Hyperspectral Molecular Orientation Mapping in Metamaterials

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Abstract: The four polarisation method is adopted for measurement of molecular orientation in dielectric nanolayers of metal-insulator-metal (MIM) metamaterials composed of gold nanodisks on polyimide and gold films. Hyperspectral mapping at the chemical finger printing spectral range of 4–20 μm was carried out for MIM patterns of 1–2.5 μm period (sub-wavelength). Overlay images taken at 0, π/4, π/2, 3π/4, orientation angles and subsequent baseline compensation are shown to be critically important for the interpretation of chemical mapping results and reduction of spurious artefacts. Light field enhancement in the 60-nm-thick polyimide (l in MIM) was responsible for strong absorption at the characteristic polyimide bands. Strong absorbance A at narrow IR bands can be used as a thermal emitter (emittance E = 1 − R), where R is the reflectance and A = 1 − R − T, where for optically thick samples the transmittance is T = 0.

Keywords: metamaterials; thin films; polarisation; FTIR; synchrotron radiation

1. Introduction

Polarisation analysis has become a powerful spectroscopic technique applied over a wide range of applications in imaging and quantisation of absorbance, molecular orientation, dichroism, birefringence and order-disorder ratio [1–5]. It can provide insights into other derived properties of mechanical, thermal, electrical, magnetic, acoustical nature of materials and phase transitions. For example, the Extended X-ray Absorption Fine Structure (EXAFS) can determine the orientation of the bond with respect to the electric field vector of the synchrotron radiation and the coordination number [6] and to reveal nature of magnetic and electric properties of crystals. Spanning THz to UV (mm to nm) wavelengths, a hierarchical organisation of materials on different scales can be revealed. Remote sensing and Earth observation satellites make use of polarised radar to perform many of their functions. Synthetic aperture radar (SAR)
imaging of the Earth utilises up to two polarisations for detection and emission (HH, VV, HV, VH) which delivers insight into ocean phenomena due to interactions between the radio waves and geometrical features on the surface [7,8]. This allows determinations of the first three Stokes parameters for polariscopic characterisation of the surface. More recently, hybrid compact polarometric (HCP) SAR satellites, which transmit circular polarisation and revive H and V, have been launched for both Earth and Lunar observations. This allows for all four Stokes parameters to be determined [9,10]. Hence, the state of polarisation of light is known upon reflection (scattering) from surface (interface). Recognition of breaking waves due to their nonpolarizing reflectivity in satellite imaging can shed new light in understanding of energy exchange at the sea-atmosphere interface, which is one of the major factors in weather and climate formation [8]. Correlation between the wind speed and changing reflectivity of the ocean surface was observed for altimeter reflection (one polarisation) [11]. This can be an indication of a changing surface curvature of the sea surface due to wind direction. Wind speed and wave height are some of the main parameters required to measure and monitor to help development reliable climate change models [12]. Space based technologies are evolving fast and are increasingly important in agriculture, climate change, deforestation and ocean wave monitoring with the next-generation altimeters incorporating the capability to detect polarisation [13]. For IR astronomy, they are based on detection of absorption and scattering anisotropy induced by large volumes of low density materials with strongly expressed polarisation effects [14], while for the Earth observation, reflection/scattering from the surface is monitored for absorption and polarisation changes. By combining several wavelengths, more precise understanding about size and shape of scattered light can be gained. In a related area of remote sensing, IR imaging at the chemical fingerprint region demonstrated strong polarisation dependence of reflected/scattered IR tunable laser radiation [15] and could be used for determination of material morphology and alignment on the surface and sub-surface down to ~10–20 µm (industrial, defence, environmental applications). In material science, molecular alignment as well as pattern formation (different mass density, out-of-plane structures) can be detected beyond the spatial resolution as demonstrated for the IR spectral range [16]. This shows that the alignment of absorbers could be detected from a volume with a lateral cross section smaller than the diffraction limit of the optics used and even smaller than the wavelength. To detect absorbance changes from nanoscale volumes and films thinner than 100 nm is a challenge [17] but a light field enhancement by localised plasmonic resonance could be harnessed. This hypothesis was tested in this study and extended to anisotropy detection using light enhancement in metal-insulator-metal (MIM) metamaterials. Previously, silk micro-tome slices of ~1 µm thickness were mapped using IR transmission spectroscopy [18]; however, thinner polymers are challenging to characterise since thickness becomes ~λ/10–λ/100.

Here, we demonstrate a capability to detect anisotropy in dielectric nanofilms sandwiched in a metal-insulator-metal (MIM) metasurface (Figure 1a inset), engineered for plasmonic response over the IR spectral range of 4–20 µm. The plasmonic resonance wavelength is tuned over this IR window by changing the diameter of the gold nanodisk pattern. The light field enhancement under the nanodisk couples with insulator (polyimide) IR absorption bands. The four polarisation method [19] was applied to demonstrate the capability to detect molecular alignment, if any, down to the IR wavelength scale (from sample areas of ~6 µm cross sections per pixel on the hyperspectral chemical image map). The top pattern (nanodisks layer) of the MIM is chosen to be isotropic with a triangular lattice arrangement. Therefore, the absorbance anisotropy of the polyimide nanolayer can be probed, rather than the nanodisk response. Nanofilms of polyimide are known to have anisotropy and where chosen for this study.
2. Experimental: Setups and Samples

2.1. Four-Polarisation Method

The four polarisation method was demonstrated for IR absorbance mapping using linearly polarised light and measuring transmittance $A(\theta) = -\lg(T(\theta))$ at angles $\theta = 0, \frac{\pi}{4}, \frac{\pi}{2}, \frac{3\pi}{4}$ [19]. Three (out of four) Stokes parameters can be obtained from the transmitted intensities $I_0, S_0 = I_{\pi/2} + I_0$ (full intensity), $S_1 = I_0 - I_{\pi/2}$ and $S_2 = I_{3\pi/4} - I_{\pi/4}$ (the normalised set is $s_0 = 1, s_1 = S_1/S_0, s_2 = S_2/S_0$). Different reflectivity and absorbance for the $E_x$ and $E_y$ components at the interface cause polarisation to become elliptical with the azimuth angle (orientation) $\psi$ of an ellipse determined by $\psi = \frac{1}{2} \arctan(S_1/S_2)$. The phase angle $\delta$ between the two perpendicular $E_x$ and $E_y$ components determines the ellipticity, which can be extracted when the $S_3$ parameter is determined for which the intensity of the right-circular (RC) and left-circular (LC) polarisations has to be measured $S_3 = I_{RC} - I_{LC}$. Then, the $\tan \delta = S_3/S_2$ and the ellipticity $\chi = \frac{1}{2} \arctan(S_3/(S_1 + S_2))$. For the four polarisation method, only linearly polarised light is used.

Further development of the method allows separation of birefringence $\Delta n$ and dichroism $\Delta \kappa$ caused by changes in transmitted intensity where the complex refractive index is $n = n + i\kappa$ [20,21]. This can be achieved by virtue of angular dependence of transmittance $T(\theta)$, which has a $2\theta$ angular dependence for birefringence and $\theta$ for absorbance. The absorbance follows a $\cos \theta$ dependence (Beer-Lambert law, 1729), while the birefringence has $\cos(2\theta)$ dependence (Malus law, 1809). The two laws are accounted for by multiplication [20]. The $\cos(2\theta)$ dependence of $\Delta n$ reflects the fact that $T$ has a minimum when the light’s $E$-field is aligned with, or is perpendicular to, the two parallel polarizers. The absorbance meanwhile is always defined by the $E$-field projection onto the axis of the dipole transition, hence the $\cos \theta$ dependence for $\Delta \kappa$.

Anisotropy of absorbance due to orientation of the absorbers (dipoles) is defined by the Malus law $\cos^2 \theta$ and has dependence of $\cos(2\theta)$ (i.e., $\cos^2 \theta = [\cos(2\theta) + 1]/2$). By fitting the angular dependence of transmittance $A(\theta) \propto \text{Amp} \times \cos(2\theta - \theta_0)$, the amplitude of absorbance $\text{Amp}$ and the initial orientation angle $\theta_0$ of the dipoles are obtained from the best fit of $T$ at four angles $\theta = 0, \frac{\pi}{4}, \frac{\pi}{2}, \frac{3\pi}{4}$ [19] (more angles can be used for the fit [21]). Only the data from fits with a regression coefficient $R^2 > 96\%$ were selected for plotting as in previous the study [21]. The four polarisation method was used for characterisation of biopolymers and tissue [18,22].

2.2. Gold-Polyimide-Gold MIM Metasurface and Properties

The MIM structure was made on Si wafer coated by 200 nm of gold by evaporation (inset in Figure 1a). Then, vacuum polymerization of polyimide was carried out onto the gold film. Polyimide was formed using vapour deposition polymerization of pyromellitic dianhydride (PMDA) and 4,4’-diaminodiphenyl ether (ODA) at temperatures of 150 °C (PMDA) and 110 °C (ODA) with substrate at 30 °C [23,24]. After 30 min of deposition, thermal imidization treatment was carried out at 150°C in air for 1 hour. Polyimide layer formation was confirmed using infrared reflection-absorption spectroscopy and its thickness was measured by ellipsometry (Figure 1). The top layer of gold nanodisks arranged into a triangular lattice was fabricated using electron beam lithography (EBL), electron beam evaporation of 50 nm of gold and a lift-off process. Reflectivity and absorbance of MIM patterns was expected to be dependent on the portion of gold nanodisks occupied on the surface, which can be estimated as the area ratio of gold per unit cell $S_{Au} = \frac{1}{2} \pi (\frac{d}{2})^2$ and the area of the unit cell $S_{un} = \frac{\sqrt{3}}{4} \Lambda^2$. $S_{Au}/S_{un} = \frac{8 \pi}{9 \sqrt{3}}$ for $\Lambda = 1.5d$ and is independent on $d$. 

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Figure 1. Sample and method. (a) FTIR absorbance $A_{bs} = -\log(T)$ map (x-y values in pixels) of metal-insulator-metal (MIM) metasurfaces at a single wavenumber [cm$^{-1}$] (wavelength [nm]) (see geometry in the top inset). Diameters $d$ ranged from 500 nm (pattern #1) to 1600 nm (#22) with $\Delta d$ nm the diameter increment changing from 10 to 100 nm ($d$ is marked on the map). The triangular lattice period of the nanodisk pattern was $\Lambda = 1.5d$. Thicknesses of MIM layers: Au film was 200 nm, Au nanodisk was 50 nm, and polyimide layer was 60 nm, single pixel on the sample was $25 \times 25$ µm$^2$. (b) The integrated absorbance over multiple pixels of the #18 area at four polarisation angles $0^\circ$, $\pi/4$, $\pi/2$, $3\pi/4$ vs. wavenumber. $0^\circ$ is the horizontal x-axis on the image.

The Fourier transform IR (FTIR) spectral imaging was carried out with a PerkinElmer Spotlight 3000 spectrometer (Spectrum One, PerkinElmer Inc., Waltham MA, United States) with an IR microscope, the automatic xyz-stage with a sample holder, and $16 \times 1$ linear detector array of Mercury Cadmium Telluride (MCT) sensors with a square pixel size of 6.25 µm. Spectral analysis was carried out with 4 cm$^{-1}$ spectral resolution.

Polyimide has several bands whose orientation can be used for determination of molecular alignment: 1780, 1745, 1520 and 1400 cm$^{-1}$ bands are for the C=O symmetric (chain axis), C=O asymmetric (ring tilt), $C_6H_5$ aromatic rings (phenyl) tangential vibrations, and C-N-C axial stretch, respectively [25–27]. The parallel (to film) bands are at 1491 cm$^{-1}$ [$\nu C–C$; skeletal vibration of 1,2,4-trisubstituted benzene ring in diamine moieties] and 1501 cm$^{-1}$ [$\nu C–C$; skeletal vibration of 1,4-disubstituted benzene in diamine moieties], while the perpendicular band is at 1724 cm$^{-1}$ [$\nu C=O$; out-of phase asymmetric stretching of carbonyl bonds in imide rings] [25–27]. These bands are typically used for evaluating the molecular anisotropy of PMDA and ODA. The tilt of PMDA ring units and the chain axis shows a preferential orientation for films thinner than 15 nm [27]. This structural anisotropy decreases rapidly as a function of increasing film thickness but the chain axis direction maintains a constant value even for thick films, indicating that a good degree of anisotropy exists [27]. Upon crystallisation, the C=O stretching mode decreases by 8 cm$^{-1}$ from 1725 to 1717 cm$^{-1}$ due to an increase in chain conjugation in the ordered state [27]. Films thinner than 15 nm have lower packing efficiency, evidenced by the decrease in the transverse C-N-C stretch (1117 cm$^{-1}$) for the thinner films. A better packing induces a higher degree of ring coplanarity and increased conjugation. Anisotropy and the main chain orientation at a range of temperatures (10–570 K) for polyimide films (0.1–300-µm-thick) of different compositions were directly measured by temperature wave analysis (TWA) [28]. Temperature diffusivity has a strong increase at temperatures below 20 K due to an increase of the phonon mean free path (from 0.8 to 3.1 nm) in an amorphous phase. Temperature diffusivity differed ~10 times due to the main chain orientation in the transverse direction of the film with anisotropy larger for thinner films [28]. A large anisotropy of temperature
diffusivity for the in-plane and out-of-plane modes were observed in an industrial grade polyimide [29]. It is expected that anisotropy of polyimide nanofilm can be exploited for polarisation properties of MIM emitters at IR wavelengths.

3. Results and Discussion

3.1. 4-pol. Chemical Mapping: Image Shifts and Baseline Correction

Figure 1a shows an absorbance map of MIM areas with diameters \( d \) ranging from 500 nm (pattern #1) to 1600 nm (#24) with increment \( \Delta d = 50 \text{ nm} \). The triangular lattice period was \( \Lambda = 1.5d \) with a single pixel on the sample being \( 25 \times 25 \mu \text{m}^2 \). Figure 1b shows the corresponding integrated spectra from area #21 at four polarisations. At the magnification used, the side length of each area was approximately 10 pixels (pattern area \( \sim 250 \times 250 \mu \text{m}^2 \)). The integrated absorbance over the sample area, showed strong differences in the MIM regions with different diameters recognisable by the blue-yellow (weak-strong) absorbance map; quantitative analysis at specific wavelengths is presented further in the text. Absorbance amplitude at specific absorption bands were polarisation dependent (b), which provides a direct motivation to apply the four polarisation method. The strongest absorbance band for C=O stretch at 1810 cm\(^{-1}\) was chosen for the orientation analysis (Figure 2a). Orientation angle \( \theta_O \) for the best fit of the absorbance at the four \( \theta \) angles by \( A(\theta) \propto \text{Amp} \times \cos(2\theta - 2\theta_O) \) is shown in Figure 2b. The length of arrows is proportional to the amplitude of the absorbance (the strongest absorbance). It is apparent that the strongest orientation changes were observed at the very edges of the MIM regions where absorbance changed over 2–3 pixels (\( \sim 50 \mu \text{m} \)). This indicates the importance of alignment of the images taken at different orientations of the polarisation grid. Slight lateral shifts occur when polariser is rotated, primarily due to noninfinity corrected optics in the spectrometer (beam had a slight convergence at the mesh-grid polariser plane).

Next, chemical mapping was carried at a larger magnification (a smaller field of view) with pixel size of \( 6.25 \times 6.25 \mu \text{m}^2 \). Since there were small lateral shifts between images taken at four different orientations \( \theta \), we applied lateral xy-plane compensation shifts as illustrated in Figure 3a. The central cross sections of the absorbance map along x and y-axes were used for alignment compensation of the overlay Figure 3c. The judgement of best compensation was carried out by maximising the area of overlap (below the cross section curve) at four polarisation angles.

Once lateral compensation of image overlay was made (Figure 3), the integrated absorbance was baseline corrected. For this, a central region of the pattern where absorbance is maximum was selected (two edge pixels were not included in calculating the average absorbance at 1810 cm\(^{-1}\)).

Figure 2. Orientation mapping. (a) FTIR Absorbance \( Abs = -\lg(T) \) map of metal-insulator-metal (MIM) metasurfaces at the 1810 cm\(^{-1}\) polyimide band (see Figure 1b). (b) Orientation angle \( \theta_O \) extracted from a fit to the absorbance at four polarisation angles by \( \text{Amplitude} \times \cos^2(\theta - \theta_O) \). The length of arrow is proportional to \( \text{Amp} \) of absorbance and the orientation of absorbing dipoles is \( \theta_O \); \( 0^\circ \) is x-axis (horizontal).
absorbance spectrum). The average spectra are shown before and after baseline correction in Figure 4. First, the region where absorbance does not change (out from the absorbance bands at 3250 cm\(^{-1}\)) was set as the minimum and was intensity shifted for all four spectra to match. In this particular example (Figure 3), it was corresponding to the zero absorbance \(A = 0\). Spectra measured at all four polarisations was set to the the same minimum to correct for the baseline.

Figure 3. Compensation for xy-plane shift in four-polarisation maps. (a) Principle of x and y-shifts for centring the maps; the images for all four polarisations was overlayed. (b) Absorbance maps of only two MIM regions (larger magnification as compared with Figure 2). One pixel is 6.25 \(\times\) 6.25 \(\mu\)m\(^2\) on the sample. (c) The cross-sectional absorbance for four polarisations \((0, 45, 90, 135)\) before and after compensation shifts.

Figure 4. Baseline correction for the integrated absorbance; integration was carried out over the most uniform part of MIM region excluding the edge regions where strongest absorbance changes occurred. The most transparent spectral region was set as the same minimum for all four polarisations (without normalisation nor amplitude change). The negative \(A\) values were obtained at a 2380 cm\(^{-1}\) CO\(_2\) band and it is a normalisation artefact.

After the lateral compensation and baseline correction, the four polarisation fit was carried out for every single pixel in the hyperspectral data set. The amplitude of absorbance
Amp and the orientation angle $\theta_O$ were extracted. Inset in Figure 5 shows the result in two MIM regions (patter #1 and #2). The difference in gold nanodisk diameter $\Delta d = 50$ nm and period $\Delta \Lambda = 1.5d = 75$ nm contributed to a spectral shift in plasmonic band. This shift is visualised by plotting all the four polarisation absorbance spectra from both MIM regions (enclosed in the red boxes in the inset). Separate families of four polarisation spectra are most clearly distinguishable at the 3860 cm$^{-1}$ O-H stretch and 2985 cm$^{-1}$ vs. 2735 cm$^{-1}$ alkyl C-H bands. The plasmonic band defines location of the C-H band due to the E-field enhancement defined by an spectral overlap of the spectrally wide C-H and plasmonic bands. There is a weak absorbance at these bands which can be observed for the $d > 0.5$ µm which shifts the plasmonic band into smaller wavenumbers (longer wavelengths). The absorbance values at the maximum of the bands $\sim 3000$ cm$^{-1}$ are proportional to the local field enhancement and their spectral form is defined by the localised plasmon; the band centred at 2750 cm$^{-1}$ ($\lambda = 3.64$ µm) and bandwidth of $\pm 250$ cm$^{-1}$ (at the baseline) corresponds to the plasmonic spectral bandwidth of 0.67 µm or 6 meV. By placing nanodiscs of different diameters over nanothin polymer film, the weak absorbance can be quantified. This also implies, that by creating anisotropic patterns of top-layer nanostructures in MIM metasurfaces, a strongly anisotropic response is expected as observed by using nanoparticles [30]. Enhancement of E-field component perpendicular to the surface (aligned with direction of propagation) is a feature which can probe not only lateral in-plane field enhancements [31].

![Figure 5](image_url)

**Figure 5.** Absorbance map (top inset) and region-averaged absorbance spectra at different spectral windows: wide and narrow (at four polarisations after compensation shift and baseline correction). The spectra from the pattern #2 and #1 ($d = 550$ nm and 500 nm, respectively) are overlaid. See Figure 6 for detailed orientation map. One pixel is $6.25 \times 6.25$ µm$^2$ on the sample.

More crowded absorption bands and lower wavenumbers are better resolved on the zoomed-in (right) spectrum in Figure 5. Clear spectral shifts are discernible due to plasmonic band interaction with polyimide absorbance bands around 1400 cm$^{-1}$ where shifts by $\sim 15$ cm$^{-1}$ occurred; eye guide lines in the Figure 5b. It is however recognisable that there was no apparent difference between spectra measured at different polarisations. This implies that orientation of polyimide was not pronounced. This is understandable since the way the polyimide was formed is known to produce amorphous films. The orientation of polyimide is visualised next by plotting orientation angle $\theta_O$ at several absorption bands (Figure 6). A random orientation was obtained from the best fit by four
polarisation orientation measurement at the 3850 cm\(^{-1}\) O-H stretch band depicted by orientation of a bar while the length of the bar is proportional to the absorbance amplitude of the cos-fit at for orientation angles. More ordered absorbers were mapped at the 2735, 1400 and 1320 cm\(^{-1}\) bands. Importantly, there was no obvious edge effect in orientation maps which were observed at lower magnification even without compensation of image shifts due to orientation of polarisers (Figure 2b).

3.2. Anisotropy, Orientation Maps and Absorbance Line-Shapes

From the 4-pol. fit the orientation of absorbers \(\Theta_0\) can be extracted. For the larger disk diameters \(d\), the plasmonic resonance and field enhancement in the polyimide 60-nm-thick film occurs at the longer wavelengths (smaller wavenumbers) with rich spectral features (Figure 1b). Figure 7 shows orientation maps \(\Theta_0\) in colour for the regions #22 and 21 at several absorbance bands. Apart from the edge effects (edges are different on left-right sides as compared with the top-bottom for the triangular lattice pattern), there were apparent orientation patterns for the 2735 cm\(^{-1}\) C-H alkyl band and surprisingly for the O-H (water) band at 3850 cm\(^{-1}\). There was approximately 90° orientation difference between the two. Since polyimide is water permeable material \([32]\), there should be preferential adsorbed water orientation inside polyimide film. As described previously in Section 2, polyimides have anisotropy with preferential molecular alignment in the plane of film and perpendicular to it. More detailed measurements of the absorption at the C-H alkyl bands were investigated where anisotropy was present. The large planar PMDA segment of polyimide has a C-H predominantly aligned in the direction perpendicular to the molecular chain (vertical in the chemical structure shown in Figure 7).

Figure 8a shows 4-pol. data plotted for the all segments #1-22 after the position shift and baseline correction were made as previously described. There was a distinct pattern of the absorbance peaks blue-shifted (higher energy/wavenumber) for the 0° (horizontal) orientation while the largest red-shift was for the 90° (vertical) orientation in back-reflected signal. This tendency was consistent over the entire O-H and C-H bands 3700–2700 cm\(^{-1}\) window and extending to the low energy 1000 cm\(^{-1}\) spectral range where isotropic absorbance was detected (see Figure 7). This polarisation response can be explained by the plasmonic pattern which has larger separation between Au-disks in horizontal direction as compared with vertical, \(\Lambda_H > \Lambda_V\). As we showed for the rectangular pattern with different periods in horizontal and vertical directions \([33]\), the absorbance along the larger period of nanodisks was blue-shifted and vice versa or visible near-IR spectral range. The same scaling was observed in the case of MIM patterns for IR wavelengths (Figure 8a). The orientation of absorbing dipoles \(\Theta_0\) determined from the 4-pol. method at a particular wavenumber was found to be dependent on the polarisation and wavelength at which it was measured (Figure 8b). This is a consequence of two contributions: (1) the cross-coupling between plasmonic bands of different separation between nanoparticles (discussed above) and (2) phase changes around the absorption band. Apart of the purely plasmonic nature of nanodisks (1), these small \(\sim 15\) cm\(^{-1}\) spectral shifts for the two perpendicular polarisations can be additionally affected by the very nature of the phase changes (2) around the absorption band of polyimide discussed next.
Figure 6. Sub-wavelength mapping of MIM metasurface. Absorbance maps at selected wavelengths in the region #2 and #1 overlaid with orientation angle $\theta$ map (spectra are shown in Figure 5). One pixel is $6.25 \times 6.25 \, \mu m^2$ on the sample. Each pixel contains approximately 6–8 periods of the MIM structure: #1 has $d = 0.5 \, \mu m$ and period of $\Lambda = 1.5d = 0.75 \, \mu m$, while the wavelength is 7.14 $\mu m$ at the 1400 cm$^{-1}$. 
Figure 7. Orientation angle $\theta_0$ obtained from the 4-pol best fit at different absorption bands (see wavenumbers) for the #22, 21 regions (see Figure 1). The top-inset shows chemical formula of PMDA-ODA polyimide.

Figure 8. Spectral absorption lineshape dependence on the polarisation (for compensated shifted and baseline corrected spectra). (a) Cumulative spectra from all #1-22 regions at four polarisations; the inset shows the absorption map. The quality factors of the resonance bands is $Q \equiv \omega_0/\Delta \omega = 1/(2\gamma) \approx 11$. (b) The single polarisation $0^\circ$-horizontal (red) and $90^\circ$-vertical (blue) absorbance maps at the maximum of the corresponding absorbance (see, (a)). Line-markers show the orientation measured from 4-pol. angles overlaid on the absorbance map at the particular wavenumber. The inset shows phase change $\phi$ at the resonance $\omega_0$ of harmonic oscillator at different damping $\gamma = 0.05$ (weak) and 0.5. The E- and H-field orientations for reflection from a surface with refractive index $n > 1$ and $n < 1$ are shown; subscripts “in” and “re” stands for the incident and reflected, $k$ is the wavevector.
The phase change around the absorption band of material with complex refractive index \((\hat{n} = n + i\kappa)\) have the phase change due to real part (a phase delay) and due to change of phase at the resonance. For the considered here case, polyimide and gold optical properties are important. The phase change of the reflected field \(E_r\) (in air) from the surface with refractive index \(n\) is defined by \(E_r = -\frac{n-1}{n+1}E_{in}\), where \(E_{in}\) is the incident E-field; the “-” sign means the opposite phase or the \(\pi\)-shift. When \(n > 1\), there is a \(\pi\)-shift between the incident and reflected E-fields of light (see the inset in Figure 8b). Since the real part of refractive index of gold \(n < 1\) for the visible-IR spectral range, there is no phase change between \(E_r\) and \(E_{in}\). For polyimide with \(n \approx 1.5\), there is \(\pi\)-shift upon reflection. Metamaterial reflectors are designed to harness vectorial nature of reflection [34].

Since the optical absorbance measurements of MIM structures were carried out in reflection, the phase changes in 60-nm-thick polyimide were enhanced due to double thickness (optical path) and the E-field enhancement which was 10-100 for intensity \(E^2\). This contributed to a stronger absorption. At the absorbing dipole resonance at a cyclic frequency \(\omega_0\), there is a phase change from 0 to \(\pi\) as frequency \(\omega\) is increasing. From the mechanical oscillator analogy, the phase change is \(\phi = -\arctan \frac{2\gamma \omega_0}{\omega^2 - \omega_0^2}\) for \(\omega < \omega_0\) and \(\phi = -\pi + \arctan \frac{2\gamma \omega_0}{\omega^2 - \omega_0^2}\) for \(\omega > \omega_0\) modulo \(2\pi\), where \(\gamma\) is a dimensionless damping factor defining the quality \(Q = \frac{\omega_0}{\gamma \omega}\) of the resonance; the equation of mechanical motion is defined as \(m \ddot{x} + 2m \gamma \omega_0 \dot{x} + m \omega_0^2 x = F_0 \sin(\omega t)\) for inertial mass \(m\), \(F_0\) is the force amplitude acting at cyclic frequency \(\omega\), \(\omega_0\) is the resonance frequency and \(x, t\) are the space and time coordinates, respectively. The inset in Figure 8b shows the phase change \(\phi\) at the resonance. In the MIM structure, reflection from the top-Au disks and bottom-Au film will have a change of phase due to absorption in the polyimide (I-part in MIM); there is no phase change due to reflection from Au. For the aligned absorbers in polyimide, the red-shifted absorbance wing will have a less reduced intensity as compared with the blue-shifted absorbance wing where phase is lagging by \(\pi\). Hence, absorbance anisotropy due to molecular alignment is affected by the phase change and asymmetry in the absorption peak. This phase change around the absorbing line can be also coupled with birefringence to cause polarisation change of the back-reflected light. The spectral line shapes of the absorption bands are also dependent on the measurement technique for measurements in transmission, attenuated total reflection or near-field scattering due to their different sensitivity to real and imaginary part of the refractive index [35–37].

### 4. Conclusions and Outlook

It was demonstrated that the four polarisation method can be applied to characterise thin film (60 nm polyimide) in MIM metamaterial patterns. The plasmonic band was designed for plasmonic response at a specific IR wavelength defined by the diameter of nanodisks and period of the lattice. By choice of isotropic triangular array of nanodisks, the orientation effects, if any, in the nanofilm of isolator/dielectric in MIM metasurface can be determined from the orientation maps of \(\theta_O\). The plasmonic band of nanodisks and the triangular lattice has isotropic plasmonic response. It was shown that a lateral shift compensation and baseline correction were critically important to obtain reliable fits since the matching pixels in the four images were compared for the absorbance values. With this alignment compensation, there were no edge artefacts observed in the orientation maps.

The plasmonic band is shown to affect the absorbance however does not impose orientational anisotropy in the detected absorbance. The field enhancement typical to such structures is on the order of 5–10 for the local E-field at the edges of nanodisks and below it. This enhancement is responsible for detection of minute absorption changes in the nanofilm of polymer. Plasmonic spectral tunability of E-field enhancement and absorbance is promising for design of spectrally narrow emitters for the IR band. Indeed, the Kirchhoff’s law defines reciprocity between the absorbance \(A\) and emittance \(A = E\), where \(E = 1 - R\) for transmittance \(T \rightarrow 0\). We experimentally tested it for the chemical mapping IR region [38]. For the MIM design with reflectance \(R \rightarrow 0\) a perfect absorber \(A = 1\) can be made, which will be an equally efficient emitter. This can be useful for IR and
visible plasmonic sensors \cite{39,40}. Metasurface based filters and emitters are promising for the space applications where faster, cheaper, and lighter are driving practical solutions.

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