR_{\text{Si}} \approx 1.7$), thus would render significant anchoring effect [113] and brings some difficulties to confirm the verticality of nano disks fabrication.

Traditionally, the pure LC spatial light modulation calls for LC thickness no less than $\lambda/\Delta n > 5\lambda$ for the complete control either in amplitude or phase.

LC thickness can be expected dramatically reduced when the metasurface is introduced for its enhancement effect. Most of the LC based metasurfaces reported so far are designed for the lower frequencies like THz and microwave with LC layers thicker than $5\ \mu\text{m}$ [4, 64, 108], which could be much larger than the extension distance of anchoring effect on the LC alignment, thus only weakly influences the optical performance. However, considering the large resistivity of liquid crystal about $10^{10}\ \Omega/\text{cm}$, high voltages above 40 V is needed to saturate the thick layer LC switching within nano structure areas [65, 114, 115]. For the higher frequencies like the visible light, LC layer thickness can be reduced which would be advantageous to improve the device performance in optical modulation [116], LC pixel sizes reduction and power consumption [117, 118]. However, performance of the LC based tunable all dielectric metasurface for visible light modulation is still challenging considering the complicated fabrication process and the less reliability of optical performance. The interaction between resonant Mie scattering with both passively and actively manipulated LC optical anisotropy is worthy to be discussed.

The mechanism of LC alignment anchored on the polymer surface structures like the polyimide of rubbed layers has been discussed based on two possible reasons: one is attributed to the static electric interactions between the LC molecules and surface polymer chains [119], while the other one is attributed to the mechanic distortion of LC molecules induced by the surface structures like the groove or trenches [116, 120]. Therefore, the LC alignment will be expected to be influenced by the surface nano structures. As discussed above, the elastic energy of the liquid crystal can be expressed based on the splay, twist and bend deformation parameters as:

$$F_{elas} = \frac{1}{2} \int \{K_{11} \cdot (\nabla \cdot \mathbf{n})^2 + K_{22} \cdot (\mathbf{n} \cdot [\nabla \times \mathbf{n}])^2 + K_{33} \cdot (\mathbf{n} \times [\nabla \times \mathbf{n}])^2 - \epsilon_0 \epsilon (\mathbf{E} \cdot \mathbf{n})^2\} dV \quad (21)$$

in which $\mathbf{n}$ represents the director of the LC alignment [121]. Thus, we can receive an equilibrium configuration of the static systems' energy as the sum of the LC elastic energy and the surface energy: $F_{stat} = F_{elas} + F_{surf}$. So far, several theoretical studies have been gradually extended on the LC alignment

performance within the nano structures. The first model to define the surface energy is proposed by Berreman, by whom the surface anchoring of the linearly rubbed surface is approximated to be a sinusoidal shape and the unit strength can be expressed as:

$$F_{\text{surf}} = \frac{1}{4}KA^2q^3 \sin^2 \varphi, [116] \quad (22)$$

or $W\sin^2\varphi$ in Rapini-Papoular model [118, 122] for simplification in which the W represents the anchoring strength and φ defines the angle between the surface easy axis and LC alignment. For the Berremans's model as given in Ref. 116, the LC distorted system has the elastic energy contributed by splay (f_1), twist (f_2) and bend (f_3) deformations is expressed as: $f_1 = \frac{1}{8}K_1q^3A^2 \sin^2 \varphi$, $f_2 = \frac{1}{8}K_2q^3A^2 \sin^2 \varphi \cos^2 \varphi$ and $f_3 = \frac{1}{8}K_3q^3A_2 \sin^4 \varphi$. Later, Fukuda *et al* found that for the scratched surface, the LC aligns nearly parallelly and the splay and twist deformations are quite weak [118]. Thus, it leads to a major contribution of the bend deformation of the LC alignment near the surface, namely proportional to $\sin^4 \varphi$ with respect to the easy axis. For the 2D layouts, in which the anchoring effect induced by the surface geometry can be expected from orthogonal directions as shown in Figure 2.13, the surface antennas have the perpendicular gaps along x and y -axis directions, therefore can be expressed with the surface energy efficient, *e.g.* W_1 and W_2 , and $W_1=W_2$ for symmetric geometries. Therefore, for analysis of the LC alignment in certain kind of LC cell sample

Figure 2.13 Schematic illustration of LC alignment within the nano structured cells under the influence of both the surface anchoring effect and top alignment energy by either rubbing or photoalignment

with three kinds of energy considered: the LC molecules' elastic energy, the rubbing/photoalignment layer energy and the influence from the other places, the unit surface anchoring energy can be expressed as:

$$F_{\text{surf}} = W_1 \sin^4 \varphi + W_2 \cos^4 \varphi. \quad (23)$$

For the LC cell under the electrical fields, the energy of the whole system can be expressed as:

$$F = F_{\text{elas}} + F_{\text{surf}} + F_{\text{e}} = F_{\text{stat}} + \left(-\frac{1}{2} \int \text{Re}(\mathbf{E} \cdot \mathbf{D}) dV\right) \quad (24)$$

which can be also referred to the Equation 12 in this chapter [59]. Details of the relations between the LC alignment and surface anchoring effect energy will be discussed in Chapter 6.

Chapter 3: Magneto-optical spatial light modulation based on MnBi thin film

3.1 Introduction

As given in Section 2.1, the magneto-optical effect can be introduced into design for advanced spatial light modulation functions. To obtain more significant polarization switching signals spatially distinguishable, the Kerr effect happens in perpendicular magnetic materials is more appreciated due to the larger E - M interaction momentum between the incident electric field and the magnetization. So far, kinds of magnetic materials have been studied for magneto-optical (MO) devices like the metals (Co, Fe and Ni), the transition metal oxide composites (YIG, Mn oxides, Fe_3O_4 etc.) and magnetic alloys (CoFeB, CoFe, MnBi etc.) (see Section 2.1 of Chapter 2). However, magnetic materials with strong perpendicular magnetization will be preferred for such kind of performance.

Low temperature phase (LTP) MnBi (see Figure 3.1a) has been found a competitive candidate for applications with a large perpendicular magnetization ($\sim 500 \text{ emu/cm}^3$), large Kerr rotation angle ($\sim 1^\circ$) as well as high spin polarization rate ($\sim 60\%$) [97]. Normally, LTP MnBi thin films were fabricated by thermally annealing the $[\text{Mn/Bi}]_x$ multilayer at high temperatures ($>350^\circ \text{C}$) (see Figure 3.1b), leading to the hexagonal NiAs-like structure ($P63/mmc$) with $a=b\sim 0.43$

Figure 3.1 (a) structure of low temperature phase MnBi lattice; (b) Mn and Bi thermal annealing process for MnBi fabrication

nm, $c \sim 0.61$ nm, $\alpha = \beta = 90^\circ$, $\gamma = 120^\circ$ which is characterizable below the curie point $T_c \sim 628$ K (355 °C) [123]. It's been thought the local magnetic moment of the LTP originates from the Mn ($3d^5$) ~ Bi ($6p^3$) orbits interaction, which induces an average moment of $\sim 3.6 \mu_B$ on the Mn atoms [124].

However, some obstacles are still waited to be overcome for the LTP MnBi thin film's application: the flatness of Mn and Bi sublayers' deposition for the uniformity of the final MnBi alloy assembling, the instability of magnetization due to the environmental oxidation and minimized pixilation and the coercivity for driving energy. In this chapter, we will focus on the magneto-optical spatial light modulation properties based on the MnBi alloy thin films.

3.2 Experimental results

Experimental results including the sample fabrication, elemental content analysis, micro-structure characterization, magnetic and magneto-optical measurement will be given in this section. The list of equipment was given in Figure 3.2. The thin films were prepared by magnetron-sputtering deposition (UHV Chiron), followed by a thermal heating annealing above 350 °C with a homemade vacuum oven setup. X-ray diffraction with Cu K α radiation (Philips

Figure 3.2 Some equipment for MnBi thin film fabrication: (a) magnetron-sputtering system, (b) homemade vacuum oven for thermal annealing, (c) AES system, (d) AGM system (e) optical microscope

X'pert XRD system) meter and optical microscope were used to determine the phase of the MnBi films. Auger Electronic Spectrum (AES: HSMART200) testing was applied to determine the element concentration throughout the whole thickness. The surface morphology was with the Atomic Force Microscope (the Digital Instruments Atomic Force Microscopy Dimension 3100). Room temperature magnetization was measured using an alternating gradient magnetometer (AGM) with the fields up to 20 kOe and the Quantum Design product: Super-conduct Quantum Interfere Device (SQUID). The magnetic domain's transition was verified with the magnetic force microscopy (MFM).

3.2.1 Fabrication of MnBi thin films

Mn and Bi layers were alternatively deposited by DC and RF modes of magnetron-sputtering system (UHV Chiron) (see Table 3.1). Mn was deposited under the pressure of 1.5 mTorr and 100 W at the rate of about 6.6 nm/min. Hexagonal Bi layer of 30 nm was first deposited under 4.5 mTorr and 10 W (Figure 3.3a). However, MnBi was not crystalized after thermal annealing based on this condition since the zigzag-like surface of Bi could lead to an uneven distribution of Mn/Bi stoichiometry (Figure 3.3b and c). As the result, the MnBi phase is difficult to form due to the heterogeneous Mn and Bi elemental distribution. The surface morphology was much smoother when Bi was deposited by RF mode at slower rate (3.8 nm/min) than the DC mode (14.9 nm/min) for 4.5 mTorr and further being optimized under a much smaller 1.32 nm/min for 1.15

Table 3.1 Parameters for Mn/Bi thin films fabrication

Material	Mode	Pressure (mTorr)	Power (W)	Deposition rate (nm/min)
Mn	DC	1.5	100	6.6
Bi	DC	4.5	10	14.9
Bi	RF	4.5	10	3.8
Bi	RF	1.5	10	1.86
Bi	RF	1.15	10	1.32

Figure 3.3 (a) XRD pattern of 30 nm Bi as deposited; (b) XRD pattern of MnBi (Mn/Bi = 15/30 nm) thermally annealed; Step profilers of Bi layers deposited at (c) DC mode for 4.5 mTorr and RF mode for (d) 1.5 mTorr and (e) 1.15 mTorr

Fig. 3.4 XRD patterns of Bi single layers with (a) 20 nm, (b) 30 nm and (c) 40 nm thicknesses, and (d) 20/40 nm and (e) 10/20 nm Mn/Bi films after thermal annealing in vacuum at 350 °C for 2 hrs.

mTorr and 10 W (Figure 3.3d and e). As given in Figure 3.4a to c, the hexagonal Bi (000 l) is only observable when the thickness of Bi is thicker than 30 nm.

Then the Mn/Bi bilayer with different contents characterized by the thickness ratios was studied. It has been reported a window of Mn/Bi thickness ratios from 0.4 to 0.6 for the LTP MnBi crystallization and detectable perpendicular magnetic performance. Here, the thickness ratios of Mn/Bi were initially set at 0.5: 10/20, 15/30, 20/40 and 30/60 nm. As given in Figure 3.4d, the typical (000 l) peaks in XRD patterns confirms the LTP MnBi fabrication. After annealing process, the LTP MnBi peaks become unclear for samples with Bi thinner than 30 nm (see Figure 3.4e), confirming a limitation of thickness to form the Bi texture (> 30 nm). Then we prepared the samples with different Mn/Bi thickness ratios (12/40, 14/40, 16/40, 18/40, 20/40, 22/40 and 24/40 nm). Some of the XRD patterns were given in Figure 3.5. MnBi peaks of XRD patterns only appear in 18/40, 20/40 and 22/40 nm samples, namely the Mn/Bi thickness

Figure 3.5 XRD patterns of MnBi thin films with Mn/Bi thickness ratios as (a) 24/40 nm, (b) 22/40 nm, (c) 20/40 nm and (d) 16/40 nm after thermal annealing in vacuum. The black dots represent the peaks of wafer substrate. The peaks of MnBi and Mn oxides were marked in the patterns.

ratios between 0.45 to 0.6, which almost coincides with the reported results. Mn metal is easy to be oxidized. Based on the results of optical microscope capture with 100x magnification (see Figure 3.6a), for 24/40 nm thickness ratio sample, the metallic Mn oxide was densely condensed (see the small blue spots). For samples within the fabrication window of MnBi, the MnBi can be observed (see the gray area circled). For sample thickness ratios below the window (<0.45), such MnBi phase almost disappeared, indicating a decreased amount of MnBi phase. The depth profile of the MnBi with 20/40 and 22/40 nm ratios were measured by AES systems, showing the comparative percentage of Mn Bi and O elements (see Figure 3.6b). For the 20/40 nm MnBi sample, the Mn and Bi element ratios are almost consistent throughout the whole thickness of thin film. Comparatively, the Mn shows obvious higher percentage than Bi for the 22/40

Figure 3.6 (a) Microscopic images of MnBi surface morphology with Mn/Bi thickness ratios from 24/40 to 14/40 nm; The circle marks the MnBi phase. (b) AES cross sectional depth profile of 20/40 and 22/40 nm MnBi film for O, Bi, Mn and Si.

Figure 3.7 XRD patterns of $[\text{Mn/Bi}]_x$ multilayer MnBi films for (a) $x=10$, (b) $x=4$, (c) $x=2$ and (d) $x=1$; the dots mark the diffractive peaks of the silicon wafer

nm, corresponding to the thicker Mn thickness. To be noted, the oxygen content markedly increased in 22/40 nm sample than the 20/40 nm sample.

To realize a thorough diffusion of Mn and Bi layers, $[\text{Mn/Bi}]_x$ ($x=2, 4, 10$) multilayers were fabricated based on 20/40 Mn/Bi thickness ratio with a total thickness of 60 nm. As given in Figure 3.7a to d, the peak intensity generally increased with an increased periodicity of the layers, showing a well inter-diffusion of Mn and Bi with a thicker Bi layer to form the hexagonal texture, thus a better formation of the LTP-MnBi phase after thermal annealing.

3.2.2 Perpendicular magnetization of MnBi thin films

The M - H hysteresis loop was measured for one of the fabricated MnBi thin film samples (Mn/Bi=20/40 nm) at room temperature by superconducting quantum interference device (SQUID, Quantum Design Inc.) and Micromag Alternating Gradient Magnetometer (AGM). The comparison of the results is given in Figure 3.8. The sample was measured under magnetic field both parallel and perpendicular to the film sample's surface. For the SQUID measurement, the

Figure 3.8 Magneti hysteresis loop of MnBi thin film measured by SQUID and AGM under magnetic fields perpendicularly and parallelly to the sample's surface

sample was measured under high magnetic field up to 5T. As given in Figure 3.8, for the perpendicular field, a saturation of magnetization (M_s) around 250 uemu can be observed with a coercivity around 10 kOe. The high level of spontaneous perpendicular magnetization alignment ($\eta = M_r/M_s > 0.95$) reflects a near-perfect alignment of the magnetic LTP MnBi crystal in thin film. For the field parallel to the sample's surface, the magnetization cannot saturate even under high field as much as 5 T. The results indicate a perpendicular magnetic anisotropy (PMA) of the thin film, confirming the true fabrication of the LTP phase of MnBi. For the AGM measurement, field as much as 2 T was applied. The measured hysteresis loops are almost closely overlapped, proving the conformity of the measured results under the two systems. For the following work, the results are measured by the AGM system for various Mn/Bi thickness ratios and receive the maximized saturated magnetization around 480 emu/cm³ was obtained for the sample 20/40 nm Mn/Bi thickness ratio (see Figure 3.9), which corresponds to the crystal structure analysis in Figure 3.4 and 3.5. Saturated magnetization reduced with a further deviation of the component ratios. The results correspond to the certain amount of the magnetic phase components within the sample. The M - H loop of the substrate is also measured with an almost negligible magnetization, excluding the possible influence of the substrate on the sample

Figure 3.9 PMA magnetic performance of wafer substrate and the MnBi thin film with Mn/Bi thickness ratio from 24/40 to 16/40 measured by the AGM system

magnetization. Coercivity as much as 6 kOe was obtained for the sample with sufficient magnetic phase. For the 24/40 nm MnBi sample and the substrate, quite small magnetization and coercivity was obtained, showing the tiny amount of magnetic phase.

Figure 3.10 Training effect of PMA MnBi measured 4 repeats of process under magnetic fields of 20 kOe

For the magnetic devices, performance of the magnetic unit for repeated training is vital to be considered. Here, a new MnBi thin film sample with the best component ratio (20/40 nm) was fabricated according to the condition collected as above, and repeatedly trained under the perpendicular magnetic field as much as 2 T. The sample was measured with the saturated magnetization M_s as much as 480 emu/cm³ and coercivity of 6 kOe for the first round and almost consistent with the previous results (see Figure 3.10). When the sample was repeatedly trained, the M_s generally reduced to 390 emu/cm³ and the coercivity was increased to 8 kOe, confirming a reduced amount of the magnetic phase.

Figure 3.11 PMA magnetic performance of MnBi thin film exposed without the capping layer

As shown in Figure 3.6, the metallic Mn would result in the oxidation at the surface. Therefore, the capping layers are necessary for sample protection due to that the materials easily to be influenced by the ambient environment like the metal and alloy. Here, the magnetic performance of pure MnBi sample was measured with a 14-day interval in the ambient environment. As given in Figure 3.11, the magnetization is reduced by 35% from 430 emu/cm³ to 280 emu/cm³ for the 20/40 nm MnBi thin film, revealing possible degradation of the magnetic content, while the M_s reduced more dramatically by 79% from 140 emu/cm³ to 30 emu/cm³ for the 22/40 nm MnBi thin film. For the coercivity, H_c increased by a 23% increment from 6.6 to 8.1 kOe after the 14-day interval exposure for the 20/40 nm sample, while increased by 120% from 3.5 to 7.7 kOe for the 22/40 nm MnBi sample. These results confirm the significant influence of the ambient oxidation. The details of the oxidation effect will be discussed in the Section 3.3.2.

Ta and Ru are typical candidates of the capping layer for sample protection due to the stable physics and chemistry properties. Here, we chose the Ta and Ru respectively as the capping layer and deposited on the MnBi thin film before thermal annealing. In Figure 3.12, the magnetic performance of the protected samples was shown and compared with the capping layer free sample. For the Ta

Figure 3.12 PMA magnetic performance of the MnBi thin film with Ta and Ru capping layer and compared with the capping layer free sample

Figure 3.13 PMA comparison of MnBi with the Ta capping layer before and after 14-day exposure in air

protected sample, the magnetization can be almost well preserved. However, for the Ru protected sample, the magnetization almost disappeared. When checking with the XRD patterns (not given here), there is no MnBi phase for the Ru protected sample. Comparatively, the atom size of Bi is smaller than Ta, but larger than Ru. During the thermal annealing process for MnBi fabrication, the Ru would be easily diffused into the MnBi lattice, which would prevent the formation of MnBi microstructure. For Ta, the atoms are blocked on top of the MnBi layers, playing a role of the protector. Later, the Ta protected MnBi was measured between a 14-day interval of ambient exposure. As given in Figure

Table 3.2 Design of the MnBi thin film pixilation scale and fill factor

Pixel pitch: 10 μm				
D500S1500	D540S1460	D580S1420	D620S1380	D660S1340
FF=0.0625	FF=0.0729	FF=0.0841	FF=0.0961	FF=0.1089
D700S1300	D750S1250	D800S1200	D900S1000	D1000S1000
FF=0.1225	FF=0.1406	FF=0.16	FF=0.2025	FF=0.25

Figure 3.14 AFM surface morphology of the pixilated MnBi microstructures of (a) and (c) D500/S1500 and (b) and (d) D1000/S1000

3.13, the magnetic properties can be well preserved for the Ta protected MnBi with the M_s of larger 490 emu/cm^3 and the H_c of smaller 4.9 kOe , confirming an effective role it played as the capping layer.

Pixilation of the microstructure patterned nano thin films are essential for practical application. Fill factor (FF), given by $FF = (D/P)^2$, is defined as the ratio of the light sensitive area (D^2) versus the total area of the pixel pitch (P^2), in which D and P give the linear scale of the effective component and the whole pixel lattice. Based on the fabrication process given above, the silicon wafer coated with a layer of $20/40 \text{ nm}$ MnBi was dry etched by focused ion beam etching (FIB) method after the 350°C . Surface morphology of the pixilated MnBi was scanned by the atomic force microscope (AFM, Bruker Inc.) (see Figure 3.14). It can be confirmed that the linear size of each pixel pitch is around $10 \mu\text{m}$, with D and S stand for the length of near-square pattern and the spacer between the nano antennas. The FF dependence of the PMA of pixilated MnBi was illustrated by AGM measurement with out-of-plane magnetic field. The selected pixels are fabricated with FF patterned from 0.0625 (D500S1500) to 0.25 (D1000S1000) (see Table 3.2). The numbers represent the relative values of 10

Figure 3.15 (a) PMA of pixilated MnBi thin films with pixel size 1 μm and continuous film (fill Factors of 0.25 and 1); (b) FF dependence of coercivity (H_c) and saturated magnetization (M_s)

μm pitch. Comparison of M - H loops as captured for selected MnBi pixilated structures are shown in Figure 3.15. We first compare the continuous film with the pixilated sample ($FF=0.25$), seeing a decreased M_s from 236.5 emu/cm^3 to 68.28 emu/cm^3 , while coercivity (H_c) increased from 10.44 kOe to 16.83 kOe after pixilation process. From the AGM results, a rise in fill factor resulted in a decrease in coercivity from 17.23 kOe to 15.63 kOe, followed by an increase to 16.83 kOe. Moreover, an increase in fill factor results in a rise in of M_s from 74.31 emu/cm^3 to 135.3 emu/cm^3 and then fall to 68.28 emu/cm^3 .

Figure 3.16 (a) MOKE results of MnBi with different Mn/Bi thickness ratios; (b) Comparison of Kerr rotation and PMA magnitude depending on the Mn/Bi thickness ratios

3.2.3 Magneto-optical performance of MnBi thin films

The magneto-optical Kerr rotation (θ_k) was measured at room temperature by a home-made magneto-optical tester setup with a 633 nm light source. Signal of the pure substrate was tested beforehand to exclude the influence on MOKE in exception of the MnBi. As given in Figure 3.16a, the MOKE signal was tested for samples with different Mn/Bi components ratios. The Kerr rotations are almost maximized for 20/40 nm MnBi sample with Kerr rotation of 0.1 degree and coercivity about 5 kOe, which almost corresponds to the PMA hysteresis loop results. For samples near the optimized ratio, obvious Kerr rotation signal

Figure 3.17 (a) Surface morphology characterized by the optical microscope with 100X magnification for $[\text{Mn}/\text{Bi}]_x$ with $x =$ (i) 10, (ii) 4, (iii) 2 and (iiii) 1; (b) Kerr rotation signal of the multi-layered MnBi thin films

can be obtained, which corresponds to the strong PMA behaviors of the MnBi thin film (see Figure 3.16b). For Mn/Bi ratios deviated from the critical window, almost no Kerr signal was observed, which corresponds to the weak magnetization. As interpreted by the principle of MOKE (see equation (1) to (8) in Chapter 2), the Kerr rotation is determined by the perpendicular magnetization factor. Normally the MOKE is more influenced by the magnetic phase at the surface area around 30 nm in depth [125]. The magnetic phase size especially at the surface would be vital for the MOKE performance. As discussed in section 3.2.1, the existence of LTP MnBi phase can be improved by multi-layer $[\text{Mn}/\text{Bi}]_x$

deposition before thermal annealing, for which the Mn and Bi atoms can be more thoroughly diffused. Here, the $[\text{Mn/Bi}]_x$ multi-layer with $x = 10, 4, 2$ and 1 were characterized by the optical microscope under $100\times$ magnification and then measured by the MOKE setup (see Figure 3.17). As given in Figure 3.16a, the gray areas stand for the MnBi phase domain [124]. For the $x=1$, the MnBi phase domain size is fragmentally distributed with each no larger than $1\text{ }\mu\text{m}$. When x increases from 1 to 10 , the domain size of the magnetic phase gradually increases and almost links up into a large stretch. This observation well confirms a more uniform MnBi phase formation when Mn and Bi layers are more densely interlaced. For MOKE measurement in Figure 3.17b, when the number of interlaced layers decreases from 10 to 1 , the Kerr rotation generally decreased from 0.1 to 0.08 degree, corresponding to the reduced magnetic phase formation in sample.

3.3 Discussion

3.3.1 Condition for LTP MnBi fabrication

As shown above, the LTP MnBi thin films can be well fabricated with the magnetron sputtering method followed by a 2hrs thermal annealing. Certain thickness above 30 nm is essential to form the hexagonal structure of Bi layers. RF mode is suitable for the Bi fabrication due to the low conductivity and it would be difficult to control the Bi ion flow under the DC mode. The thermal annealing above $300\text{ }^\circ\text{C}$ is important for the plenary interlayered diffusion of Mn and Bi thus to form a uniform MnBi lattice structures. The Mn/Bi layer thickness ratio is optimized for $20/40\text{ nm}$. Strong perpendicular magnetization about 480 emu/cm^3 is obtained for the 60 nm MnBi thin film, which confirms a correct composition of the MnBi phase of the thin film sample. The strong perpendicular magnetization is an important precondition for a better MOKE performance, which is also observed in the MOKE test results. Surface oxidation would be significant for the Mn components in the sample [126, 127]. Protection will be important for the thin film sample and further the devices based on it.

3.3.2 Magnetic properties of MnBi

As measured and given in Section 3.2, strong perpendicular magnetization is obtained together with an obvious MOKE performance for the optimized component thickness ratio of Mn/Bi=20/40 nm. Those results confirm a good quality and magnetic performance of the LTP MnBi thin films. The decreased magnetization of MnBi out of the optimized window of thickness ratio indicates a decrease share of the magnetic phase. To be noted, when the sample was trained for several times, the magnetic coercivity reduced, showing a decrement of the magnetic domain size. Similar reduction is also observed in the pixilated sample. The smaller the aspect ratio of the pixel pitch, the smaller coercivity and magnetization received, corresponding to the reduced magnetic domain evolution after the process.

An obvious oxidation influence is critical here for the magnetic properties. As given above, the ambient oxygen may play an important role in influence the

Figure 3.18 XRD patterns of (a) as-deposited Mn/Bi/SiO₂/Si, (b) Sample 1 and (c) Sample 2 when fabricated, (d) Sample 1 and (e) Sample 2 after the 14-day exposure to air, and (f) bare MnBi films with Mn thicknesses of (i) 20 nm (Sample 1), (ii) 22 nm (Sample 3) and (iii) 24 nm (Sample 4) after the 14-day exposure to air. The unmarked peaks represent the wafer substrate.

Figure 3.19 Depth profile of elemental distribution of (a) Sample 1 and (b) Sample 2. The dashed lines (orange) give the Mn/Bi atomic ratio.

crystal structure and thus that the magnetic properties of the MnBi thin films. The appearance of pure Bi phase in the MnBi thin film may be due to either the peritectic reaction during the Mn-Bi solidification process above the Bi melting

point ($\sim 260^\circ\text{C}$) or the decomposition of MnBi phase [123, 128]. In the XRD results (see Figure 3.18), the diffraction peak of Bi only appeared in MnBi thin films without the capping layer after the 14-day exposure to air, and the Bi peak becomes more significant while the peak of the MnBi phase is reduced in the samples with higher Mn content (see Figure 3.18), presenting a large reduction of M_s (see Figure 3.9 and 3.16). Kharel *et al* noticed the similar behavior that the intensity of Bi (012) peak increased and MnBi (002) peak decreased with certain Pt concentration, which was attributed to the substitution of Pt into MnBi lattice [129]. Considering the electron configuration of Mn ($3d^5$) $\sim$ Bi ($6p^3$) bonding, Mn in MnBi can be easily oxidized due to the unpaired electrons in $3d$ orbits [130]. Referring to the AES results (see Figure 3.19), after the 14-day exposure to air, the oxygen further diffused into the inner area where more MnBi content would exist. The oxidation process of Mn in MnBi could be the possible origin of the decomposition of MnBi as well as the reduction of M_s . When the oxygen diffusion was suppressed by the Ta capping layer (see Figure 3.19b), the MnBi content ratio can be effectively reserved, further maintain a higher M_s .

As given above (see Figure 3.11), the coercivity H_x can be enlarged after the 14-day exposure to air. Referring to the microstructure, the grains of all the samples have the similar size of about 100 nm before and after the exposure (see Figure 3.20). According to the spherical particle model, the critical diameter of MnBi single domain was calculated to be 300-500 nm [131], which is obviously larger than the grains observed. The magnetization of the samples in Figure 3.20 could be regarded as rotating coherently within the single grain region. For the MnBi thin films when fabricated, the sizes of the magnetic domains are much

Figure 3.20 AFM and MFM images of (a) Sample 1 when fabricated, (b) Sample 1 and (c) Sample 2 after the 14-day exposure to air

Figure 3.21 Illustration of magneto-crystal anisotropy and inter-grain exchange energy across the domain boundaries. The hexagons define the magnetic domain areas and the red dash squares represent the boundaries' areas.

larger than the size of grains. After the exposure to air, average size of the domains in the Sample 1 decreased to less than 1 μm , while almost retained unchanged for the Sample 2. The alignment of magnetic moments is normally regulated by the interplay between magnetic crystalline anisotropy (K_a) and inter-grain exchange interaction (J_{ex}) [132]. For areas across the boundaries of the inter-grain coupling systems, the moments can be deviated from the crystal axis to align with the external field due to the J_{ex} , and the subdomains can thus form a larger magnetic domain. As shown in Figure 3.20, the magnetic domain images (MFM in the figure) were captured simultaneously at the same position. The small magnetic domains divided by the non-magnetic boundaries are close to the grains in shape (dashed squares in Figure 3.20b). When the magnetic coupling becomes weaker between the MnBi grains due to the oxidized non-magnetic boundaries, the movement of domain wall moments will be restricted. As given in Figure 3.21, to align the moments parallel align the external field, greater fields are needed for the propagation of domain wall moments at the non-magnetic boundaries, which leads to a larger coercivity and saturation field. For the Sample 2 protected with Ta capping layer, even after 14-day exposure to air, its inter-grain exchanges were almost unaffected due to the significant oxidation. Therefore, Sample 2 can maintain larger magnetic domain size and lower coercivity than Sample 1.

3.3.3 Enhanced MOKE of MnBi thin films with dielectrics

It has been proved that the insertion of dielectrics can help to enhance the MO activity due to the light confinement. Based on the MnBi thin films, the TiO_2 dielectrics is introduced. The optical and magneto-optical performance of MnBi based metal/dielectric bilayer structures were numerically calculated and discussed. The calculation model was referred elsewhere [133]. The refractive index (n , k) and magneto-optical parameters (Q_1 and Q_2) of the reported MnBi film at red (632.8nm), green (532nm) and blue (473nm) wavelengths were derived and listed in Table 3.3 ($\text{MO} = Q_1 + iQ_2$) [134, 135]. To better differentiate the refractive indexes between MnBi and dielectrics, we chose the TiO_2 ($n \sim 2.6$) which is lossless in visible light range. Four stacks were designed to study the influence from dielectrics. The MO properties of MnBi films were simulated in terms of Kerr rotation ($2\theta_k$), reflectivity and figure of merit (FOM: MO rotation

vs reflectance) at the above red (R), green (G) and blue (B) wavelengths and listed in Table 3.4 and summarized in Table 3.5 and shown in Figure 3.22a to f.

According to the results, the TiO₂ significantly enhanced the Kerr rotation, *e.g.* from $2\theta_k = 0.86^\circ$ without TiO₂ to a maximum 29.6° with TiO₂ of $t=114.4\text{nm}$

Table 3.3 (n, k) and (Q₁, Q₂) parameters setting of the reported MnBi film at RGB wavelengths in simulation.

RGB wavelength (nm)	Refractive index		MO parameter	
	n	k	Q ₁	Q ₂
632.8 (R)	1.72203	2.62325	0.037667	0.063705
532 (G)	1.53417	2.37527	0.046007	0.0398
473 (B)	1.43051	2.21415	0.045552	0.029428

Table 3.4 MnBi-based stacks designed for the simulation of MO properties.

No.	Stack structure (<i>t</i> - thickness; unit in nm)
#1	TiO ₂ (<i>t</i>)/MnBi(60)/SiO ₂ (1000)/Si(substrate)
#2	TiO ₂ (<i>t</i>)/MnBi(60)/Al ₂ O ₃ (25)/Ag(150)/SiO ₂ (1000)/Si(substrate)
#3	MnBi(60)/TiO ₂ (<i>t</i>)/Al ₂ O ₃ (25)/Ag(150)/SiO ₂ (1000)/Si(substrate)
#4	TiO ₂ (<i>t</i>)/MnBi(60)/TiO ₂ (100)/Al ₂ O ₃ (25)/Ag(150)/SiO ₂ (1000)/Si(substrate)

at 473nm in stack #2. Due to the light localization within the dielectric layers, the enhanced MO performance can be expected for certain thickness with the fractional relation of incident wavelengths, which can be proved by the periodic peaks of MO signals in Figure 3.22. The special behaviors are almost diminished in stack #3, on which MnBi was the first layer deposited. To be mentioned, light localization is significant since the reflectivity is greatly reduced from 50% at

Table 3.5 Simulated MO properties of four different MnBi-based stacks

No	Kerr Rotation ($2\theta_k$)			Reflectivity			Figure of Merit (FOM)		
	632.8 nm	532 nm	473 nm	632.8 nm	532 nm	473 nm	632.8 nm	532 nm	473 nm
#1	9.5° t=35.4nm	17.7° t=135.9nm	23.8° t=114.3nm	3.55% %	1.73% %	1.16% %	0.0010	0.0016	0.0019
#2	17.6° t=41.0nm	23.1° t=134.7nm	29.6° t=114.4nm	2.73% %	1.49% %	0.78% %	0.0025	0.0023	0.0019
#3	1.37° t=40.7nm	1.71° t=57.5nm	1.80° t=46.1nm	51.1% %	55.0% %	51.4% %	0.0003	0.0005	0.0005
#4	16.4° t=39.9nm	22.9° t=134.5nm	27.6° t=115.0nm	4.3% %	1.6% %	0.67% %	0.0035	0.0025	0.0014

Figure 3.22 Dependence of MO properties of MnBi-based stack structures #1-#4 on the TiO_2 thickness (t): (a) to (c) Kerr rotation ($2\theta_k$) at RGB wavelengths; (d) to (f) Reflectivity at RGB wavelengths

RGB wavelength in stack #3 to less than 5% after TiO_2 inserted. The pure MnBi shows higher reflectance while smaller Kerr signals since no dielectric layer is deposited with the magnetic layer. New methods are waiting to be developed for the trade-off between the Kerr rotation and reflectivity to achieve higher figure

of merit (FOM). Such enhanced performance can be expected by introducing the dielectrics based nano structures.

3.3 Summary

In this chapter, the LTP phase MnBi thin film with perpendicular magnetic anisotropy was successfully fabricated. Surface morphology, microstructure, and magnetic properties including the perpendicular magnetization and MOKE Kerr rotation performance was accordingly tested and discussed. MnBi was fabricated by magnetron sputtering deposition of the $[\text{Mn/Bi}]_x$ multilayers and then thermally annealing at 350 °C for 2 hrs in vacuum. The Bi has a high resistance and the flat Bi layer was deposited by RF mode with a much lower deposition power compared with the DC mode at the rate of 1.32 nm/min with a lower 1.15mTorr background pressure, while the Mn layer was deposited by DC mode at the rate of 6.6 nm/min. Hexagonal lattice structure can be only textured with the Bi thickness no thinner than 30 nm. Multi-period $[\text{Mn/Bi}]_x$ interlaced deposition would help for a uniform formation of magnetic MnBi phase.

MnBi shows the best phase crystallization and perpendicular magnetic anisotropy for Mn/Bi thickness ratio of 1/2 with 20/40 nm, receiving a saturated magnetization M_s of 490 emu/cm³ and the coercivity around 5 kOe. The M_s reduces with the deviation of the Mn/Bi components ratios from the optimized window. Training effect shows that the MnBi PMA would reduce with repeated cycling under the magnetic field. The M_s of MnBi alloy obviously decreases with the interval of exposure in air, showing a sensitivity to the influence of ambient oxidation. Ru would be easy to infiltrate into the MnBi lattice and is not suitable for protection. Ta layer shows an effective capability as the capping layer with almost negligible decline even after long time exposure in air. Pixilation influence is critical on the magnetic properties. The magnetization reduces and coercivity increases for pixels with smaller Fill Factors. MOKE test shows a close correlation with the PMA results, and maximized at the 20/40 nm MnBi sample with a large MOKE signal in visible wavelength range, confirming the origin of MOKE effect with the perpendicular magnetization.

The evolution of magnetization can be interpreted by the interplay between the MnBi magnetic crystalline anisotropy and the inter-grain exchange energy.

For sample with large continuous magnetic domains, the magnetic moments can be saturated with smaller field due to the coherent rotation of moment within the single domains. When the magnetic domain size reduces due to the insufficient phase formation or broken by oxidation or repeated training, the exchange energy across the magnetic domains would be increased to rotate the moments at the boundaries due to the larger magnetic exchange interaction, leading to the enlarged coercivity and saturation field.

According to the numerical calculation, the Kerr rotation can be dramatically enhanced from $2\theta_k = 0.86^\circ$ without TiO_2 to a maximum 9.5° at 633 nm with a dielectric inserted TiO_2/MnBi multilayer, and an even large increment to a maximum 17.6° with a reflection enhanced $\text{TiO}_2/\text{MnBi}/\text{Al}_2\text{O}_3/\text{Ag}$ multilayer. The enhancement of MOKE due to the insertion of visible lossless dielectric TiO_2 can be attributed to the focus the light intensity in vicinity of the magnetic layer.

Albeit showing excellent magneto-optical performance compared with other MO materials, the MnBi received is still insufficient for practical application due to the large coercivity, which would dramatically increase the driving cost for high frequency devices. Besides, the sensitive reaction to the ambient influence and the degrade magnetization of pixilation would further prevent the application of such MOSLM design especially for the high-density resolution devices with small size pixilation.

Chapter 4: Optical performance of TiO₂ nano disks metasurface

4.1 Introduction

Metasurface has been used for subwavelength modulation of light properties like the amplitude, phase, polarization via the tailoring of electric-magnetic modes, which has been proved to be an effective platform for development of manually designable spatial light modulator as tiny as the subwavelength scale. A metasurface showing strength in both high efficient transmission/reflection and phase control would be a potential platform for the development of metasurface based SLM for applications like the holographic 3D display and wave-front shaping *etc.* As given in Chapter 1 and 2, the all dielectric metasurface shows merit of low-loss light modulation based on the Mie scattering effect. Compared with the silicon material, TiO₂ has a wider band gap and is lossless within the visible range (Si: $E_g \sim 1.1$ eV, TiO₂: $E_g \sim 3.2$ eV, *vis.* light: $E > 1.6$ eV), which can be preferred as one of the candidates for further research. Some studies in amplitude and phase modulation have been reported in TiO₂ metasurface and show capability of highly efficient light modulation within *vis.* range [136, 137]. To develop an effective metasurface for *vis.* light modulation, it would be challengeable to fabricate the antennas of small sizes for the short wavelength. Here, we will fabricate the metasurface and carry out the following discussion based on the TiO₂ nano cylinder atoms.

In this section, the optical response of TiO₂ nano cylinders based metasurface will be studied in numerical simulation and experiments. The optical response, including the transmittance and phase shift to the nano antennas' geometry and incident polarization will be thoroughly discussed to show the relations of electro-magnetic resonance within the nano cylinder atoms. Electric and magnetic dipole resonance evolution will be decomposed along nanoantennas' periods for interpretation of the light output. Besides, based on the optimized window, the TiO₂ nano cylinders based metasurface will be fabricated, measured and compared with the numerical analysis to verify the optical performance. Finally, the optical response depending on the variation of optical

environment will be also discussed for exploration of the possibility of tunable optics based on metasurface.

4.2 Numerical design of TiO₂ metasurface

4.2.1 Numerical setup for calculation

The optical response of TiO₂ nano cylinders metasurface was numerically analyzed beforehand by finite-difference time-domain (FDTD) method of Lumerical Inc.. The setup of simulation model was sketched in Figure 4.1 captured from the FDTD software interface. One single unit-cell contains a disk of TiO₂ with a periodic boundary for calculation. The periodic pitch was set $P=360$ nm in both the x and y directions to simulate the layout of the antennas' array for the excitation of the resonance within the visible light range, and further the effective subwavelength tailoring of light. The parameters of the TiO₂ cylinders were set variously in the height (H) and radius (R). The refractive index of TiO₂ was given beforehand by actual sample ellipsometry measurement and loaded into the materials' database. A 1.1 mm soda lime glass substrate with a ITO surface layer about 23 nm was attached below the TiO₂ nano disk, which

Figure 4.1 The model of numerical calculation for FDTD simulation

Figure 4.2 The transmittance and reflectance spectra of TiO₂ nano cylinder ($P = 360$ nm, $R = 160$ nm and $H = 188$ nm) for $\varphi = 0^\circ$, 45° and 90° incidences. The value of the plot represents the percentage of the output intensities normalized to the incidence.

strictly respects the actual measured thickness of the commercial product. The monitors are set $3.5 \mu\text{m}$ to the metasurface to approximate the far-field situation. The cut-off point was set $1/1000$, and a tiny mesh resolution as small as 2 nm was applied for the calculating areas aiming to obtain a precise simulation result.

4.2.2 Numerical optical performance of TiO₂ based on nano disk atoms

First, the transmittance (T) and reflectance (R) of the TiO₂ nano disks were simulated under the incidence with $\varphi = 0^\circ$, 45° and 90° polarizations (see Figure 4.2). For example, the geometry of the nano disks was set with the radius $R=160$ nm and height $H=188$ nm. It shows the spectral resonances located at $\lambda \sim 620$ nm and $\lambda \sim 640$ nm for either the transmission or reflection. At the resonance positions, the transmission reduces to the minima almost close to 0% , while the reflection was maximized to above 80% . The large transmission about 80% indicates the high efficiency of TiO₂ metasurface modulation for *vis.* range. A small amount about 10% of the output efficiency difference at the resonances ($100\% - T - R$) accounts for the absorption of the metasurface. For $\varphi = 0^\circ$, 45° and 90° incident polarizations, either the transmittance or reflectance spectra are almost well

Figure 4.3 The electric and magnetic dipole resonances detection for the $\varphi = 0^\circ$, 45° and 90° incidences: (a) the spectra of electric and magnetic resonant dipole; (b) electric dipole resonance along the x and y directions; (c) magnetic dipole resonance along the x and y directions. The values of the plots represent the excitation magnitude of the dipoles' amplitude normalized to the incidence field.

overlapped. It can be attributed to the symmetric structure of the TiO_2 nano disks. Then, the decomposed electric and magnetic dipole resonances of the excitation are figured out according to a point-monitor set in the center of the nano disk for illustration of the evolution of the resonances. As given in Figure 4.3a, the peak position at $\lambda \sim 620$ nm is for the electric resonance, while the peak at $\lambda \sim 640$ nm is for the magnetic resonance. The spectral curves for either electric or magnetic modes show an almost overlapping for variant incident polarizations. The resonant excitation can be regarded as the enhancement of the output components over the original input. Therefore, to obtain the excitation strength of both the electric (E) and magnetic (M) modes, the amplitudes for both E and M have been normalized by the non-resonant incident intensity: ~ 1 for the electric field and $\sim 5 \times 10^{-4}$ for the non-resonant incident magnetic field. The magnetic intensity shows a much smaller value than the electrical field, showing a comparatively weak secondary effect from the electric dipole excitation. After the normalization process, as shown in Figure 4.3a, the electric and magnetic excitation magnitudes are close, showing a comparable resonant effect along the two directions. As given in Figure 4.3b, for the dipole resonances excitation along x and y directions,

an anisotropic performance can be observed. Normally, the resonances are excited along the periodicity of the nano structures. For the $\varphi = 0^\circ$ incidence, almost all the electrical dipole resonance lies along the x -direction (E_x), while only negligible amount lies along the y -direction (E_y), showing a major distribution of electrical excitation along the incident polarization. When the incident polarization rotated from $\varphi = 0^\circ$ to 90° , the electrical components along the y -direction generally boost up, while the x -directional components ebb away. For the $\varphi = 45^\circ$ incidence, the electrical components along the x and y -directional periods are nearly equal. The spectral curves are almost well overlapped for both the x and y directional components as given in Figure 4.3b. As the secondary effect of electrical excitation, the magnetic resonant excitations will happen perpendicularly to the electrical components. For $\varphi = 0^\circ$ incidence, the magnetic dipole resonance majorly lies along the y -direction. For $\varphi = 45^\circ$ incidence, the H_x and H_y curves are almost overlapped. For confirmation, incident polarizations from 0 to 180° were applied to the same structure ($P=360$ nm, $R=160$ nm and $H=188$ nm) for calculation (see Figure 4.4). The resonance positions are almost not shifted in spite of the incident polarizations,

Figure 4.4 (a) Transmittance, (b) Electric and (c) magnetic dipoles resonances of TiO_2 metasurface for various incident polarizations from $\varphi = 0^\circ$ to 180° . The value in (a) represents the percentage of transmittance normalized to the incident intensity and value in (b) and (c) represents the excitation magnitude of the dipoles' amplitude normalized to the incidence field.

Figure 4.5 The electric (E) and magnetic (H) field distribution (top view) for incident polarization of $\varphi = 0^\circ$, 45° and 90° . The radius of the cylinder is set $R = 160$ nm. The value of the plots represents the dipoles amplitude normalized to the incidence field.

corresponding to the symmetric geometry of the nano cylinders. indicating an equivalent effect of the electrical excitation along the x and y -directional periodicities. To be noted, even for different incident polarizations, the resonance position of the dipole components almost not shifts, either along the x or y directions. The electrical dipole resonance lies at $\lambda \sim 620$ nm (Figure 4.4b) and the magnetic dipole resonance lies at $\lambda \sim 640$ nm (Figure 4.4c). The electrical dipole magnitude is defined as the quadratic sum of each component along the axes' coordinates: $|E| = \sqrt{E_x^2 + E_y^2 + E_z^2} \approx \sqrt{E_x^2 + E_y^2}$, in which the normal excitation is negligible ($E_z \approx 0$). Combined with the results above, the intensity and spectral position of the electric or magnetic dipole resonances are not changed for different incident polarizations. As shown by the top view field distribution of the nano cylinder (see Figure 4.5), the electric fields distribute along the directions of incident polarizations within the area of the nano cylinder, while a perpendicular direction for the magnetic fields. The overlapped spectral positions of the x and y -axis directional components may correspond to the similar periodicity of nano structures along the two directions.

In Figure 4.6a and b, when the height of the nano disks varies from 185 to 200 nm, the electric dipole resonances only slightly red-shift from $\lambda \sim 620$ nm to $\lambda \sim 625$ nm in spectra, while the magnetic dipole resonances red-shift faster from $\lambda \sim 630$ nm to $\lambda \sim 650$ nm. By comparing the amplitude of the dipole components,

Figure 4.6 (a) Transmittance, (b) reflectance, (c) E_x , (d) E_y , (e) H_x and (f) H_y of the TiO₂ metasurface for various nano disk height from 185 to 200 nm for $\varphi = 0^\circ$ incident polarization. The radius of the nano disks was set 160 nm. The value in (a) and (b) represents the percentage of transmittance and reflectance normalized to the incident intensity and value in (c) to (f) represents the excitation magnitude of the dipoles' amplitude normalized to the incidence field.

the electric dipoles are majorly distributed along the x -direction due to the $\varphi = 0^\circ$ polarization, and accordingly to receive a y -direction magnetic dipole distribution.

Then, spectral response evolution of the TiO₂ metasurface with the radius parameters was analyzed as given in Figure 4.7. For T and R spectra (see Figure 4.7a and d), when the radius increases from 146 to 164 nm, the electrical resonances red-shift from $\lambda \sim 680$ nm to $\lambda \sim 630$ nm, showing a faster shift than the magnetic resonance from $\lambda \sim 625$ nm to $\lambda \sim 650$ nm. The electric dipole shows a more sensitive response to the changes of the in-plane diameters. Details of the relations between the geometry and the E and H resonances will be discussed in the Section 4.5 of this chapter.

As introduced in Chapter 2, the TiO₂ based metasurface show capability of high efficient phase modulation. Here, the phase shift response was calculated based on the TiO₂ nano cylinders design and compared together with the transmittance spectra to verify the relations between resonance excitation within the atoms and optical response. Normally, up to 1π phase shift is obtainable

Figure 4.7 (a) Transmittance, (b) reflectance, (c) E_x , (d) E_y , (e) H_x and (f) H_y of the TiO_2 metasurface for various nano disk radius from 146 to 164 nm for $\varphi = 0^\circ$ incident polarization. The height of the nano disks was set 188 nm. The value in (a) and (b) represents the percentage of transmittance and reflectance normalized to the incident intensity and value in (c) to (f) represents the excitation magnitude of the dipoles' amplitude normalized to the incidence field.

Figure 4.8 Simulated results of the transmittance spectra (red curve) for the TiO_2 nano disk with geometry parameters: array pitch of 360 nm, radius of 160 nm, disk height of 188 nm for $\varphi = 0^\circ$ incident polarization, together with the corresponding 1.5π phase shift response (blue curve) with two steps located at the resonances of $\lambda \sim 620$ nm and $\lambda \sim 640$ nm in spectra.

for the single direction's mode. To better distinguish the distribution of electric and magnetic dipole resonance, we chose the geometry: $P = 360$ nm, $H = 188$ nm and $R = 160$ nm, which is out of the window of Huygens' condition, for study. As given in Figure 4.8, the transmittance and phase shift were compared across the resonant spectra for $\varphi = 0^\circ$ incident polarization. The phase response was leveled-up by unwrapping and subtracting the LC background signal and shows two-step phase shift about 1.5π . The shift steps are aligned in spectra with the transmittance resonances at $\lambda \sim 620$ nm and $\lambda \sim 640$ nm, which corresponds to the phase jumping due to the electro-magnetic excitation across the subwavelength topology. The strength of phase shift for each resonance mode is almost comparable, which on the other way confirms the close magnitude between the electric and magnetic excitations.

The Figure 4.9 shows the near-field distribution of the electric and magnetic dipole resonances. For the resonance at $\lambda \sim 640$ nm, the electric field excites normalized to the incoming plane wave values. The sketch at the right illustrates the setup of xy , yz plane for field distribution monitoring along the incident

Figure 4.9 Near-field maps of the (a) top view (xy plane) and (b) side view (yz plane) of the nano disk array with the optimized geometry ($P=360$ nm, $R=160$ nm and $H=184$ nm) for the wavelength $\lambda \sim 640$ nm, showing a perpendicular electric (blue arrays) and magnetic field (yellow arrays) distribution in the plane. The value of the plots (a) and (b) represents the dipoles amplitude normalized to the incidence field.

Figure 4.10 The simulated data of phase change response for the range of (a) H and (b) R parameters. The black dash lines indicate the evolution of the dipoles' resonances with the variance.

polarization direction near the surface area of the atom. The magnetic field aligns perpendicularly to the electric field at the center of the cylinder.

The phase shift response depending on the variation of H and R was given in Figure 4.10. A two-step phase shift can be obtained with less than 1π phase change for each mode. Compared with the Figure 4.6 and 4.7 results, the positions of phase shift coincide with the resonance evolution for both the electric and magnetic dipole resonances. Therefore, the phase shift response is adjustable via the design of the nano antennas' geometries.

4.3 Experiments

4.3.1 Fabrication of TiO₂ based metasurface

The TiO₂ nano disks metasurface was fabricated on the TiO₂ films deposited on the commercially available ITO-coated soda lime glass using the standard nanofabrication techniques, which is patterned by electron-beam lithography (EBL, Elionix ELS-7000) followed by inductively-coupled plasma reactive ionetching (ICP-RIE). The ITO thickness was measured $t \approx 20$ nm. The amorphous TiO₂ layer was deposited on the surface of ITO glass by the ion assisted deposition system (Oxford Optofab 3000). For etching process, a thin layer chromium (thickness $t \approx 30$ nm) and the polymethyl methacrylate (PMMA) e-beam resist films were sequentially deposited on top of the TiO₂ films to work as the mask layer for EBL. The nano disks were etched using a reactive ion

Figure 4.11 (a) Side view of the SEM capture of the TiO_2 nano disks fabricated; Top view of the (b) 130, (c) 140, (d) 150 and (e) 160 nm radius nano disks etched under the 0.84 exposure dosage.

etching process (ICP-Fluorine, Oxford OIPT Plasmalab System 100) followed by cleaning with the oxygen plasma and dipped in an etchant solvent to remove the remaining PMMA and Cr resist. The microstructure of the pattern was checked later by the scanning electron microscope (SEM, Hitachi SU8000).

The TiO_2 nano disk arrays have a size of $50 \times 50 \mu\text{m}^2$. The nano disks were arranged in a square periodic lattice with a pitch of $P=360 \text{ nm}$. As given in Figure 4.11a, the almost perfect patterning of nano disks was received according to the SEM observation. To be noted, for larger diameters, the edges of the cylinders were incompletely etched due to the limited spacers between disks (see Figure 4.11b to e). The exposure dosage is a key factor for etching results. As shown in Figure 4.12, the array fabricated under the 0.84 exposure dosage during EBL process is observed and captured via the optical microscope. For 160 nm array, an obvious over etched area is observed in the center, which, as referred to the

Figure 4.12 Capture of arrays fabricated under 0.84 exposure dosage for atoms with designed radius of 160, 150 and 140 nm captured by optical microscope

Table 4.1 measured radius of the TiO₂ nano disks fabricated under different exposure dosages from 1.0 to 0.8 (Radii unit: nm)

	1.0	0.96	0.92	0.88	0.84	0.8
120 (nm)	131.5	128.8	125.7	124.2	122.6	121.2
130 (nm)	142.2	139.2	137.5	137.5	133.6	131.5
140 (nm)	151.8	148.3	147.4	147.2	144.2	142.5
150 (nm)	NA	NA	NA	NA	156.4	155.2
160 (nm)	NA	NA	NA	NA	NA	NA

Table 4.1, corresponds to an unrecognized atom geometry due to the over-dose issue. Here we used PMMA as the positive resist to form the mask for patterning. For high dosage exposure, the mask will be more etched thus lead to a wider scale of the antennas. As given in Table 4.1, the radii of the cylinders are still larger than designed requirement even for 0.8 dose. For smaller exposure dosages, the radius patterned will decrease. For the following fabrication, the sample is patterned with an even smaller dosage (0.74) for a better control of the geometry.

4.3.2 Measurement methods

Optical transmission and reflection spectra of the fabricated sample were characterized using a customized micro-spectrometry setup described in detail elsewhere [93]. The measurement setup is given in Figure 4.13a, combined with the microscope (Nikon Ti-U), CCD camera and the spectrometer (Andor SR-303i). The sample was illuminated using a halogen lamp, focused through a 5x dark-field objective lens with a numerical aperture NA=0.15 and thus closely mimicking normal incidence conditions, with a linear polarization state adjustable using a rotatable wire-grid polarizer. The transmission was then directed into the spectrometer with a 400×1600 pixels EMCCD detector (Andor Newton).

The phase shift measurement setup was established based on the typical Mach-Zehnder interference optical path (see Figure 4.13b). The schematic diagram is plotted in Figure 4.14. The metasurface sample was inserted in one of the collimated beams split by the beam splitter (BS) cubic. During measurement,

Figure 4.13 Measurement setup for the spectral and phase signal detection. The spectrometer consists of the microscope, spectrometer detector and CCD camera.

a spectral tunable laser light source ($\lambda \sim 550\text{-}700\text{ nm}$) with a spectral resolution of 0.5 nm was applied, and the interference output was captured by the 12-bit high resolution CCD camera. Schwider-Hariharan Five Steps Measurement method was applied for the calculation of the phase shift data. A motor nano-stage is used for a continuous 5-steps movement of adjustable mirror.

There have been kinds of phase-measuring algorithms reported [138], like the 3-bucket, 4-bucket, average 3&3 and 5-bucket *etc.* Here, we adopted the five step 5-bucket algorithms which offers advantages in reduced sensitivity to phase

Figure 4.14 Sketch of phase measurement optical setup (left) and logical chart for phase calculation based on the 5-frame algorithm phase-shift method (right). The 5 steps intensities were obtained via the movement of the mirror on the piezo nano stage.

Figure 4.15 The calculated (a) unwrapped and (b) wrapped phase map of TiO₂ nano cylinders array (the square inside the map) by five-step algorithm program

shifter calibration [139]. The program was coded by Python 2.7. For the five-step phase shift algorithm, the fringe images were captured by CCD for 5 times with a continuous phase step of $\pi/2$ (namely $632.8/4 = 158.2$ nm). The five frames used in the algorithms can be expressed by the intensity as: $I_i = I_0(1 + V \cos(\phi + n\beta))$, ($i=1, 2 \dots 5$, and $n = 1, 2 \dots 5$) where β is the phase step between the successive frames. Then the phase angle can be obtained by:

Figure 4.16 Comparison of calculated ($P=360$ nm, $R=160$ nm and $H=188$ nm) (black curve) and measured (red and blue curves) transmittance spectra of the TiO₂ nanodisks metasurface before the LC infiltration. The inset gives the scanning electron microscope (SEM) image of the fabricated TiO₂ metasurface.

$$\phi = \tan^{-1} \left\{ \frac{2(I_2 - I_4)}{2I_3 - I_5 - I_1} \right\} \quad (1)$$

Some example of the captured and calculated phase map before and after the unwrapping process are shown in Figure 4.15.

4.3.3 Optical performance of TiO₂ based metasurface

The transmittance was obtained by normalizing the transmission signal intensity to that of the light source. For the measured results as shown in Figure 4.16, two resonance dips can be clearly seen at $\lambda \approx 620$ nm and $\lambda \approx 640$ nm corresponding, respectively, to the electric dipole and magnetic dipole resonances supported by the nano disks in the metasurface. Good correspondence is found with numerical simulations performed using a Finite-Difference Time-Domain commercial software (Lumerical FDTD) with the diameter $D=320$ nm and height $H=188$ nm in the periodicity $P=360$ nm, almost close to the designed geometry of the layout. These resonance positions are almost identical even when the incident polarization is rotated by 45° , as shown in the graph, due to the symmetry in the metasurface.

Then, for study of the optical response of periodic layout, a sample based on the process above with the antennas' periodicity arranged along 0° and 45° was fabricated. The antennas were designed as the cylinder with the radius varies in the range from 140 to 160 nm as given in Figure 4.17. The transmittance was measured under $\varphi = 0^\circ$ incident polarization and calculated by normalizing the incident light source. Compared with the numerical results, the resonances here measured red-shift with the increased diameters. The left resonance peak, can be expected from the electric mode, moves faster than the right one. Despite the changes of the radii, the curves for both the 0° and 45° arrays are almost overlapped, confirms a symmetric fabrication of the periodicity of the nano cylinders. Besides, the transmittance at the non-resonant areas can be as high as above 80 %. The peak depth at the resonance can be larger than 60 % between 80 % and 20 %. This shows an efficient modulation of the TiO₂ materials.

The phase shift performance of the TiO₂ was tested by the setup introduced in Section 4.3.2 for $\varphi = 0^\circ$ incident polarizations. The high resolution for the laser wavelength variation and the data capture ensure the reliability of the response.

Figure 4.17 Transmittance spectra of TiO_2 nano disk ($P=360$ nm and $H=188$ nm) metasurface with the radius varies in the range from 140 to 160 nm for both the 0° (blue curves) and 45° (red curves) array layout measured by $\varphi = 0^\circ$ incident polarization. The value of the curves represents the percentage of the transmission intensity normalized to the incidence.

The 632.8 nm laser beam was illuminated into the TiO_2 nano antennas first before penetration into the attached ITO glass substrate. The phase shift response of both the 0° and 45° layout sample was measured and subtracted by the background signal. As shown in Figure 4.18, the curves for both layouts are almost well overlapped, confirming the consistent optical response due to the symmetric periodicity of the samples. It can be found, for each step of the phase shift, a magnificent about 0.5 to 1π can be obtained, which confirms the results as simulated in the numerical analysis section.

Figure 4.18 Phase shift spectra of TiO₂ nano disk ($P=360$ nm and $H=188$ nm) metasurface with the radius varies in the range from 140 to 160 nm for both the 0° (blue curves) and 45° (red curves) array layout for $\varphi = 0^\circ$ incident polarization. The value of the curves represents the unwrapped phase shift data.

4.4 Discussion

Due to a large refractive index of TiO₂ ($n \sim 2.6$), an obvious excitation can be obtained for the magnetic dipole. Here, as shown in Figure 4.2 (simulation) and Figure 4.16 (measurement), comparable magnitude of electric and magnetic dipole is excited in the TiO₂ based metasurface, which make it possible for the efficient optical modulation. According to the dependence of the geometric on resonance evolution (see the Figure 4.5 and 4.6), the magnetic dipole resonance is more significantly influenced by the height of the resonators. When the

polarized light is illuminated onto the resonators, the displacement current would be easily excited on the surface (see Figure 4.4). The magnetic dipoles are normally excited at the center of the resonators by the circular displacement current of electrical excitations. For the radius variation, the electric dipole resonance moves faster in spectra, revealing a sensitive response. As introduced in Chapter 2, the electric polariton P is related to the surface scale, or the diameter of the nano disks. The magnetic excitation $\mathbf{m}$ is excited at the center of the antennas perpendicularly to the electric dipole $\mathbf{p}$ by the antiparallel electric displacement current near the opposite surface of the nano particles as $\mathbf{m}_j = \omega/(2i) \cdot (\mathbf{r}_j - \mathbf{r}_0) \times \mathbf{p}_j$ [51, 94], which would be dramatically influenced by the comparative distance between the electric and magnetic modes, *i.e.* the parameters of the height. Due to the symmetric structure of the cylinders, the optical response of the pure TiO₂ nano cylinders metasurface is in-plane homogeneous. The phase shift is aligned in position of spectra with the resonant excitations since the phase jump is produced by the excitation along certain resonance. The phase shift response also follows the resonance evolution depending on the geometry. Therefore, the window for appropriate phase shift performance can be obtained with an optimized design of the nano cylinders' parameters.

Normally, the optical response of the tiny metasurface atoms can be tuned by either change the geometry as mentioned above, or adjustment of the refractive index of the environment. The electric field excitation by the incidence are more often considered to happen at the surface of the nano disks with a polarizability as $\alpha_E = i \frac{6\pi\epsilon_0\epsilon_d}{k_d^3} a_1$ while the magnetic mode is excited inside the nano structures with the polarizability as $\alpha_M = i \frac{6\pi}{k_d^3} b_1$ [52, 94]. a_1 and b_1 are coefficients of the expansion on the scattered field in the vector spherical harmonics, which may influence the spectral position via the change of optical environment. (k_d is the complex wave number in the surrounding environment)

In Figure 4.19, the transmittance spectra of TiO₂ nano cylinder metasurface with homogenous environment are shown and compared with the phase data accordingly. By increasing the ambient refractive index from 1 to 2, the resonance peaks red-shift due to the reduced contrast of refractive index between

Figure 4.19 (a) Transmittance and phase shift response of TiO_2 nano disk metasurface with ambient refractive index ranging from 1.0 to 2.2; (b) the decomposition of electric and magnetic dipole response of the metasurface with ambient refractive index ranging from 1.2 to 2.2. The label of the dipole resonances map represents the intensity of the resonance.

the nano cylinder and the environment, thus leading to a decreased excitation across the nano antennas. To be noted, the magnetic dipole magnitude is reduced with an increased refractive index. When the ambient refractive index is higher than 2 and becomes comparable with the index of TiO_2 , the resonance almost disappeared while the interferential performance becomes more and more significant. For these cases, the surface is generally becoming a homogenous layer. Based on these results, the metasurface can be tuned with an adjustable environment around the antennas. The idea of the metasurface in contact with a tunable optical material will be an effective way for development of the tunable metasurface devices. Details will be discussed in the next several chapters.

4.5 Summary

In this chapter, the optical response of metasurface of TiO_2 nano cylinders is discussed in numerical calculation and experiments. The light output was numerically analyzed by Lumerical FDTD method for variation of nano cylinder

geometry and incidence polarization within a periodic lattice of 360 nm. The electric and magnetic dipole resonances are excited in transmission and reflection spectra at $\lambda \sim 620$ nm (E) and $\lambda \sim 640$ nm (H) for nano cylinder with height of 188 nm and radius of 160 nm. Due to the symmetric nano antennas' structure, the spectral curves almost overlapped for transmittance, reflectance, E and H dipole responses in spite of the incidence polarizations from 0 to 180°. The resonances can be excited only along the periodicity along the x and y directions, and the components vary with the rotation of incidence polarizations. The electric dipole distributes along the incidence polarization direction at the surface of the antennas while the magnetic dipole was consequently excited along a perpendicular direction at the center of the nano cylinder. The magnetic dipole resonance shows a sensitive response to the variation of the nano cylinders' height, while the electric dipole resonance shifts more significantly to the changes of nano cylinders' radius. Phase shift close to 1π can be excited by either the electric or magnetic dipole resonances and shift accordingly in spectra with the geometric variation, which almost well corresponds to the transmission (reflection) spectra.

The TiO₂ metasurface of nano cylinders was fabricated with the standard nano fabrication process. Size of nano antennas geometry fluctuates within a small range due to the inhomogeneity of exposure dosage. The resonances were excited at $\lambda \sim 620$ nm and $\lambda \sim 640$ nm, which corresponds to a geometric size of periodic pitch $P=360$ nm, height $H=188$ nm, radius $R=160$ nm. Phase control close to 1π was received for each resonance mode. The experimental results of both the transmission output and phase control closely corresponds to the numerical simulation, confirming a correct design of the optical response.

The electric and magnetic dipole resonances can be in spectra with a variation of environment refractive indices. The resonances almost disappear when environment refractive index gets close to the index of TiO₂ of 2.6. For increased refractive within a short range from 1 to 2, the resonances red shift from around 600 nm to 730 nm, which can be attributed to the reduced contrast of refractive index between TiO₂ and the environment. Thus, the tunable metasurface and optical response can be inspired by actively controlling the optical environment of the devices.

Chapter 5: Optical performance of thin layer nematic LC infiltrated TiO₂ nano disks metasurface

5.1 Introduction

In Chapter 4, the TiO₂ cylinders based metasurface is successfully designed and fabricated with strong excitation of electric and magnetic dipole resonances and phase change, which shows potential for further development of the metasurface based high efficient spatial light modulation devices. Traditionally, the pure LC spatial light modulator calls for LC layers with the thickness no less than $\lambda/\Delta n$, namely the effective optical distance difference equivalent to the unit wavelength, for the complete control either of the amplitude or phase due to the full accumulation through the effective optical distance. However, consider the large resistivity of liquid crystal about $10^{10} \sim 10^{12} \Omega/\text{cm}$, high voltages above 40 V would be needed to saturate the thick layer LC switching with nano structure areas [65, 114, 115]. Similar optical performance can be retained with LC thickness dramatically reduced when the metasurface is introduced into the device with enhancement effect, which could bring advantages like the lower driving voltages together with the smaller aspect ratio for pixilation during the packing process to abate the crosstalk. People found that the microstructures on the surface will influence the LC alignment in vicinity, which can be called as the surface anchoring effect, thus the LC would deviate from the preset alignment direction defined by rubbing or photoalignment. For most of the LC based metasurfaces reported so far, they are designed for the lower frequency ranges like THz and microwave, and the LC layers is thicker than 5 μm [4, 64, 108]. That could be much larger than the extension distance of the anchoring effect by surface structures, and only weakly influences the optical performance of the device. For the higher frequency ranges like the visible light, there is no need of thicker LC layers, which would be advantageous to improve the device performance in optical modulation [116], and the reduction of LC pixel sizes and power consumption [118, 140]. However, performance of the LC based tunable all dielectric metasurface for visible light modulation would be challengeable considering the complicated fabrication process and strong anchoring effect,

which brings less reliability of the output response. In this chapter, the passive optical response of TiO_2 nanodisk metasurface after LC infiltration will be systematically discussed, including the numerical design, fabrication and optical measurement. A refined model of LC alignment will be proposed for better simulation of the situation of LC infiltrated metasurface.

5.2 Numerical analysis of LC based TiO_2 metasurface

5.2.1 Numerical analysis of optical response of TiO_2 metasurface with liquid crystal for perfect alignment

Numerical study was carried out based on the results of the Lumerical finite-difference time-domain (FDTD) simulation. Simulation model was adopted referring to the Figure 4.1 in Chapter 4 with the TiO_2 nanoantennas infiltrated with a layer of commercial E7 LC product, which is initially set parallel to the x -axis along the TiO_2 nano cylinders' periodicity, *i.e.* an azimuth angle $\varphi = 0^\circ$.

Figure 5.1 Sketch of electrically tunable transmission type TiO_2 metasurface with LC infiltration sandwiched by ITO-coated glass substrates. The LC, in the absence of any applied voltage, is aligned by the photoalignment layer defined as x -axis coated onto the top ITO glass surface (the photoalignment direction is given by the white arrow). LC alignment near the nanostructures can be altered by its presence influenced by both the photoalignment layer and the anchoring effect of nanostructures.

Considering the variant dispersive relation below 800 nm [141], the list of LC refractive index' data sheet referred from Merck companyy was input to the simulation model. The 1.1 mm soda lime glass substrates with a 23 nm ITO layer on the surface were also included to mimic the real structure of fabricated devices. In the simulation model, the TiO₂ nano cylinder unit was built with an in-plane periodic boundary in the lattice size $P=360$ nm. LC anisotropy axis was set parallel to the metasurface, *i.e.* a zenith angle $\theta = 90^\circ$, representing the case before applying the voltages, namely the OFF state, while $\theta = 0^\circ$ for the case when being switched ON. The sketch of the transmission type cell is given in Figure 5.1.

Normally, the resonance is excited in the nanoantennas. Here, to clearly observe the evolution of the dipole resonances, we first chose the nano cylinder units based on the fabricated geometry in Chapter 4 for analysis: period 360 nm, height 188 nm and radius 160 nm. Then, TiO₂ nano-disks metasurface simulation model was setup with a 1.5 μm LC layer with LC set along the x -axis ($\varphi = 0^\circ$) for

Figure 5.2 (a) Numerically calculated transmission spectra of LC infiltrated TiO₂ metasurface for nano-disks' height ranging from 180 to 204 nm, with a fixed radius of 160 nm. The dashed lines indicate the evolution of electric and magnetic dipole resonances. (b) The resonance amplitude of both electric (E) and magnetic (H) dipoles. The value in (a) represents the percentage of transmittance normalized to the incident intensity and value in (b) represents the excitation magnitude of the dipoles' amplitude normalized to the incidence field.

different nano-disks' height ranging from 180 to 204 nm. The calculated transmittance and dipole resonances spectra are given in Figure 5.2. Compared from transmittance in Figure 4.5, both the electric and magnetic resonances red-shift after the LC infiltration. This is due to the increased refractive index of LC. As given in Figure 4.19, the resonances red-shift in the increased refractive index of the environment and thus the decreased refractive index contrast with the TiO_2 ($n \sim 2.6$). Similar to the pure TiO_2 metasurface before infiltration, the magnetic resonances shift faster than the electric resonance with the variation of the nanoantenna's height due to the change of surface displacement electric current with the magnetic excitation at the center of the disks. When the height of the nano disks varies from 180 to 204 nm, the electric resonances shift from $\lambda \approx 692$ nm to $\lambda \approx 698$ nm, while the magnetic resonances shift from $\lambda \approx 686$ nm to $\lambda \approx 700$ nm, for which the tuning range is only slightly expanded than in the ambient environment. To be noted, after the LC infiltration, *e.g.* the $H = 185$ nm, the electric resonance moves from $\lambda \approx 620$ nm to $\lambda \approx 692$ nm while the magnetic

Figure 5.3 (a) Numerically calculated transmission spectra of LC infiltrated TiO_2 metasurface for nano-disks' radii ranging from 140 to 170 nm, with a fixed height of 188 nm. The dashed lines indicate the evolution of electric and magnetic dipole resonances. (b) The resonance amplitude of both electric (E) and magnetic (H) dipoles. The value in (a) represents the percentage of transmittance normalized to the incident intensity and value in (b) represents the excitation magnitude of the dipoles' amplitude normalized to the incidence field.

resonance moves in a narrower range from $\lambda \approx 640$ nm to $\lambda \approx 686$ nm. As introduced in Section 2.2.3 of Chapter 2, compared with the magnetic dipole, the electric dipole shows sensitive response to the refractive index which shows a significant sensitivity to the optical environment. Then we fixed the height $H = 188$ nm and adjust the radii of nano disks from 140 to 170 nm. The calculated transmittance and dipole resonances spectra for $\varphi = 0^\circ$ polarization incidence are given in Figure 5.3. For the radius increased from 140 to 170 nm, the electric resonance shifts from $\lambda \approx 668$ nm to $\lambda \approx 705$ nm, while the magnetic resonance shifts with a narrower range from $\lambda \approx 668$ nm to $\lambda \approx 695$ nm, which corresponds to the electric field distribution depending on the in-plane ranges. The electric and magnetic excitations are obtained by normalizing the output fields with the non-resonant incident field as done in Chapter 4. As given in Figure 5.2b and 5.3b, the excitation amplitude for both electric and magnetic components are

Figure 5.4 Numerically calculated transmission spectra of LC infiltrated TiO_2 metasurface (Periodicity 360 nm, Height 188 nm, Radius 160 nm) for the $\varphi = 0^\circ$, 45° and 90° polarized incidence. The LC is set aligned along with the $\varphi = 0^\circ$ parallel to x -axis direction.

comparable, which provides the possibility to obtain the high efficient modulation performance across the Huygens' condition. As seen in Figure 5.2a and 5.3a, the E and M modes get close in spectra within the window of: $H = 188$ to 200 nm, $R = 160$ nm, or $H = 188$ nm, $R = 140$ to 160 nm, leading to visually single dip in spectra within the resolution of the peak width. Higher transmittance above 25% is obtained for geometry of $H = 196$ nm and $R = 160$ nm, while only 0% transmittance is obtained for the other parameters, indicating a better aligned overlapping of the electric and magnetic resonances in spectra.

The LC was set along the x -axis direction, which lead to an in-plane anisotropy of refractive index, or the permittivity along the x and y -axis periodicities, which would influence the optical response for various in-plane polarized lights. Here, we chose $H = 188$ nm and $R = 160$ nm as the nano cylinders' geometry based on the parameters of the fabricated sample mentioned in Chapter 4. An optical anisotropy is defined by the extraordinary $n_x = n_e$ and

Figure 5.5 (a) Numerically calculated evolution of electric and magnetic dipole excitation under incidence from $\varphi = 0^\circ$ to 90° ; (b) Evolution of electric dipole components along x and y directions. The value of the plot in (a) and (c) represents the excitation magnitude of the dipoles' amplitude normalized to the incidence field.

ordinary $n_y = n_z = n_o$ refractive indices for the $\varphi = 0^\circ$ LC alignment along the x -axis direction. Transmittance spectra of the array calculated for in-plane incident light polarization parallel to $\varphi = 0^\circ$, $\varphi = 45^\circ$ and $\varphi = 90^\circ$ directions are given in Figure 5.4. The evolution of the electric and magnetic dipole resonances was identified by recording the electric and magnetic fields at the center of the nanoantenna using a point monitor and analyzed as given in Figure 5.5. For the incident polarization along x -axis ($\varphi = 0^\circ$ incidence), the electric and magnetic dipole resonances are almost overlapped at $\lambda \approx 688$ nm, which explains the single dip observed in the transmission spectrum. For the incident polarization along y -axis ($\varphi = 90^\circ$ incidence), the electric resonance blue shifts to $\lambda \approx 662$ nm, while the magnetic resonance only slightly shifts to $\lambda \approx 682$ nm and thus two dips in transmission are observed. The observed blue shifts of the resonances for the orthogonal polarization can be attributed to the reduced refractive index from n_e to n_o along the polarization direction. As discussed above, the magnetic resonance shows less sensitivity to the refractive index change than the electric one. This effect is known to be related to a higher confinement of the magnetic dipole mode inside the particle [142] and thus its lower sensitivity to the optical environment. By analyzing the electric and magnetic dipole resonances separately (see Figure 5.5), one can see a co-existence of two electric dipole resonances at $\lambda \approx 662$ nm for n_o and $\lambda \approx 688$ nm for n_e during the incident polarization rotation from $\varphi = 0^\circ$ to 90° . The component ratio between the two electric dipoles depends on the rotation angle of incident polarization. To be noted, an obvious splitting of magnetic mode is also observed for incident polarization angles between $\varphi = 15^\circ$ and 75° incidence. This can be explained by the anisotropy of the LC. In polarization states having components both along the ordinary and the extraordinary axes. Two different dipolar resonances are excited with spectral positions corresponding to the different refractive indices felt in the anisotropic optical environment [42]. For the $\varphi = 45^\circ$ incidence, the excitation components along x and y -axes become nearly equivalent and, thus, the transmittance spectrum shows an obvious combination of those observed under $\varphi = 0^\circ$ and 90° incidence, further corroborating the influence of the anisotropic optical environment with respect to the two directions (see the Figures 5.5b).

5.2.2 Refined numerical analysis introducing the influence of nanoantennas' anchoring effect

In section 5.2.1, we consider the ideal situation with LC aligned along with the x -axis of the rubbing or photoalignment direction. It has been previously reported that LCs may preferentially align along a certain direction defined by the surface energy of nanostructures [59]. This, so called, anchoring effect of LC can be expected to significantly affect the LC alignment near the nanoantennas, introducing in-plane deviations in the LC alignment from the preset rubbing or photoalignment direction [4]. A refined model considering such effect would be appreciated for better interpretation of the LC alignment performance in the devices. Here, in the refined model for numerical calculation, the LC was separated into two layers: the first layer of 200 nm in vicinity of the TiO_2 nano pillars which would be almost influenced under the domination of the anchoring effect of the nanoantennas, while the second layer of the rest 1300 nm attached above to work as the pure LC layer.

Considering the combined effect of the photoalignment and nanostructure anchoring effect, we proposed two models, which we name the parallel (*pa.*) and twisted (*tw.*), to simulate the LC alignment (see Figure 5.6). Similar to the setup in Section 5.2.1, the spatial LC alignment is expressed by both the zenith (θ) and

Figure 5.6 (a) The coordinates of LC alignment with TiO_2 nano cylinder metasurface; (b) illustration of LC infiltrated TiO_2 metasurface models of (i) parallel (*pa.*) and (ii) twist (*tw.*) alignment for simulation. The in-plane angle φ defines the influence due to the surface nanoantennas' anchoring effect on the LC molecules.

Figure 5.7 Calculated transmittance percentage for the (a-c) parallel (*pa.*) and (d-f) twisted (*tw.*) model of LC alignment for incident polarization along $\varphi = 0^\circ$, $\varphi = 45^\circ$ and $\varphi = 90^\circ$ directions. The alignment angles are defined by the LC molecules orientation angles near the nanostructures from 0 to 45 degrees representing the influence of the anchoring effect. The data is given in percentage of the transmission normalized to the incident intensity.

azimuth (φ) angles which defines the refractive index of the optical environment surround the nanoantennas. The models are distinguished by the comparison of strength between the photoalignment (or rubbing in other cases) and nanostructure anchoring effect. For the *pa.* model, the LC molecules retain the same direction across the whole LC cell from the nanoantennas to the top layer. This represents the case of strong anchoring effect with a large extension distance.

For the *tw.* model, the LC continuously twists across the cell from the given direction near the nanoantennas to being fully parallel to the photo-alignment direction (x -axis) at the top layer, indicating a balanced competition between the anchoring effect by the nanoantennas and the alignment induced by the photo alignment layer. The twist LC refractive index was set based on the rotated matrix calculation model setup in FDTD. For numerical simulation, the in-plane azimuth angles (φ) of the LC alignment are continuously increased, out of the

Figure 5.8 (a) Calculated transmittance spectra of TiO₂ nano disks metasurface after LC infiltration for variation of in-plane LC alignment angles ranging from 0° to 90° with respect to the photoalignment direction (x -axis) using the parallel ($pa.$) alignment model. The incident light is polarized along the x -axis (0° pol.); (b) Electric and (c) magnetic dipole resonances and the excited electric dipole components along (e) x and (f) y directions for the incident polarization parallel to $\varphi = 0^\circ$ with LC in-plane alignment directions varied from $\varphi = 0^\circ$ to 90° to the x -axis corresponding to (a).

consideration of spatial symmetry of optical environment, from 0° to 45° to show the different levels of anchoring strength (see Figure 5.7).

In the parallel model, the anisotropic effective refractive index can be approximately expressed as $n_x = n_o + \Delta n \cdot \cos \varphi$, $n_y = n_o + \Delta n \cdot \sin \varphi$ and $n_z = n_o$ (see the definition of φ in Figure 5.6a). To be specific, the calculated transmittance of $pa.$ model for $\varphi = 0^\circ$ polarized incidence is shown in Figure 5.8 for LC alignment from 0° to 90°, together with the electric and magnetic components. Due to the spatial distribution of parallel LC alignment, the evolution of transmittance spectra for $\varphi = 0^\circ$ and 90° incident polarizations are almost symmetrical about the 45° LC alignment. As it can be seen from Figure 5.8, the electric dipole resonant response along x -axis (E_x) continuously blue-shifts with the LC alignment rotation from $\lambda \approx 688$ nm for $\varphi = 0^\circ$ to $\lambda \approx 662$ nm for $\varphi = 90^\circ$ (circle-dotted curve in Figure 5.8a). This can be explained by the continuous reduction of the refractive index along the excitation direction (x -axis) from the extraordinary, n_e , to the ordinary one, n_o . The magnetic resonance, in turn,

slightly shifts from $\lambda \approx 688$ nm for $\varphi = 0^\circ$ LC alignment to $\lambda \approx 682$ nm for $\varphi = 90^\circ$. Interestingly, when the LC alignment rotates to $\varphi > 15^\circ$, the orthogonal electric resonance mode (E_y , square dot curve in Figure 5.8a) is observed and oppositely red shifted with LC rotation. To be noted, the orthogonal component of the electric resonance appears due to the polarization rotation induced by the phase retardation associated with LC birefringence [52, 108].

For the twisted model (see Figure 5.7d-f), the effective refractive index can be approximated as the integral accumulation of birefringence of each differential LC layer. In this case, the electric resonance blue shifts with the LC alignment rotation from $\lambda \approx 686$ nm for $\varphi = 0^\circ$ to $\lambda \approx 670$ nm for $\varphi = 45^\circ$, which is a little bit narrower the range of tuning. Compared with the parallel model, the birefringence change due to LC alignment is smaller in twisted model. As the example shown for the 0° incident polarization, the E_x component of the electric dipole is more pronounced, while E_y is less evident for small LC rotation angles with respect to x -axis, which helps to differentiate between the two models. Figure 5.7 also shows these dependences for different incident polarizations rotated by 0° , 45° and 90° with respect to x -axis.

5.2.3 Numerical analysis of optical response for the rotated nanoantenna's periodicity layout

As given in Figure 4.14 in Chapter 4, the TiO_2 nano disks metasurface before LC infiltration shows an in-plane symmetric response to the incident polarization directions due to the nanoantennas' geometry and the homogenous optical environment. For LC infiltrated sample, anisotropic response would be considered when metasurface layout is contacted with the LC. As discussed in Section 5.2.1, for the $\varphi = 0^\circ$ LC alignment which is parallel to the nano antennas' array periodicity along the x -axis, the optical response to the incident polarizations shows a perfect reaction to the birefringent optical environment from n_e for $\varphi = 0^\circ$ polarization to n_o for $\varphi = 90^\circ$ polarization. When considering the layout of nano disks with $\varphi = 0^\circ$ periodicity direction, the trenches of the gap between nano disks would be along either x or y -axis directions, in general would lead to an averagely 45° anchoring to the LC near the nano structures. For comparison, we setup the $\varphi = 0^\circ$ periodic arrays and set LC aligned along 45°

Figure 5.9 Calculated transmittance spectra of LC infiltrated TiO₂ metasurface for incident polarization from $\varphi = 0^\circ$ to 180° for (a) 0° array with LC along 45° direction (x -axis) and (b) 45° array with LC along 0° direction. The value of the plots represents the percentage of the transmission normalized to the incident intensities.

with respect to the x -axis. As given in Figure 5.9a, the transmissive resonances almost stay around $\lambda \approx 650$ and $\lambda \approx 680$ nm for incident polarizations from 0° to 180° , almost follows an in-plane homogeneity of the response. To be noted, for variation of the incident polarizations, the resonance evolutions slightly distorted for both the electric (left) and magnetic (right) components (the position can be referred from Figure 5.8). Besides, A slight broaden of the resonance happens for the incidence around $\varphi = 135^\circ$ polarization, together with a slight blue shift of the magnetic resonance. Comparatively, for the $\varphi = 45^\circ$ polarization, the magnetic resonance shows a slight red-shift. Details will be further discussed in Section 5.5 in this chapter.

Later, we set another model of the $\varphi = 45^\circ$ periodic arrays and the LC aligned along 0° along the x -axis. Similar to the case in Figure 5.9a, the optical response for incident polarizations from 0° to 180° almost follows an in-plane homogeneity of the response with the resonances stay around $\lambda \approx 650$ and $\lambda \approx 680$ nm (see Figure 5.9b). But, unlike the case of $\varphi = 0^\circ$ periodic arrays with 45° LC alignment in Figure 5.9a, a slight broaden of electric resonances happens around $\varphi = 90^\circ$, together with the blue shift of the magnetic resonances. Details will be further discussed in Section 5.4 in this chapter.

5.2.4 Numerical phase modulation of TiO₂ metasurface by LC

As discussed in Chapter 4, the phase shift of the TiO₂ metasurface is produced due to the resonant scattering within the nano antennas. The significant phase shift more often happens at the resonant positions in spectra corresponding to the transmission spectra. As introduced in Section 2.2.3 of Chapter 2, 1π phase range can be covered by the excitation of resonance along one direction. In plasmonic devices, the 2π phase shift can be obtained via two independently tuned resonances within some specially designed 2D structures like the “L” or “V” shape antennas. For Mie-type scattering all dielectrics, the comparable resonances can be excited simultaneously along the perpendicular directions, thus, to obtain a 2π phase shift when the resonances are overlapped in spectra.

As shown in Figure 5.2, a higher transmittance above 25% is obtained for cylinders’ geometry of $H = 196$ nm and $R = 160$ nm. Under the condition of the spectral resolution, it can be regarded close to a situation with overlapped E and M resonances responses in spectra. For comparison, the calculated phase shift is given in Figure 5.10, with a continuous 2π phase shift across the resonance

Figure 5.10 Comparison of numerically simulated transmittance (red curve) and phase shift (blue curve) results of optimized geometry nanoantennas ($P = 360$ nm, $H = 196$ nm and $R = 160$ nm) for LC aligned along the x -axis and $\varphi = 0^\circ$ incidence polarization. The black dash line marked the resonant position for both the transmittance and phase shift in spectrum.

position around $\lambda \approx 696$ nm. The phase data is unwrapped and leveled up by the background signal (similarly processed hereinafter).

As discussed above, the resonances can be tuned by changing the geometry of the nano antennas, showing a behavior of shift in spectra. Therefore, the phase shift response can be adjusted via the design of atoms' geometry parameters either. In Figure 5.11, the phase change is calculated in TiO_2 cylinders by varying the (a) height and (b) radius of the atoms. A full period of $0 \sim 2\pi$ phase shift is obtained within the window of geometry parameters of $H = 188$ to 200 nm, $R = 160$ nm, or $H = 188$ nm, $R = 140$ to 160 nm. The parameters almost correspond to the window with nearly overlapped E and M modes in spectra. Within the window, continuous 2π phase shift can be still obtained even for those not perfectly aligned, showing a tolerance range of the phase shift response. For the geometries far from the window, similar to the transmittance spectra in Figure 5.2 and 5.3, a double-dip behavior occurs due to the deviated E and M resonances positions in spectra, with about π phase shift for each mode, corresponding to the

Figure 5.11 Numerically calculated phase shift of LC infiltrated TiO_2 metasurface for nano cylinders' (a) height from 180 to 204 nm, with a fixed radius of 160 nm, and (b) radii from 140 to 170 nm, with a fixed height of 188 nm. The dashed lines indicate the evolution of electric and magnetic dipole resonances.

Figure 5.12 Numerically calculated phase shift of LC infiltrated TiO_2 metasurface ($H = 188$, $R = 160$ nm) for incident polarizations from $\varphi = 0^\circ$ to 180° with arrays of (a) 0° periodic layout infiltrated with 45° LC and (b) 45° periodic layout infiltrated with 0° LC

independent resonance along the singer direction of either E or M mode.

For comparison, the phase shift spectra performance for the varied incident polarizations from 0° to 180° is also calculated based on the array with 0° and 45° periodic layout as the model in Figure 5.9. Similar to the transmittance spectra in Figure 5.9, the phase shift happens around the wavelength of $\lambda \approx 650$ nm $\lambda \approx 670$

Figure 5.13 Numerically calculated phase shift of LC infiltrated TiO_2 metasurface ($H = 188$, $R = 160$ nm) with a coherent in-plane LC alignment from 0° to 45° shown in (a) the stacks of phase shift spectra for 0° , 15° , 30° and 45° LC alignment and (b) the mapping of the continuous evolution for $\varphi = 0^\circ$ incident polarization.

nm for both the 0° array with 45° LC alignment and 45° array with 0° LC alignment, echoing the excitation of the resonances (see Figure 5.12). About $0.5\sim 1\pi$ phase change can be obtained for each resonance. To be noted, similar to the evolution of resonance in spectra, a slight shifting of the shift position is also observed from $\lambda \approx 675$ nm to $\lambda \approx 665$ nm with an increased in-plane polarization angle from $\varphi = 0^\circ$ to 180° for 0° array with 45° LC alignment.

The phase shift response for the parallel model (as introduced in Figure 5.7 and 5.8) with coherent LC alignment from 0° to 45° is also calculated. The results for the $\varphi = 0^\circ$ is given as the example in Figure 5.13. The position evolution of the phase shift well matches the resonance in transmittance spectra. Compared with Figure 5.8, for LC alignment direction angle $\varphi < 30^\circ$, the continuous phase shift close to 2π corresponds to the nearly overlapped electric and magnetic dipole resonances. When the LC aligns $\varphi \geq 30^\circ$, a derivative phase shift happens around $\lambda \approx 675$ nm with a reduced phase shift below 1π for each resonance. Details will be further discussed in Section 5.4 of this chapter.

5.3 Experiments

5.3.1 Fabrication process of thin layer liquid crystal based TiO_2 metasurface

For LC-metasurface sample fabrication, the TiO_2 nano disks metasurface was patterned beforehand on the soda lime ITO glass. The infiltration and

Figure 5.14 Fabrication process of LC cell for the transmissive type TiO_2 metasurface on ITO glass substrates

Figure 5.15 The equipment for LC fabrication process: (a) glass cleaning tank, (b) heater oven, (c) sealant drawer, (d) rubbing stage, (e) spacers sprayer, (f) hot-press stage, (g) vacuum LC infiltrator

packaging process of LC cells was carried out according to the standard as shown in Figure 5.14. Some of the equipment used for fabrication is given in Figure 5.15. The commercial soda lime ITO glass was cut into small pieces with 2×1.5 cm² size to work as the substrate for either the metasurface growth or alignment

Figure 5.16 (a) The CCD capture of LC background aligned with (i) & (iii) photoalignment and (ii) & (iv) rubbing alignment before and after applying voltages. The alignment direction was marked with the white arrows. (b) The micro-optical images captured by optical microscope for *aso* dye solvent coated ITO glass under (v) 3000, (vi) 4000 and (vii) 5000 rpm.

Table 5.1 Thickness and roughness of alignment layer by rubbing and photoalignment for different coating conditions

	Photoalignment (aso-dye based layer)				Rubbing alignment (polyimide)	
Coating speed (rpm)	2000	3000	4000	5000	2000	3000
Thickness (nm)	71.6	59.3	47.9	38.6	102.4	89.6
Roughness (nm)	15.3	12.4	9.8	6.9	32.4	23.5

layer coating process. Considering the tiny LC layer thickness required, the glass slices were then rinsed by ultrasound in the cleaning agent for 1 hr (see Figure 5.15a), followed by 200 °C oven-dry for 30 min (see Figure 5.15b) to prevent the residual water, grease or dust. The edge of the ITO was chemically etched to prevent the shortcut due to the residual conductive slags possibly exist at the glass substrates' edges.

Traditionally, the LC alignment in the LC cells are rubbing process, namely by rolling the velvet fabric or cloth to scratch the trenches for LC via the anchoring effect of the grooves (see Figure 5.15d). However, significant surface roughness and electricity is unavoidable and would bring serious influence especially for the thin layer LC cells (see Figure 5.16a and Table 5.1). For comparison, the photoalignment technology brings the form of quite thin and flat alignment polymer layer (see Table 5.1) with non-contacting method. The photoalignment solvent was prepared with a 1% *wt* azobenzene sulfuric dye SD1 dissolved in 2-ethoxyetanol chemical. Then the solvent was coated onto another piece of soda lime ITO glass at 5000 rpm for 30 s for a uniform surface of the film with the thickness measured being thinner than 50 nm, and then baked at 60 °C for 30 min to evaporate the residual liquid. After that, a blue light LED (460 nm) was used for 30 min illumination. According to the properties of *aso dye* base chemicals, the molecule chain prefers to align along the direction perpendicular to the incidence polarization of the blue light [143].

In the meantime, for another piece of ITO glass substrate with the TiO₂ nano disk metasurface patterned, the 1.5 μm silica sphere spacers were sprayed onto the surface by machine (see Figure 5.14e and inset of 5.16a). 0.02g spacer powders were measured by electronic balance and blown into the chamber with an electric field applied to regulate the direction of flow. To avoid the overlying of the spacer spheres on the nano antennas, a simple hand-made shelter was put to cover the array areas. Sealant glue was drawn on this piece to set the area for LC infiltration (see Figure 5.15c) and then hot-pressed at 120 $^{\circ}\text{C}$ for 40 min with another piece with spacers for curing package (see Figure 5.15f). The gap size for LC infiltration can be well retained according to the spacer's diameters. For example, for the 1.5 and 6 μm spacers, the gap size is close to the thickness we designed based on the direct cross-section scanning of SEM (see Figure 5.17a). Interference spectra were also measured to confirm the thickness: as given in Figure 5.17b, the thickness of the nominal 1, 5 and 8 μm cells can be measured and calculated as 1.12, 4.71 and 7.59 μm based on the spectral relation of interference $n \times d = \frac{1}{2} \times \frac{\lambda_1 \lambda_2}{\lambda_1 - \lambda_2}$ ($n \times d$ represents the optical distance of the resonant gap and the λ_1 and λ_2 positioned the wavelength of neighbor

Figure 5.17 (a) SEM images of the cross-section of the sealed ITO cell with 1.5 and 6 μm gaps for LC infiltration. The inset gives the image of ITO glass sprayed with 1.5 μm silica sphere spacers via the optical microscope. (b) The interference spectra of sealed ITO cell with gaps nominally of (i) 1.5, (ii) 5 and (iii) 10 μm .

interference peaks). For LC infiltration in ambient environment, the air bubble would densely exist inside the LC layer. Here, we used a vacuum chamber (see Figure 5.15g) and pumped to below 5 Pa to prevent the interfusion of the air into the LC. Then the cell gap was contacted with the commercial E7 LC liquid ®Merck and the LC can be capillary infiltrated into the cell. After infiltration, the sample was heated in oven at 80 °C (above the E7 clearing point: 58 °C) for 15 min for a uniform alignment of the LC molecules along with the top layer photoalignment (see Figure 5.16a).

Figure 5.18 Measured transmission of the fabricated LC cell. (a) Transmission of the bare LC cell without metasurface for incidence polarization varied from $\varphi = 0^\circ$ to 90° with respect to the photo-alignment direction (x -axis). The spectra are detected through a polarizer oriented perpendicular to the incident polarization. This configuration allows measuring a cross-polarized transmission induced by LC birefringence. The transmission signal is maximized for 45° and is almost zero for 0° and 90° polarization incidence indicating a well aligned LC orientation along the photo-alignment direction. (b) Captured LC cell image under 0, 0.5, 1, 2, 3 and 4 V with transmission passed through polarizers and analyzer before and after the cell set perpendicular to each other (cross-polarized light detection). The incident polarization is rotated 45° with respect to the LC photo-alignment direction (white arrow). The transmission can be almost blocked above 3 V indicating a complete switching of LC molecules to the vertical orientation (along the z -axis). (c) Transmittance percentage of the bare LC cell under electrical voltages from 0 to 8 V with the photoalignment direction 45° to the polarizer. The measurement setup is the same as in (b).

5.3.2 Optical performance of LC based TiO₂ metasurface

The LC based TiO₂ metasurface is measured by the setup as introduced in Chapter 4. The transmittance of the bare LC layer background was measured beforehand to determine the LC alignment outside the metasurface region. For that, we placed a rotatable wire-grid polarizer before the detector oriented perpendicularly to the photoalignment direction (x -axis). We analyze the transmission when the incident polarization is rotated from 0° to 90° with respect to the x -axis. The transmittance reaches the highest value, above 80%, for $\varphi = 45^\circ$ incidence, while approaches 0% for the $\varphi = 0^\circ$ and 90° incidence, indicating a well aligned photoalignment parallel to the x -axis direction (see Figure 5.18a). Then the tuning performance of the pure LC background was measured under the $\varphi = 45^\circ$ incidence with a polarizer inserted in the beam path as the analyzer

Figure 5.19 Transmittance of LC infiltrated TiO₂ nano cylinders with the designed radius varying from 120 to 160 nm fabricated with 0.8 exposure dosage. The figures show the results of 0° layout for $\varphi =$ (a) 0°, (b) 45°, (c) 90° polarizations and (d) 45° layout for $\varphi = 0^\circ$. The dash lines show the evolution of E and M resonances.

oriented at 90° with respect to the x -axis (see Figure 5.18b). Due to the thin layer of the material, the LC cell can be driven at small voltages below 1 V. Transmittance of light through the bare LC backgrounds decreases from above 80% to almost 0% when the voltage is increased above 3 V (see Figure 5.18b and c), indicating a saturation of switching of LC.

Then, the optical response of the metasurface with LC infiltration was measured under the polarized incidence. A metasurface sample was designed with periodicity along 0° and 45° with respect to the x -axis and fabricated with a nominal dosage level of 0.8 (see Table 4.1) with the radius varying from 120 to 160 nm. Transmittance of groups of LC infiltrated TiO_2 nano cylinders were measured and shown as in Figure 5.19. The measurement was carried out under incident polarizations of $\varphi = 0^\circ$, 45° and 90° . The optical environment was defined by the birefringent LC alignment. Compared with the results in Chapter 4, the resonances red-shift after LC infiltration due to the reduced refractive index contrast between the nano structure material and environment. For the 0° array layout under the $\varphi = 0^\circ$ polarization (see Figure 5.19a), the electric dipole resonance shifts faster in spectra from $\lambda \approx 630$ nm to $\lambda \approx 665$ nm while the magnetic dipole resonance only shifts from $\lambda \approx 660$ nm to $\lambda \approx 680$ nm. Interestingly, for the 0° array layout under the $\varphi = 45^\circ$ and 90° polarization, the electric dipole resonance shifts, although faster than the magnetic mode, with a same range in spectra from $\lambda \approx 630$ nm to $\lambda \approx 665$ nm. The magnetic dipole resonance shifts $\lambda \approx 660$ nm to $\lambda \approx 680$ nm. For the 45° array layout under the $\varphi = 0^\circ$ polarization, the electric dipole resonance shifts in spectra from $\lambda \approx 630$ nm to $\lambda \approx 670$ nm and the magnetic dipole resonance shifts from $\lambda \approx 660$ nm to $\lambda \approx 680$ nm, which is almost close to the performance for the 0° array layout. Details of the performance will be discussed in the following section 5.4 in this Chapter.

Then, we take the $H = 188$ nm and $R=160$ nm cylinders referring to the geometry in Figure 4.15 of Chapter 4 with the layout 0° and 45° with respect to the x -axis as the example and focus on the LC infiltrated array measured for various incidence polarizations. The transmittance of 0° array layout is given in Figure 5.20a for $\varphi = 0^\circ$, 45° and 90° polarization incidence. For $\varphi = 0^\circ$ polarized incidence, the resonances of the transmission spectrum locate at $\lambda \approx 660$ nm and $\lambda \approx 680$ nm. For $\varphi = 45^\circ$ polarized incidence, the resonances shift to $\lambda \approx 675$ nm

Figure 5.20 (a) Measured transmittance spectra of 0° array after LC infiltration for the $\varphi = 0^\circ$ (black curve), 45° (red curve) and 90° (blue curve) incidences; (b) Comparison between the simulated (red curve) and measured (blue curve) results for $\varphi = 0^\circ$ polarization incidence. The green dash line gives the measured transmittance of the pure ITO soda lime glass substrates.

and $\lambda \approx 680$ nm. Then for $\varphi = 90^\circ$ polarized incidence, the resonances of the transmission spectrum locate at $\lambda \approx 660$ nm and $\lambda \approx 680$ nm, which is almost close to the position for $\varphi = 0^\circ$ polarized incidence. By comparison with the numerical simulation with the measured spectral response for the 0° array, poor correspondence is obtained for the model of $\varphi = 0^\circ$ in-plane LC alignment along

Figure 5.21 Transmittance of LC infiltrated arrays of (a) 0° and 45° periodic layout with incidence polarization rotated from $\varphi = 0^\circ$ to 180° and compared against the numerical simulations. The dash lines show the evolution of the resonances in the transmittance spectra. The value of the plots represents the percentage of the transmission normalized to the incident intensities.

the photoalignment direction (see Figure 5.20b), which indicates an abnormal LC alignment within the array areas. Later, we extend the measurement range for incidence continuously from $\varphi = 0$ to 180° as given in Figure 5.21. For the 0° array layout, as given in Figure 5.21a, the resonances locate at $\lambda \approx 660$ nm and $\lambda \approx 680$ nm for $\varphi = 0^\circ, 90^\circ$ and larger degrees incidence polarization directions. For $\varphi = 15^\circ$ to 135° incidences, the resonances shift closer at $\lambda \sim 675$ nm and $\lambda \approx 680$ nm. For the 45° layout array, when the incidence polarization rotates from $\varphi = 0^\circ$ to 90° , the E and M resonances continuously blue shift from $\lambda \approx 670$ nm and $\lambda \approx 682$ nm to $\lambda \approx 664$ nm and $\lambda \approx 680$ nm. The blue shift tuning indicates the limited reduced refractive index of the LC along the polarization directions from $\varphi = 0^\circ$ to 90° for the 45° array layout. When the incidence continues to rotate from $\varphi = 90^\circ$ to 180° , the resonances red shift to $\lambda \approx 670$ nm and $\lambda \approx 682$ nm, which almost revert to the same position for $\varphi = 0^\circ$ polarization incidence. The discussion of the LC alignment performance and the comparison between both layout will be extended in the discussion section.

A new TiO_2 metasurface sample was fabricated and study for the phase modulation performance under before and after applying the electrical excitations. Details of both the phase response of passive and dynamic modes will be discussed in section 7.3.2 of Chapter 7.

5.4 Discussion

In this section, the fabrication and optical response of LC infiltrated TiO_2 cylinders metasurface is studied. Similar to the TiO_2 metasurface before LC infiltration, the resonances for the LC infiltrated sample also red-shift with an increased cylinders' geometry either of the radius or height due to an enlarged typical size for the Mie scattering. Comparatively, the resonances only excite from the period of the cylinder atoms' array but can be shifted in spectra by changing the optical environment. The faster shift of resonance in spectra is observed of the electric dipole with the change of cylinders' radius, while the magnetic dipole with the height. Due to the increased refractive index of LC compared with the ambient, the contrast of the optical environment between the cylinders and the surrounding is decreased and thus red-shifts the resonance position in the transmittance spectra. Dependence of the incident polarization

Figure 5.22 Illustration of birefringence within LC infiltrated 0° and 45° layout arrays for $\varphi = 0^\circ$ polarization incidence. The blue line across the atoms indicates the assumed LC's extraordinary direction with n_e . The angle φ defines the rotated LC alignment with respect to the x -axis.

direction is sensitive on the optical response. As shown in Figure 5.5, the excitation can be only happened along the periods of the nano structure, thus the resonances can be tuned by the rotation of the incident polarization with the varied components of incident electric field along the periodicity.

For the coherent LC in-plane rotation, the components of refractive index along the x and y -axis changes, thus lead to a symmetric evolution of the resonances position between the $\varphi = 0^\circ$ and 90° incident polarizations. To be noted, although the polarization is aligned along the periodic x or y -axis direction, the phase retardation of LC molecules will help to produce some derivation of the electrical components along the perpendicular direction. Therefore, for spectra analysis, the resonant excitation along both x and y -axis directions need to be considered.

It has been found the surface nano antennas would produce a deviation of the LC alignment from the preset rubbing/photoalignment direction along the x -axis. We first assume a model of the 45° LC deviation in 0° array consider the periodicity of the nano antennas along the perpendicular x and y -axis directions. Based on the simulation in Figure 5.9, the optical response almost not changed

for various incident polarizations between the restrict 0° array with 45° LC alignment and the 45° array with the 0° LC alignment. As shown in Figure 5.22, for both cases, the refractive index has an equivalent component along the two periodic directions. For the 0° array illuminated by a $\varphi=0^\circ$ polarized light, the electric field would experience an equivalent refractive index about $n_{\text{eff}} = n_e \cos 45^\circ + n_o \sin 45^\circ$ along the 0° direction (x -axis). In 45° array for $\varphi = 0^\circ$ polarization, they will experience the same projection of the refractive index along both periodicities. In Figure 5.8a, for the larger angle of polarizations about $\varphi = 135^\circ$, the expanded electric resonance can be the results of the increased derived mode due to the larger phase retardation from the LC birefringence $\Delta n = n_e - n_o$. For the 45° array with 0° LC alignment in Figure 5.9b, the expansion happens at about $\varphi = 90^\circ$ polarizations with a maximum birefringence.

The poor fitness between the simulation results based on the 0° LC alignment and the experimental results reveals a significant deviation of LC alignment. To uncover the mystery of the LC alignment in the sample, the measured optical response for varied incident polarization was compared with the preset refined model with parallel and twist LC alignment. A coherent 30° in-plane alignment is proposed here which gives the best agreement to the experiment values (see

Figure 5.23 Calculated results of transmittance of LC infiltrated TiO_2 cylinders with the $\varphi = 30^\circ$ LC in-plane alignment for incident polarizations varied from 0° to 180° . The value of the plot represents the percentage of the transmission normalized to the incident intensities.

Figure 5.24 Calculated electric and magnetic dipole resonances in the parallel model for the varied incident light polarizations with LC alignment set 30° with respect to x -axis. (a) Electric dipole response for the incidence polarization varied from $\varphi = 0^\circ$ to 180° with respect to x -axis; (b) Comparison between the excited electric dipole components along x and y directions; (c) magnetic dipole response for the incidence polarization varied from $\varphi = 0^\circ$ to 180° with respect to x -axis. The intensity of the dipole resonance was normalized by the incident fields.

Figure 5.23). As it can be seen from the comparison of the excited electric and magnetic dipoles in Figure 5.24 with the transmittance spectra in Figure 5.21a, the electric resonance along x -axis (E_x) excited at $\lambda \approx 675$ nm is dominant for incident polarizations varied from $\varphi = 15^\circ$ to 90° . This corresponds to the higher effective refractive index for $\varphi = 30^\circ$ LC alignment. On the other hand, the electric resonance oriented along y -axis excited at $\lambda \approx 664$ nm dominates for incident polarizations varied from $\lambda = 105^\circ$ to 180° and corresponds to the lower effective refractive index.

In the measured transmittance spectra in Figure 5.21b, a slight blue-shift

happens from $\varphi = 0^\circ$ to 90° incident polarization in the 45° array, which can be the reason of reduced effective refractive index due to a slight deviation of LC alignment from the x -axis of the 0° direction.

5.4 Summary

In this chapter, the LC infiltrated TiO_2 metasurface was studied in numerical simulation, fabrication and measurement of optical response. As compared with the pure TiO_2 metasurface of the nano cylinder, the spectral resonances red shift for LC infiltrated metasurface due to the increased refractive index of the environment. Based on the spectral analysis for various incidence polarizations, the electric and magnetic dipole resonances excited along the periodic direction and the magnitude of each directional component varies with the rotation of the incidence polarization. Due to the anisotropic birefringence of the LC, the resonance position shifts when incidence polarizations rotated from x to y direction as the result of the shifted refractive index along the periodicity. Coexistence of electric dipole resonances can be excited for intermediate incidence polarization directions from 30 to 60 degrees to x -direction due to the comparable projection of electric mode along the periodic directions, and consequently induces the bimodal of the magnetic resonances. Phase shift can be excited accordingly at the resonances position of the transmission spectra and can be tuned by refractive index variation of LC. An enhanced 2π phase shift can be obtained in TiO_2 nano cylinders samples of 140 nm radius and 195 nm height for 0-pol incidence due to the overlapped electric and magnetic resonances which may indicate a possible Huygens' condition in spectra.

For sample fabrication, the TiO_2 metasurface was patterned on the ITO glass and then packaged and infiltrated with @merck E7 LC by the standard LC cell packaging process. The 1.5 μm LC cell was fabricated and measured, confirming a good in-plane LC alignment defined by the photoalignment.

For optical measurement of the 1.5 μm LC based TiO_2 metasurface with increasing geometry of the radius, red-shift of both electric and magnetic resonances happens with different shifting rate and can be overlapped for a nominal 140 nm radius cylinder sample. The electric resonance locates at $\lambda \sim 664$ nm for both 0-pol and 90-pol incidences and shift to $\lambda \sim 675$ nm for 45-pol

incidence. The $\lambda \sim 675$ nm resonance can be retained for incidence from 15-135 pol, and the $\lambda \sim 664$ nm exists for the incidence of 0-pol and 90 to 180-pol. The coexistence of the bimodal of electric dipole resonance can be the comparable components along the two periodic directions. For comparison, the electric dipole resonances only slightly blue shifted from 670 to 664 nm for incidence of 0 to 45-pol for the nano cylinder array patterned with the periodicity 45 degree to the x -direction, which can be attributed to the limited reduced refractive index change for excitation direction of the electric dipole.

The measured results obviously disagree with the calculation based on 0-degree LC alignment parallel to the photoalignment. Simulation model is setup with LC parallelly or twistedly aligned from 0 to 90 degrees. A nearly 30° in-plane LC alignment was proposed by comparison between the measurement and calculation, indicating a possibly strong anchoring effect of the nano cylinder surface via the surface energy analysis based on Frank-Oseen model. Details of the influence of the nano structure geometry will be discussed in the next chapter.

Chapter 6: Alignment of LC infiltrated in the nano structure

6.1 Introduction

As discussed in Chapter 5, the LC in vicinity of the nanostructures tends to align with a 30° in-plane deviation from the photoalignment direction, which confirms a significant anchoring effect from the nano structures. It has been reported by groups about such LC misalignment performance, which would influence the optical performance in the LC based metasurface. It's thought that the misalignment normally happens enslaved to the surface geometry, including the shape and size parameters [113]. Such unexpectable misalignment will deviate the output response from the design. However, the report of nano structures' influence on the LC alignment and the optical response are not many. As introduced in Section 2.3, the LC alignment anchored by the scratched surface can be predicted via a minimization of the system energy balanced between the LC elastic distortion energy and surface energy with the Frank-Oseen model. Therefore, it's necessary to systematically study the relation between LC alignment and the nanostructure's geometry, thus guiding to improve the design of the LC based metasurface devices. In a LC cell, the liquid crystal molecule chains are polarized and arranged orderly via the electrical interactions. Therefore, upon the combined influence of the top layer photoalignment/rubbing and the nanostructures' anchoring effect, the alignment of the LC molecules will be defined by the lowest elastic energy of the system, which would lead to some misalignment of the LC when the nanostructures' anchoring effect is unparallel to photoalignment/rubbing direction. The LC's energy in system, based on the Frank-Oseen model, can be described as the sum of LC elastic energy and the anchoring effect for both the nanostructures and the photoalignment.

In this chapter, the LC based metasurface is fabricated with different TiO_2 geometries. The optical performance is measured and analyzed via the CCD capture, transmissive spectral and Raman spectral measurement. The LC alignment within the TiO_2 arrays are characterized, further to deduce the relation between the LC alignment with the TiO_2 nano geometries.

6.2 Experiments

6.2.1 Fabrication of LC based TiO₂ metasurface of different atom geometries

Here, to introduce various geometric influence on the LC alignment, the surface nano structures was laid out with different atom dimension and the related angle with respect to the preset alignment direction. The dimension the nano atoms is given below in Table 6.1, with a comparison between the nano blocks (marked as Group A) and blocks (marked as Group B). To simulate the most likely layout of the in-plane geometry, the nanoantennas were designed with variation of parameters into three series: 1. the varied aspect ratios from 1:1 to 1:4 with a long edge length of 320 nm; 2. the 1:1 aspect ratio with the varied edge length from 80 to 320 nm; 3. The rotated periodicity from 0° to 90° with respect to the x -axis for 1:1 arrays with a long edge length of 320 nm. Hence, as an example, A6 array represents the group of square block atoms with the 280 nm side length and B10 array represents the cylindroids atoms with the axes of 320 and 160 nm. Micro-structure of the patterned TiO₂ atoms were captured by SEM to confirm the geometry. Some of the atoms' images were shown in Figure 6.1.

The periodicity of the nanoantennas is set 360 nm as before. Generally, the fabrication of the antennas was confirmed uniformly for the periods and shapes as required. Details of the geometry parameters were measured, with the error below 10% with the designed specifications, which further confirm the correct fabrication of the samples.

Table 6.1 List of designed TiO₂ antennas geometries

Series 1	1	2	3	4	5	6	7
(nm)	80/80	120/120	160/160	200/200	240/240	280/280	320/320
Series 2	8	9	10	11	12	13	
(nm)	80/320	120/320	160/320	200/320	240/320	280/320	
Series 3	14	15	16	17	18		
	15°	30°	45°	60°	75°

Figure 6.1 Sample of micro-structure of TiO_2 nanoantennas with different geometric parameters for (a) to (d) rectangular and (e) to (h) cylindroid shapes captured by scanning electron microscope (SEM)

Then the LC was infiltrated into the sample following the standard process as introduced in Section 5.3 of Chapter 5. To control the strength of the LC alignment, we adopted rubbing process for the top layer. The strength was controlled by repeating the rubbing process with 1 and 2 cycles' scratch. The

Figure 6.2 Measured Raman spectra of pure LC aligned along x -axis ($\varphi = 0^\circ$) illuminated by the 488 nm blue light. The peaks of the typical LC chemical bonds have been marked by symbols.

rubbing was processed along the x -axis direction parallel to the periodicity of the nano antennas. To correspond to the previous experimental results, a $1.5\ \mu\text{m}$ LC layer was infiltrated with the nanoantennas. The sample of double repeat of rubbing process was systematically measured beforehand and then was compared with the sample with 1-cycle rubbing process.

6.2.2 LC alignment in vicinity of TiO_2 nanoantennas

The LC alignment within the microstructures was detected by the image capture from CCD camera and the Raman spectrometer. Due to the Raman scattering responds to the certain chemical bond in spatial position, the LC molecules can be detected by Raman spectrometer with certain position in spectra representing the typical chemical components and the intensity of the signal varies with the spatial configuration of the molecules. As shown in Figure 6.2, the Raman spectrum was obtained for the pure LC background with the incident polarization along the x -axis ($\varphi = 0^\circ$). The LC was aligned along with the rubbing direction parallel to x -axis. As introduced in Chapter 2, the LC molecules consist of four parts: the alky group ($-\text{C}_x\text{H}_y$), the C-N cyan bond, the C-C skeletal bond and the benzene ring, which accordingly locate at $\sim 3500\ \text{cm}^{-1}$ (not shown here), $\sim 2232\ \text{cm}^{-1}$, $\sim 1608\ \text{cm}^{-1}$ and the tiny peaks around $\sim 1200\ \text{cm}^{-1}$.

Figure 6.3 (a) Measured Raman spectral curve of pure LC with different incident polarizations. The inset sketches the relations between incident polarization and LC alignment. (b) The measured Raman signal intensities for incident polarizations from -90° to 150° with respect to x -axis. All the Raman signals were normalized with the 0° signal (I_0)

¹ in the Raman shift spectra. Normally, peak at 1608 cm^{-1} for the benzene ring is more significant in intensity than other peaks. For various LC alignment directions, the intensity will change, which corresponds to the anisotropic response of Raman scattering with respect to the LC directions.

In Figure 6.3, the Raman spectra for various LC alignment was measured and targeted at the 1608 cm^{-1} position. For incident polarization along the LC long axis (0°), we can receive the largest intensity, while the smallest for the $\pm 90^\circ$ directions. As given in Figure 6.3b, the intensity shows a cosine dependence with the relative angular directions. This relation can be referred for the further definition of the LC alignment for different areas as discussed in the following sections.

Then, the array with 280 nm square atoms was captured and measured with LC infiltration for $\varphi = 0^\circ$ incident polarization. The LC was first aligned by a double repeat of rubbing process. In Figure 6.4a, the peaks of the typical LC are all observed. As shown in the insert of Figure 6.4a, the LC alignment is coherently aligned within the array while the LC background is well aligned along the x -axis of rubbing process. An obvious difference of brightness is observed between the LC background and the array area, indicating a possible misalignment of LC from the x -axis within the array. For the Raman spectrum

Figure 6.4 (a) Measured Raman spectrum of A6 array. The inserts show the capture of the array for the $\varphi = 0^\circ$ incident polarization. (b) The Raman spectra measured at different points of the array as indicated in the insert of (a) and the LC background for $\varphi = 0^\circ$ and 90° incidences.

within the array, the peaks are almost overlapped, confirming a uniform alignment of LC within the array. By comparing with the LC background of 0° and 90° , the intensity of the array areas is about 90% of the maximum intensity of the LC, which can be expected a 25° deviation with respect to the rubbing alignment directions. Referring to the discussion in the Chapter 5, such misalignment of LC can be regarded due to the influence of surface geometry. Therefore, the LC alignment could be decided under the regulation of the geometric parameters.

6.2.3 LC alignment influenced by TiO_2 nanoantennas' geometry

As introduced in the section 6.2.1, the sample was designed with rectangular and cylindroid atoms of different parameters (see Table 6.1). We first captured the images of the LC infiltrated TiO_2 arrays by the CCD combined in the commercial Nikon microscope system which is also used for measurement in results of Chapter 4 and 5 (see Figure 4.12 of Chapter 4). A set of cross-aligned polarizers were inserted before and after the metasurface sample in the optical path, working as the polarizer and analyzer. The LC alignment can be directly expected via the darkness of the images. In Figure 6.5, we gave the CCD captured arrays of both the squares and cylinders of 1:1 aspect ratio. As shown in the figure, the LC background is well aligned along the x -axis with almost no transmission

Figure 6.5 Capture of 1:1 aspect ratio's array of squares and cylinders with dimension from 160 to 320 nm (sample 3 to 7) with LC. The dimension is defined by the length of the side for square and the diameter for cylinder. The setup of polarizer (P) and analyzer (A) is given by the arrows at the lower right corner.

observed. For the array areas, certain amount of the transmission was detected, indicating the LC alignment deviation from the x -axis. For both geometry groups (square and cylinder), the transmission intensity varies with the change of the atoms' size. The transmission brightness gradually increased when the side length a increases from 160 to 200 nm, while decreases when a increases for samples from 240 to 320 nm, showing a possible variation of the alignment directions with the nanoantennas. For brighter arrays, the LC can be regarded with more significant misalignment from the rubbing directions along x -axis. For the 320 nm square sample, the brightness almost becomes as low as the LC backgrounds, indicating a possible well aligned LC molecule along the antennas' periodicity and rubbing direction. Similar to the square atoms, the brightness in cylinders increase first for increased diameters from 160 to 240 nm while decreased for larger diameters to 320 nm. Comparatively, the capture inside the 320 nm diameter cylinder array is a little bit brighter than the square array, showing a slight deviation of the LC alignment with respect to the x -axis direction. Besides, the brightness for $D=160$ and 200 nm samples is obviously lower than the square samples, indicating an alignment closer to the preset rubbing directions.

For comparison, Raman spectra were measured for arrays of varied side length (see Figure 6.6). The changes of the intensity of the 1600 cm^{-1} peaks for

Figure 6.6 (a) Measured Raman spectra for arrays of different length from 160 nm to 320 nm for the $\varphi = 0^\circ$ incident polarization. (b) The intensity of 1600 cm^{-1} peak for different geometry length normalized to the LC background of 0° alignment.

different geometry parameters confirm a non-negligible influence on the LC alignment. In Figure 6.6b, the intensity of the 1600 cm^{-1} peaks first decrease from 160 to 200 nm, and then increases for side length of the squares from 240 to 320 nm, which corresponds to the results as captured in Figure 6.5. Refer to the results of Figure 6.3b, the LC alignment can be expected with an in-plane deviation from $\varphi = 25^\circ$ to 35° for the varied geometries. For comparison with the cylinder arrays, larger misalignment can be expected than the squares with the same aspect parameters. Proof will be given in the following section.

Then, the images of the atoms with different aspect ratios in the varying range from 1:1 to 1:4 were captured and shown in Figure 6.3. The dimension is defined by the length of side (represented by a and b for short and long sides) for the rectangular and axial diameters (represented by the D_1 and D_2 for short and long axis) for the cylindroid. As a result, the atoms were patterned with a fixed 40 nm narrow space along the x -axis direction, while various sizes of the gaps along the perpendicular short sides (*e.g.* see Figure 6.1c). The brightness, compared with Figure 6.5, is quite low for these samples (see Figure 6.7), together with a limited range of changes for different geometries, indicating a negligible misalignment of LC parallel or perpendicular to the polarizer under the combined effect of the nanoantennas' geometry and rubbing. To be noted,

Figure 6.7 Capture of rectangular and cylindroid arrays of aspect ratios from 1:4 to 1:1 with dimension from 120/320 to 320/320 nm (sample 2 to 7) with LC. The dimension is defined by the length of the side for the rectangular (a/b) and the axis for the cylindroid (D_1/D_2). The setup of polarizer (P) and analyzer (A) is given by the arrows at the lower right corner.

Figure 6.8 (a) Measured Raman spectra for arrays of different aspect ratios from 1:4 to 1:1 with dimension from 120/320 to 320/320 nm with LC infiltrated for the $\varphi = 0^\circ$ incident polarization. (b) The intensity of 1600 cm^{-1} peak for different geometry length normalized to the LC background of 0° alignment.

although slight, the brightness also experiences a maximum for the sample with a 200 nm atom length along the short side of rectangular arrays, and 240 nm gap for the cylindroid arrays. This relation can be echoed by Raman spectra measurement as shown in Figure 6.8. A dip of the smaller intensity of 1600 cm^{-1} peak is obtained for the 200/320 nm rectangular, which is coincident with the captured results as given in Figure 6.7. The higher intensity ratios compared with the results in Figure 6.6b indicates a better alignment close to the rubbing direction along x -axis.

To intuitively present the misalignment of LC alignment inside the nano array, the sample was rotated by 30° , 45° , 60° and 90° with respect to the x -axis. The captured results with the side length from 160 to 280 nm (sample arrays from A3 to A6) are given in Figure 6.9 (geometry can be referred to the Table 6.1). For 90° position, the brightness exists in the series of arrays like the 0° position. For the 0° and 90° position, the LC directors were aligned with either the polarizer or the analyzer directions. When the sample is rotated, the brightness, although not consistent with the LC background, is shading to the darkest when rotated from 90° to 30° position, revealing an alignment close to 30° with respect to the rubbing direction (x -axis) inside the array. To be noted, the darkness inside the array is changed for different geometric arrays, showing a slight deviation of the LC alignment. For most of the array areas, the brightness is uniform, which

Figure 6.9 Capture of rotated square arrays with LC of 1:1 aspect ratio with dimension from 160 (A3) to 280 nm (A6) defined by the side length of the square. The rotation is set $\varphi = 30^\circ, 45^\circ, 60^\circ$ and 90° with respect to the x -axis. The setup of polarizer (P) and analyzer (A) is given by the arrows at the lower right corner.

confirms a coherent LC alignment in vicinity of the antennas. However, there are still some small areas of inhomogeneity, showing an existence of singular LC alignment between the large size LC clusters.

To directly observe the LC alignment within a certain array area, mapping measurement of the Raman spectra was scanned for the A6 array (280 nm square). 8×8 points have been chosen along x and y -axis directions. The points at the periphery are near the LC background. The LC alignment angle can be calculated by comparing the Raman signal intensity with the pure LC background signal ($\varphi = \cos^{-1} I_{//} / I_{\perp}$). [143] As shown in Figure 6.10, the scanned image of A6 array with LC aligned by one (Figure 6.10a) and two repeats (Figure 6.10b) of rubbing process are given. Uniform LC alignment along about 20° – 30° with

Figure 6.10 The calculated LC alignment angles with respect to the x axis reflected by the Raman spectral mapping of A6 (280 nm square) array with LC infiltrated after (a) one and (b) two repeats of rubbing process. The angles are calculated based on the 1600 cm^{-1} peak of spectra scanned for the 8×8 points along X and Y directions. The dash line frames the array area.

respect to the rubbing direction along x -axis is obtained for the twice rubbed sample, while a larger angle about $30\sim 40^\circ$ is observed for the one-repeat rubbed sample. The larger angle indicates a weaker influence of the rubbing alignment toward the LC molecules in the less-rubbed samples. For the periphery area outside the array, the LC tends to align parallel to x -axis, coherent with the rubbing directions. The images of A6 array under polarized microscope were also captured as given in Figure 6.11. The brighter array contrast to the background confirms the possibly larger LC alignment deviation in the less rubbed sample (see Figure 6.11b). For comparison, the mapping scanning is also carried out for the cylinders with same parameters (B6: 280 nm cylinders) (see Figure 6.11).

Figure 6.11 Images of arrays captured for A6 array with (a) two and (b) one repeats of rubbing process, and (c) A11 array with one time rubbing process

Figure 6.12 The calculated LC alignment angles with respect to the x axis reflected by the Raman spectral mapping of the arrays with LC infiltrated after one time rubbing process for (a) A4 (200 nm square), (b) A11 (200/320 nm rectangular), (c) B6 (280 nm cylinder) arrays; (d) sketched illustration of the LC alignment in vicinity of nano antennas. The dash line frames the array area.

The angle deviation is consistent with the Raman signal intensity distribution. For center area of the array, the LC alignment is expected misaligned from the rubbing direction, revealing stronger influence of the surface geometries inside the array areas. Details of geometry influence on the LC alignment will be discussed in Section 6.3. Raman scanning mapping of some samples with one time rubbing process is given in Figure 6.12. As given in Table 6.1, A4 array has a smaller side length (200 nm) than A6 (280 nm). The mapping shows a lighter deviation of LC alignment direction angles of A4 than A6, which corresponds to the geometric influence similarly as shown in Figure 6.5. The slightly wider gaps between cylinders should provide a weaker restriction to the LC stretch infiltrated. For A11 array with a longer aspect ratio (200/320 nm) along the $\varphi = 90^\circ$ in-plane direction, the large LC alignment angle above 45° with respect to the x -axis shows a stronger influence of the surface geometry easy axis along the longer

Figure 6.13 Images of one-time rubbed array captured 0°, 30°, 45° and 60° with respect to the rubbing direction

length of the rectangular. For the B6 array of the cylinders with the sample aspect ratio of A6 (320 nm), larger LC alignment deviation was observed indicating the weaker restriction energy of the surface geometry since more space exists for the gaps between nano cylinders. The LC deviation close to $\varphi = 30^\circ$ in A4 array as shown in the Raman spectra mapping (see Figure 6.12a) can be also confirmed in the direct capture with the lowest transmission for 30° rotated position (see Figure 6.13).

6.3 Discussion

The large deviation angle of LC in-plane alignment from the rubbing or photoalignment direction indicates a strong anchoring effect in the thin LC layer, which dominates over the photoalignment influence. This effect can be considered based on the surface energy of the nanostructures, which is determined by the geometry of the metasurface and its symmetries. For our rectangular or cylinder samples, the anchoring energy coefficients along the x and y -axis directions can be considered equivalent for LC alignment.³⁴ As introduced in Section 2.3.3 of Chapter 2, the LC system's energy can be expressed by the Frank-Oseen model [59, 113]. According to the Frank-Oseen model, the system energy can be consequently expressed as the sum of the elastic energy of LC (F_{elas}) the surface anchoring energy (F_s) and the photoalignment energy (F_{ph}) as:

$$\begin{aligned}
 F &= F_{elas} + F_s + F_{ph} \\
 &= F_{elas} + (W_1 \cdot \sin^4 \varphi + W_1 \cdot \cos^4 \varphi) + W_2 \cdot \cos^4 \varphi
 \end{aligned} \tag{1}$$

$$\begin{aligned}
&= \frac{1}{2} \int \{K_{11} \cdot (\nabla \mathbf{n})^2 + K_{22} \cdot (\mathbf{n} \cdot [\nabla \times \mathbf{n}])^2 + K_{33} \cdot (\mathbf{n} \times [\nabla \times \mathbf{n}])^2 - \\
&\quad \varepsilon_0 \varepsilon_a (\mathbf{E} \cdot \mathbf{n})^2\} dV + (W_1 \cdot \sin^4 \varphi + W_1 \cdot \cos^4 \varphi) + W_2 \cdot \cos^4 \varphi \\
&= \frac{1}{2} \int_0^d \left[(K_{11} \sin^2 \theta + K_{33} \cos^2 \theta) \cdot (\theta')^2 + (K_{22} \sin^2 \theta + K_{33} \cos^2 \theta) \cdot \sin^2 \theta \cdot (\varphi')^2 - \right. \\
&\quad \left. \varepsilon_0 \varepsilon_a E^2 \cos^2 \theta \right] dz + (W_1 \cdot \sin^4 \varphi + W_1 \cdot \cos^4 \varphi) + W_2 \cdot \cos^4 \varphi
\end{aligned}$$

where the K_{11} , K_{22} and K_{33} are the splay, twist and bend elastic constants of LC, ε_a is the relative dielectric constant of the LC environment, and z is the spatial coordinate integration variable, that extends along the thickness of the cell d . The illustration is sketched in Figure 6.14. The coefficient W_1 measures the strength of the anchoring energy of the nanostructures, and is the same, by symmetry considerations, along either x or y axes. W_2 is the coefficient representing the strength of the photoalignment effect. $\mathbf{n}$ represents the spatial LC director in terms of polar (θ) and azimuthal (φ) angles of alignment as $\mathbf{n} = (\sin \theta \cos \varphi, \sin \theta \sin \varphi, \cos \theta)$. A minimum system energy can be obtained according to the Euler-Lagrange equations for the system energy based on the parallel model of LC alignment at $\varphi = 30^\circ$ determined from experiments ($\theta = 90^\circ$, $\varphi|_{z=0} = \varphi|_{z=d} = 30^\circ$ and $\varphi'|_{z=0} = \varphi'|_{z=d} = 0$), as follows:

$$\begin{aligned}
&\frac{\partial F_{elas}}{\partial \varphi} - \frac{dF_{elas}}{dz} \cdot \frac{\partial F_{elas}}{\partial \varphi'} + \frac{\partial (F_s + F_{ph})}{\partial \varphi} \\
&= K_{22} \cdot \varphi'|_{z=0} + [W_1 \cdot (\sin^2 \varphi|_{z=0} - \cos^2 \varphi|_{z=0}) - W_2 \cdot \cos^2 \varphi|_{z=d}] = 0.
\end{aligned} \tag{2}$$

Figure 6.14 Sketch of the LC infiltrated nano antennas and the relations of the specific interaction for LC alignment including the LC elastic energy (F_{elas}), surface energy of rubbing/photoalignment (W_1) and the surface anchoring energy of the nano antennas (W_2).

This equation for the energy of anchoring effect W_1 and photoalignment W_2 leads to solution $W_1/W_2=1.5$, which implies a stronger influence of the anchoring effect from the nanostructures than that of the photoalignment layer in the performed LC alignment may be critical for the design of LC based tunable metasurfaces experiments. This kind of anchoring effect in the presence of nanostructures, therefore, should be considered when realizing practical devices based on those. Then, based on this model, the surface anchoring effect of each geometry can be derived based on the measured LC alignment directions captured and calculated based on equation 2 above and give below in Table 6.2. Take the example of the A3 to A7, a stronger influence of geometry is obtained at A4 array of 200 nm length with stronger anchoring W_2 than the rubbing influence W_1 . The sample was infiltrated after a twice rubbed process.

Comparatively, the rectangular geometry can be helpful for the systematical LC alignment within the array and shows a stronger regulation of the LC alignment than the cylinders with same typical geometry parameters which can be due to the strict limitation of space for the LC alignment in topology.

Table 6.2 List of the surface energy ratio for arrays of varied geometries

		Sample				
Group A		A2	A3	A4	A5	A6
	cos φ	0.92	0.84	0.78	0.89	0.96
	φ (°)	23	32	38	27	19
	W_1/W_2	1.22	1.72	1.92	1.36	1.09
		A9	A10	A11	A12	A13
	cos φ	0.92	0.90	0.88	0.86	0.94
	φ (°)	23	25	28	28	19
	W_1/W_2	1.22	1.31	1.41	1.40	1.15
Group B		B2	B3	B4	B5	B6
	cos φ	0.94	0.92	0.88	0.82	0.86
	φ (°)	19	23	28	34	28
	W_1/W_2	1.15	1.22	1.41	1.92	1.40

6.4 Summary

In this chapter, the influence of surface nano structures on the LC alignment and the optical response was studied in the LC infiltrated TiO₂ metasurface with different nano structure geometries in numerical calculation and experiments. TiO₂ nano blocks and cylinders arrays were patterned with variation in atoms' dimension and layout direction, designing to mimic the possible surface geometric environment for the LC alignment. The thickness and rubbing strength were controlled to see the energy competition between LC plastic energy and the surface anchoring effect due to the nano structures.

LC alignment was detected by both the microscope observation and Raman spectrum. LC alignment in both the background and nano structure areas was measured and compared, showing an obvious gradient variation of alignment direction for measurement points from the center of the nano structure to the background, confirming a possible nano structure induced anchoring effect induced deviation of LC alignment from the preset direction. According to the mapping data of Raman spectrum measurement, a nearly 40-degree deviation of LC alignment can be found between the nano structure center and the background area. With an increment of the thickness of LC cell, the anchoring effect induced alignment deviation can be weakened, showing a relaxed LC plastic energy across the longer distance. The stronger rubbing strength by repeated fiber scratches can compete with the surface anchoring effect of the nano structures and improve the LC alignment along the preset direction.

Chapter 7: Electric modulation of LC infiltrated TiO₂ metasurface device performance

7.1 Introduction

As given in the discussion in Chapter 4, the electro-magnetic wave resonance for the metasurface can be modulated by changing the environmental refractive index. Considering the dielectric anisotropy, the electro-magnetic wave resonance can be modulated in the LC based metasurface by rotating the LC alignment, thus the refractive index. So far, some results have been reported in the LC based metasurface. Wang *et al* realized the tunable negative refractive index by employing the LC with the plasmonic silver structures [144]. Minovich *et al* realized a dynamic tuning of optical output efficiency via a LC infiltrated gold/MgF₂/gold fishnet structures [114]. Later time, LC based metasurface has been focused on the dynamic tuning toward the Mie-scattering effect. Sautter *et al* found a dynamic tuning of E M dipoles resonance shift in silicon nano disks metasurface via the thermal-optical response of LC and systematically discussed the performance possible principle behind it [41]. Then Komar *et al* realized an electrical tuning of Si based metasurface for the near-IR wavelength range [65]. To be noted, the tunable LC based metasurface is still insufficient for application due to several reasons: 1. the principle of optics in LC-matter systems, 2. the dull control of LC tuning including the stability and power consumption, 3. the deviation of LC alignment within the microstructures, 4. efficient control of output for visible light modulation. To be specific, the voltages for driving in the LC-microstructure system reported so far are normally more than 30V due to the anchoring effect in the thickness LC films with microstructures. In the meantime, the LC prefers to be aligned deviated from the preset direction due to the limitation of surface structures, which has been specifically discussed in Chapter 6. Plus, the materials mostly studied, including the metal and silicon metasurfaces, are lossy for the vis. light range, which would prevent the efficient modulation of the output. Here, based on the progress we've obtained in the LC based TiO₂ metasurface, we would like to explore the possibility of thin layer LC based all dielectric metasurface for electrically tunable vis. light modulation with lower power consumption. In this chapter, both the electrical tuning of the spatial light

Figure 7.1 Numerical calculation of LC based TiO_2 metasurface with vertical LC rotation from $\theta = 0^\circ$ to 90° for $\varphi = 0^\circ$ incidence, mimicking the electrical switching process: (a) transmittance results, (b) comparison in spectra between transmittance and phase shift and (c) phase change results. The LC is set with $\varphi = 0^\circ$ in-plane alignment and the TiO_2 is patterned with the geometry: $H = 188$ nm, $R = 160$ nm.

modulation performance of the LC based TiO_2 nano disk metasurface, including the transmission efficiency, dipole resonance shift and phase control will be discussed both in numerical calculation and experiments.

7.2 Numerical analysis of LC switching process

As discussed in Chapter 5, the LC tends to align with a deviation from the preset rubbing alignment of x -axis. Here we took $\varphi = 30^\circ$ as the example of in-plane LC alignment due to the anchoring effect. The optical response under the electrical switching was numerically analyzed first by the FDTD method. Variation of LC alignment in polar angle directions has been defined from 0° to 90° to mimic the LC switching process under the vertical electrical fields. As

given in Figure 7.1, the contour maps show the transmittance and phase change dependence on the vertical LC alignment directions, together with the comparison in spectra between them. For simplification, the LC was initially set along x axis with $\varphi = 0^\circ$ which is parallel to the 0° incident polarization. The polar angle θ defines the relative position between the LC alignment and normal line. For ON state, the LC is switched up, which is equivalent to $\theta = 0^\circ$. For OFF state, the LC is parallel to the preset x -axis direction with the $\theta = 90^\circ$. As given in Figure 7.1a, when $\theta = 90^\circ$, the transmittance spectrum shows slightly split resonances around $\lambda = 688$ nm. When the LC is vertically switched up (decreased θ), the two peaks slightly shift oppositely and cross when LC aligns with $\theta = 45^\circ$. Interestingly, another resonance occurs at $\lambda = 660$ nm in the meantime for $\theta = 0^\circ$. When LC is switched up (increased θ), the resonance generally blue shifts from $\lambda = 660$ nm to $\lambda = 640$ nm indicating a possible reduced refractive index of LC's dielectric anisotropy. To be noted, the intensity of this peak generally reduced when the LC is switched up.

For comparison, the phase shift data was also captured based on the same condition as in calculation of transmittance (see Figure 7.1c). A slight phase shift may happen for each resonance position, corresponding to the excitation of Mie scattering in the structure, which may induce obvious phase shift of the mode. To be noted, for $\theta = 45^\circ$, the two resonances are nearly overlapped and an enhanced

Figure 7.2 Calculated dipole components along x and y -axis directions: (a) E_x , (b) H_y for the incident polarization parallel to $\varphi = 0^\circ$ with zenith LC alignment varied from $\theta = 0^\circ$ to 90° . The value of the plots represents the excitation magnitude of the dipoles' amplitude normalized to the incidence field.

phase shift close to 2π can be received, with a high transmission efficiency above 60%, which is almost close to the Huygens' condition as introduced in Chapter 2. With a continuous change of the LC environment during switching, the resonances position deviated. A slight derivative resonance peak happens for LC is switched half way with θ from 15° to 75° , which could be a result of the phase retardation when light passes through the unparallelled LC molecules. Details will be discussed later in Section 7.3 of this chapter.

To explain the resonant scattering evolution in the anisotropic LC environment, the electric and magnetic dipoles are decomposed based on the x , y and z -axis directions. The evolution of the electric and magnetic dipole resonances under the $\varphi = 0^\circ$ incidence with the OFF state of LC aligned along x -axis direction is shown in Figure 7.2. For ON state with $\theta = 0^\circ$, most of the electric field lies along the x -direction (E_x) at the resonance position near $\lambda \sim 660$ nm. For the switching process, majority of the E_x components red shift to near $\lambda \sim 680$ nm, which lead to an obvious blue shift of the H_y components. By comparing between Figure 7.1 and 7.2, the resonance at $\lambda \sim 660$ nm for ON state should be for the ordinary refractive index (n_o). When the LC is switched down to OFF state, the projection of refractive index components along either the x or y -axis increases.

7.3 Experiments and discussion

7.3.1 Electrical modulation of transmittance spectra

The electrical tuning performance of transmittance spectra is tested in the sample discussed in Chapter 5 with the geometry of $H = 188$ nm and $R = 160$ nm with a $1.5 \mu\text{m}$ thick LC layer. In experiments, the sample has been measured for incident polarizations along $\varphi = 0^\circ$, 45° and 90° . Due to the in-plane deviation of the LC alignment from the x -axis, the resonance positions are different from the 0° alignment situation. In Chapter 5, we have found a small voltage about 3V is sufficient for switching of our thin layer LC cell. Here, for the metasurface areas, the LC switching requires higher voltages indicating the influence of the anchoring effect within the nanoantennas (see Figure 7.3). The most pronounced resonance shifts are observed for incident polarization aligned at $\varphi = 45^\circ$ with respect to x -axis, the closest to the predicted LC alignment including the anchoring effect. The electric resonance blue shifts from $\lambda \approx 675$ nm to $\lambda \approx 664$

Figure 7.3 Experimental results of electrical tuning of the liquid crystal infiltrated TiO_2 metasurface for the incident light polarization directions aligned at the 0° layout array with (a) $\varphi = 0^\circ$, (b) $\varphi = 45^\circ$ and (c) $\varphi = 90^\circ$ incident polarizations, together with (d) the 45° layout array for $\varphi = 0^\circ$ polarization under the increased DC voltages from 0 to 12 V. The symbol-line curves mark out the movement of electric (red) and magnetic (yellow) resonance positions under the applied voltage.

nm and the magnetic resonance red shifts from $\lambda \approx 682$ nm to $\lambda \approx 688$ nm with applied voltages changing from 0V to 12V. Excitation of particular resonant modes under vertical LC switching can be analyzed referring to the Figure 7.2. For the 0° and 90° polarization incidence, the tuning range becomes limited with only slight blue shift of the electric resonance from $\lambda \approx 664$ nm to $\lambda \approx 662$ nm and magnetic resonance red shift from $\lambda \approx 682$ nm to $\lambda \approx 688$ nm. (see Figure 7.3a and c). As discussed in Section 5.2 of Chapter 5, for the $\varphi = 45^\circ$ polarization incidence, the electric resonance at $\lambda \approx 675$ nm for 0V corresponds to the dominant contribution of electric dipole aligned along x -axis direction (E_x) for 30° LC alignment. The blue shift of this resonance at applied voltage can be attributed to the decreased refractive index of LC environment from n_{eff} to n_o near

Figure 7.4 The evolution of resonances in transmittance spectra of LC infiltrated nano cylinders under the electrical driving from 0 to 16 V. The sample was measured with a $\varphi = 0^\circ$ incident polarization

the nanostructures. The magnetic resonances movement is small for all incident polarization directions and all applied voltages due to its lower sensitivity to the environmental change. For the 0° and 90° polarization incidence, the electric resonance at $\lambda \approx 664$ nm for 0V corresponds to the dominant contribution of electric dipole aligned along y -axis direction (E_y), with a limited refractive index change resulting in a weak resonance shift. The observed spectral response can be continuously modulated in the range from 3 V to 5 V. For voltages above 5 V, the resonance positions are almost unchanged in all cases, showing an almost saturation of vertical LC alignment providing ordinary refractive index n_o for all in-plane incident polarizations.

7.3.2 Electrical modulation of phase performance

To experimentally demonstrate the performance of electrical phase modulation based on the LC infiltrated metasurface, another sample was fabricated for the phase shift response measurement. The atoms were measured by SEM with a geometry close to $P = 360$ nm and $H = 190$ nm. A nearly cone structure with the radii gradually varied from $R = 130$ nm to 160 nm from top to bottom, which can be due to the gradient spatial distribution of the e-beam

Figure 7.5 Measured phase shift of the LC infiltrated nano cylinders of the new sample's geometry under the electrical voltages from 0 to 16 V: (a) comparison of the phase spectra for both $\phi = 0^\circ$ (blue square curve) and 45° (red dot curve) incidence; (b) The phase shift response for $\phi = 45^\circ$ at $\lambda \sim 670$ nm wavelength.

exposure. As shown in Figure 7.4, the spectra of LC infiltrated array are tunable within the range of 4 to 8 V. The incident polarization is set $\phi = 45^\circ$ with respect to the x -axis, which is introduced in Chapter 5. A shift of the resonance position from almost overlapped $\lambda \approx 675$ nm below 4 V to a pair of deviated resonances at $\lambda \approx 660$ nm and $\lambda \approx 680$ nm above 8 V. The higher starting voltage around 4 V is related to an anchoring influence of the nano antennas to the LC molecules.

The phase measurement is conducted following the methods in Chapter 4 and 5. Compared with Figure 7.3, for a near-overlapped resonance position around $\lambda \approx 675$ nm at 0V, a continuous phase shift close to 2π can be expected which corresponds to the discussion in the previous chapters (see the red dot curve of Figure 7.5a). When higher voltages were applied (~ 12 V) and the LC was switched up, the phase spectra show two-dip phase drop around $\lambda \approx 660$ and 680 nm which corresponds to the resonance position as shown in Figure 7.4. For 0V, an anisotropic response of phased shift is observed for $\phi = 0^\circ$ and 45° incidences, which results from the anisotropic LC alignment. For 12V, when LC is almost fully switched, the phase shift responses are almost become close for $\phi = 0^\circ$ and 45° incidences, confirming an homogenous in-plane refractive index. Base on the resonance shift with the electrical driving (see Figure 7.4), we chose $\lambda \approx 670$ nm as the reference point for phase shift data capture (see Figure 7.5),

where we can expect the high phase change across the resonance shift area, while still reserve a high transmission above 80%. For the starting period from 0 to 4 V, the phase shift stays close to 0, showing a static state of the LC in the infiltrated array areas. For the voltages increased between 4 to 8 V, the phase shift response dramatically changes from 0 to -1.5π , showing a sensitive and continuous change of the phase shift response due to the LC switching. For the higher voltages above 8 V, the phase shift stays at -1.5π and almost not changed, which reveals a saturated LC alignment after switching process. Based on this result, the idea of electrically tunable efficient phase modulator within the range of visible light wavelength is reliable with a large phase shift response. By designing the LC infiltrated TiO_2 metasurface with appropriate geometry parameters, the phase shift can be modulated within a range more than 1.5π at certain wavelength with the adjustment of LC birefringence upon the electrical driving, and with a high efficiency above 80%. This performance can make it possible for development of phase modulators with multi levels (0, 0.5, 1 and 1.5π). More efforts are needed on study of that issue.

7.4 Summary

In this chapter, the optical response, both the transmittance and phase shift of the 1.5 μm thin layer LC based TiO_2 metasurface under the DC voltage electrical modulation is discussed both in simulation and experiments. As in the calculation results, the resonance in transmittance spectra can be tuned significantly via the switching of the LC alignment and thus the strong birefringence. As confirmed in the experimental measurement, the resonances can be tuned within a small range of voltages from 3~5 V, indicating a strength of the thin LC layer based metasurface devices. A wide resonance shift across about 20 nm can be obtained for the 45° incident polarization due to a more significant change of the refractive index along the resonant period. A large ratio of transmission efficiency above 65% (from 15% to 80%) can be obtained across the resonance wavelength.

Another sample was fabricated to test the phase shift response. A wide 1.5π phase shift is obtained within a small range of DC voltage applied from 4 to 8 V across the 670 nm, while reserved high efficiency above 80%. For voltages

before starting (<4 V) and after fully switched (>8 V), the phase shift states can be stable due to an unchanged LC alignment upon that situation, confirming a stable performance of the device. The large phase shift with high transmission efficiency convinced us with the idea of the LC based dynamically tunable metasurface for advanced phase modulator application in future.

Chapter 8: Summary and outlook

8.1 Summary

In summary, novel spatial light modulation technology with efficient performance in minimized structures are essential for developing the advanced visible light modulator in applications like the hologram display, phase reconstruction, wave-front shaping *etc.* Here, in this dissertation, the spatial light modulation performance of visible frequency range has been systematically studied and discussed based on the magneto-optical Kerr effect (MOKE) and tunable all dielectric metasurface.

Magneto-optical spatial light modulation (MOSLM) technology based on MOKE is potential for its sensitive signal detection with a high frequency above $\sim 10^6$ Hz and a small pixilation approach submicron scale. In this work, the MOSLM was studied based on the low temperature phase (LTP) MnBi thin films, which shows a strong perpendicular magnetization as much as 500 emu/cm³ with a 60 nm thin film. A large MOKE signal above $\theta_k \sim 0.5^\circ$ is detected under a 633 nm laser incidence. The MnBi thin film sample was fabricated via a 2hrs thermal annealing at 350 °C for a complete inter-diffusion of Mn and Bi atoms to form a hexagonal lattice. The Mn/Bi stack films were deposited by magnetron sputtering before the annealing process. The Mn was deposited by the DC mode while the Bi was fabricated by the RF mode due to the small conductivity of Bi, which would hinder the uniform ion flow during DC sputtering. Varied thickness ratios were designed for the Mn/Bi in the range from 12/40 nm to 24/40 nm and received the optimized window of 20/40 nm. For pixilated MnBi antennas with a decreased scale from 10 μ m to 2 μ m, the magnetization reduced. For training effect process, both the magnetization and coercivity reduced after times of measurement under the magnetic field. Besides the Mn components are easily to be oxidized. Therefore, the MnBi alloy sample is easy to be oxidized which lead to a 40% reduction of the saturated magnetization, and more reduction percentage for higher Mn amount ratios. The reduced magnetization for the pixilation, training process and oxidation effect is attributed to the degraded magnetic domain size after the process. Besides, the large coercivity above 5000 kOe would be still power consumptive for the high frequent driving of the magnetic

signals. Magnetic optical performance of the MnBi thin film with TiO₂ based dielectric stacks was simulated with an enhancement from $2\theta_k = 0.86^\circ$ without TiO₂ to a maximum 9.5° at 633 nm.

Electrically tunable metasurface for high efficient transmission and phase modulation was numerically designed and experimentally demonstrated. The metasurface device was setup based on the all dielectric TiO₂ nano cylinders infiltrated with 1.5 μm E7 nematic liquid crystal. The TiO₂ metasurface is fabricated via a standard electronic beam lithography flow with a nano antennas' periodic scale of 360 nm. The liquid crystal layer fabrication is carried out via a standard LC infiltration process. The electric and magnetic dipole resonances are simultaneously excited for the polarized incidence with comparable magnitude due to the high dielectric constant of TiO₂ materials. High transmission above 80% for non-resonant transmission is obtained both in simulation and experiments, showing a lossless performance of the TiO₂ dielectrics. The resonances red-shift with increased geometry parameters, with a sensitive response for electric dipole resonance to the radius while for magnetic dipole resonance to the height. Phase shift close to 1π is achievable for either of the resonance at the same position in spectra. Wide resonances shift from $\lambda \sim 660$ nm to 720 nm is obtained in transmission spectra via the change of the ambient refractive index surrounded from $n=1$ to 2, while the resonance disappears for n above 2 due to a small contrast of the refractive index between the nano antennas and the environment. After the infiltration of LC, the resonances red-shift due to the increased and show in-plane anisotropic response due to the optical environment of the LC. The measured results for the sample with 1.5 LC infiltration and TiO₂ antennas of 360 nm periodicity, 188 nm height and 160 nm radius show a poor correspondence with the numerical simulation, showing a large angle deviation between the actual LC alignment and rubbing alignment. Parallel and twist LC alignment models were proposed for illustration of the LC alignment within the sample. A $\varphi = 30^\circ$ in-plane deviation of the LC alignment was found in the sample by comparing the measured data with the models. Derivation of the optical dipole response can be excited along the direction perpendicular to the incident polarization due to the phase retardation of the LC birefringence. Stronger anchoring effect due to the surface antennas is confirmed

by introducing the Frank-Oseen model for numerical analysis. Large angle deviation of the LC alignment with respect to the rubbing direction is intuitively observed by Raman spectra mapping within the whole array areas. By measuring the LC alignment in samples with varied atom geometries' parameters, the deviation is confirmed in the sample experiencing a weak-strong-weak misalignment trend with an increased atom scale from 120 to 320 nm. Stronger anchoring effect is observed in rectangular samples than the cylinders. Electrical tuning of the optical response of the sample is demonstrated in both the transmission spectra and phase shift. A wide resonance shift close to 20 nm is obtained around $\lambda \sim 660$ nm in the driving range from 3~5 V with a large transmission efficiency modulation above 65% from “<15%” to “>80%”. A wide 1.5π phase shift is obtained within the voltage tuning range, while reserved high efficiency above 80%, showing a large phase control with high transmission efficiency.

8.2 Outlook

In this work, the idea of spatial light modulation based on the magneto-optical effect and tunable all-dielectric metasurface was systematically explored. Some issues are still waited to be further studied:

- *The candidate magnetic materials with large perpendicular magnetization and smaller coercivity for the development of MOSLM.*

Small coercivity is essential for the high frequency devices considering the driving power consumption. As shown in Chapter 4, the contradiction between large perpendicular magnetization and smaller coercivity, which normally shows the opposite requirement for the magnetic domain sizes, will hinder the realization of the target. As introduced in Section 3.3.3 of Chapter 4, some nano-photonics design like the dielectric stacks can be a way for enhancement of the MO effect. Similar approaches can be also expected via the structure of magnetic photonic crystal, surface plasmon structure or dielectric metasurface for light concentration in vicinity of the nano atoms.

- *Improvement of LC cell fabrication for continuous control of LC switching during the electrical driving in LC based metasurface device.*

In Chapter 7, mismatch of LC alignment is observed between the array area and the background due to the homogeneous anchoring effect towards the LC molecules. For thin LC layers, the surface morphology of the polyimide would be significant and influence the electric field distribution for various positions of the cell. Besides, stronger rubbing or photoalignment strength would be appreciated for regulate LC molecule director along with the preset direction, thus lead to a uniform LC alignment of the designed direction.

- *Relations between LC alignment and nano antennas geometry due to the surface anchoring effect.*

In addition to the improvement of the process for LC alignment control, the study of the relations between the LC molecules alignment and the nano antennas' geometry would be valuable for understanding the principle of LC misalignment influenced by the nano antennas. Due to the comparable scale of LC molecules with the tiny gaps between the antennas for the visible wavelength. For development of vis. range LC based metasurface, the LC misalignment due to the antennas' anchoring effect would be significant which makes the output out of control. More detection methods for micro-space LC alignment and theoretical model need to be developed for better illustration of the LC alignment within the nano structures.

- *Deep learning enabled control of the optical response for the LC based metasurface.*

To realize precise control of optical output of tunable LC based metasurface, a deep learning enabled method can be introduced to enhance the efficiency of metasurface design and optics control. our method consists of two steps. In the first step, geometric structure of tunable metasurface is deduced using traditional method, which will achieve a coarse tuning of metasurface. After that, deep neural network calculation is introduced to adjust LC addressing and further the metasurface output. In the long term, a photonic neural network, for example based on the silicon process technology [145], can be fabricated for the all-optical control of the output. This problem can be formulated as a supervised machine learning problem. During training

session, both the neuron, that is, the metasurface unit geometry, and the final output optical response of metasurface can be optimized using back propagation, making the output more and more similar to the desired output results. The adaptive tuning using neural network overcomes the drawback in traditional metasurface manufacture.

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