Surface Plasmon Resonance for In-Plane Birefringence Measurement of Anisotropic Thin Organic Film

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Abstract
The measurement of in-plane birefringence ($\Delta n$) of ultrathin film is challenging due to a significant deviation of physical properties of materials in ultrathin regime as compared to that in bulk state. Surface plasmon resonance (SPR) phenomenon can be employed to measure change in refractive index of ultrathin film at a very high resolution. This article discusses simulation of SPR phenomenon in Kretschmann configuration for the measurement of $\Delta n$ in organic thin film exhibiting nematic-like ordering on the two-dimensional gold surface. The distribution of plasmonic field on the gold surface was found to be anisotropic. This suggested that the coupling plasmonic field with that of organic thin film exhibiting nematic-like ordering on the gold surface will be non-isotropic. Therefore, a nonzero difference in resonance angle (RA) was obtained from SPR measurement performed along the optic-axis (OA) and orthogonal to OA of the in-plane nematic ordering ($\Delta \theta$). A calibration surface showing the variation of ($\Delta n$) as a function of $\Delta n$ and thickness of thin organic film consisting of shape anisotropic tilted molecules exhibiting nematic-like ordering on gold surface was obtained. This calibration surface was employed for the measurement of $\Delta n$ of single layer of Langmuir–Blodgett films of cadmium stearate (CdSA) and 4’-octyl-4-biphenylcarbonitrile (8CB) deposited on SPR chips. The thickness of the LB films was estimated using X-ray reflectivity measurement, and $\Delta \theta$ was measured using a home built SPR instrument. The $\Delta n$ values were found to be 0.012 and 0.022 for ultrathin films of CdSA and 8CB molecules, respectively.

Keywords Surface plasmon resonance · Kretschmann configuration · In-plane birefringence · Langmuir–Blodgett film · FDTD simulation

Introduction
The optical phenomenon surface plasmon resonance (SPR) is very popular owing to its remarkable application in the field of sensors. The phenomenon facilitates a highly sensitive and label-free sensing for a variety of biological and chemical analytes [1–3]. The underlying principle for a SPR sensor is based on measurement of changes in refractive index (RI) at a very high resolution due to molecular interactions. The surface plasmon polaritons (SPP) can be excited at a metal–dielectric interface by an incident electromagnetic wave traveling via a coupling medium with RI greater than 1.0. The resonance can be established by matching the wavevectors of the incident and the SPP waves. At the resonance, a maximum energy will transfer from the incident wave to the SPP wave leading to extinction of the characteristic incident electromagnetic wave from the spectrum [4–6]. In the widely utilized Kretschmann configuration of SPR, a p-polarized monochromatic electromagnetic wave is allowed to incident on the metal surface via a coupling prism [7, 8]. In order to establish the SPR, the angle of incidence is varied and the reflected intensity is recorded. At resonance, the reflected intensity diminishes to minimum. The resonance angle is unique for the given metal–dielectric interface. Therefore, any adsorption of analytes at the metal–dielectric interface during sensing can alter the dielectric nature and hence resonance angle (RA) shifts. The shift in RA can be measured very precisely, and the corresponding change in RI can be calculated theoretically using the Fresnel’s relations [9]. In addition to the traditional sensing applications, the SPR phenomenon can also be used for the measurement of optical anisotropy...
in thin films [10], temperature measurement [11–13] and optical filter [14]. A typical resolution of the Kretschmann configuration-based SPR instrument lies in the range of $10^{-5}$ to $10^{-7}$ RIU [9, 15, 16]. Such a high resolution in the measurement of RI using SPR was successfully utilized for quantification of optical anisotropy in ultrathin films. Anisotropy in thin film arises due to tilt of shape anisotropic molecules (e.g., rod-shaped calamitic liquid crystal molecules) with respect to surface normal which may yield in-plane nematic ordering. In an earlier report by our group, the optical anisotropy in ultrathin films was estimated experimentally using the SPR phenomenon by measuring shift in the RA in orthogonal directions of the films exhibiting different degree of optical anisotropy [10].

The reported anisotropy in the ultrathin films was estimated from SPR angle measurements in randomly chosen orthogonal directions. In order to estimate the in-plane birefringence ($\Delta n = n_e - n_o$), the SPR measurement has to be performed along the optic axis (OA) of the thin film and orthogonal to it. The measured values of RI along OA and orthogonal to OA of a given anisotropic thin film exhibiting nematic ordering in two-dimensional plane can be defined as $\Delta \theta$. In the present work, we have modified our experimental setup by integrating a rotating platform (rotation axis along X-axis, Fig. 1) with a resolution of 0.1° to rotate the film deposited substrate and measure the SPR response in-situ as a function of angle of rotation of the film. This modification ensures alignment of optics for the measurement of $n_e$ and $n_o$ and hence $\Delta n$ of the ultrathin film. The RI of ultrathin film will be dependent on several factors including the surface density, orientation of molecules, surface morphology and the thickness of the film. Thus, the RA measured using SPR phenomenon will be dependent on such factors. Therefore, a systematic study is needed for the estimation of important optical parameter related to thin film, viz. in-plane birefringence ($\Delta n$).

The reports in the literature in general provide the value of birefringence of the bulk material; however, due to reduction of dimension of the material, the physical properties deviate largely from that of bulk. Therefore, measurement of physical properties of a material at the lower dimension is essential for material engineering followed by device fabrication. The physical properties of the low-dimensional materials like two-dimensional thin film depend on its thickness. Hence, a calibration curve is essential for quantifying the dependencies of a physical property on any such parameters. Since the SPR phenomenon can be potentially employed for the measurement of RI at a very high resolution, a small in-plane birefringence due to tilt of shape anisotropic organic molecules even in a single layer can be measured. Such film with tilted molecules may exhibit nematic organic molecules even in a single layer can be measured. Such film with tilted molecules may exhibit nematic ordering on the surface. In this article, we present a calibration surface showing the dependency of $\Delta \theta$ on $\Delta n$ and thickness of the thin organic film. The calibration surface was obtained through simulation, and it was utilized for the estimation of $\Delta n$ of single layer of Langmuir–Blodgett (LB) films of cadmium stearate (CdSA) and 4’-octyl-4-biphenylcarbonitrile (8CB) molecules. The values of thickness and $\Delta \theta$ of the LB films of CdSA and 8CB were obtained from X-ray reflectivity and a home built SPR instrument, respectively, and these values were used in the calibration surface for the estimation of the respective $\Delta n$.

![Fig. 1](image_url)

Fig. 1 A schematic of (a) simulation setup showing the major components as depicted. The plane of polarization is XY. The angle of incidence of the monochromatic light (L) is $\theta_i$, thickness of each material and detector (D) are shown and (b) a single layer of shape anisotropic molecules (rod shaped) tilted with respect to X-axis along Y-axis on the YZ plane. The projection of the molecules is shown in black. Such projection resembles nematic ordering on 2D plane with optic axis along Y-axis.
Simulation Setup

A finite difference time domain (FDTD) method was employed for the simulation of SPR phenomenon in the Kretschmann configuration using a commercial package of Lumerical [18, 19]. The FDTD method is highly reliable and advantageous over other techniques in solving Maxwell’s equations for complex geometries of materials. The simulation setup is shown in Fig. 1a.

The simulation was carried out using a monochromatic plane wave source (L) having a wavelength of 635 nm. The perfectly matched layer (PML) boundary condition with steep angle profile of 12 layers was used in order to minimize reflection from the boundary as the wave enters into the layer. Linear discrete Fourier transform monitors were used to capture reflected and transmitted electric field at 350 nm away from the interface. The source was made to incident on the gold layer via glass medium at an angle of incidence of \( \theta_i \). In order to obtain the resonance angle, the incident angle sweep was generated from 40°-48° with 251 iterations. The mesh override was selected with 251 iterations. The resolution and sensitivity of the equipment are 1.92 \( \mu \text{RIU} \) and 53°/RIU, respectively. The SPR chip consists of 0.5 mm glass plate (RI=1.51) deposited with 50-nm-thick gold film through sputtering technique. The chemicals stearic acid and 4'-octyl-4-biphenylcarbonitrile (8CB) were procured from Sigma-Aldrich. Both the molecules yield a very stable Langmuir monolayer at the air–water interface and are ideal systems for utilizing them for fundamental studies [20, 21]. A single layer of LB film of CdSA deposited at 30 mN/m can yield an average molecular tilt of \( \sim 10^\circ \) with respect of surface normal [22], and similarly, that of 8CB deposited at 4 mN/m yields an average molecular tilt of \( \sim 60^\circ \) with respect to the surface normal [23]. A single layer of LB films of CdSA and 8CB was deposited onto SPR chips at target surface pressure of 30 and 4 mN/m, respectively, using a LB trough (KSV-NIMA). The thickness of the LB films was measured by X-ray reflectivity (XRR) technique using a X-ray diffractometer equipped with thin film analysis unit (SmartLab, Rigaku).

Results and Discussion

A p-polarized electromagnetic wave was allowed to incident at the glass–gold interface as shown in Fig. 1. The evanescent wave generated in the gold film can excite the surface plasmon polaritons (SPP). Figure 2a shows the SPR curve for the gold-air interface. It exhibits the RA value of 44°. The SPR curve and hence the RA value obtained through the FDTD calculation for the gold-air interface are in agreement with the literature [3]. The two-dimensional (2D) electric field profile due to the surface plasmon polaritons at the resonance angle was obtained and is shown in Fig. 2b. According to the chosen geometry, the YZ plane corresponds to the gold-air interface and the plane of polarization is XY. The SPP are excited by the incident p-polarized electromagnetic wave. Therefore, the electric field of the incident electromagnetic wave is restricted in the XY plane and has zero component along the Z-axis. This may lead to surface distribution of the surface plasmon field to be anisotropic in nature. For a chosen 1000 nm×1000 nm mesh size, the anisotropic nature of the plasmonic field can be clearly seen in the image. This indicates that the excitation of SPP is non-isotropic and hence there is an immense possibility that coupling of such anisotropic field with optically anisotropic material will be direction dependent. Therefore, the SPR measurement of such anisotropic materials in different directions with reference to the plane of incidence can yield different resonance angle. The materials with optical anisotropy can be obtained either in bulk state or as a single layers of organic molecules exhibiting some shape anisotropy. The rod-shaped calamitic liquid crystal molecules exhibit a birefringence of \( \sim 0.2 \) in the bulk nematic phase [24, 25]. The liquid crystal molecules have great technological importance where such

Experimental

The Kretschmann configured SPR instrument was developed in the laboratory [9]. The equipment utilizes 5 mW laser of wavelength 635 nm, coupling prism (RI=1.51) and a segmented photodiode as detector. The resolution and sensitivity of the equipment are 1.92 \( \mu \text{RIU} \) and 53°/RIU, respectively. The SPR chip consists of 0.5
optical anisotropy play significant role in display device applications. When such shape anisotropic molecules are aligned onto solid substrate through self-assembly or a controlled Langmuir–Blodgett deposition technique [26], the deposited single layer can induce a degree of optical anisotropy due to a collective tilt of the molecules with respect to the surface normal. Hence, the projections of such tilted molecules can yield a nematic ordering on the two-dimensional surface. In our simulation setup, we created an organic layer of a given thickness whose RI is chosen to be anisotropic by assigning different values along X, Y and Z axes. The SPR spectra were obtained through simulation when the plane of incidence is parallel and perpendicular to the OA of the in-plane nematic ordering in thin film of organic material. The difference in RA was noted as \( \Delta \) from the SPR spectra obtained in these two geometries.

Figure 3 shows the SPR curves obtained for an anisotropic thin film of 2 nm thickness having \( \Delta n \) as 0.1. The corresponding RAs were obtained as 44.45° and 44.80° yielding \( \Delta \theta \) to be 0.35°.

In the simulation, the SPR curves are obtained for different values of \( \Delta n \) and thickness of organic film and the corresponding \( \Delta \theta \) was obtained. A calibration surface displaying the variation of \( \Delta \theta \) as a function of \( \Delta n \) and film thickness \( (t) \) is plotted in Fig. 4.

The simulated data are fitted with a surface polynomial curve

\[
\Delta \theta = P_1 + P_2t + P_3\Delta n + P_4t^2 + P_5\Delta n^2 + P_6\Delta n + P_7t^2\Delta n + P_8t\Delta n^2 + P_9\Delta n^3
\]

(1)

where \( P_i, i = 1, 2, 3...9 \) are the fit parameters. The fit indicator R-square was 0.993 which suggests a good fitting. The fitted calibration surface as represented by the Eq. 1 can be useful for the determination of \( \Delta n \) of thin films using SPR phenomenon in the very simple prescribed methodology as discussed here.

We have utilized the calibration surface (Eq. 1) for the estimation of in-plane birefringence of ultrathin films fabricated using the standard Langmuir–Blodgett (LB) technique. We fabricated a single layer of LB films of cadmium stearate (CdSA) and 8CB molecules on the SPR chips at the target surface pressure of 30 and 4 mN/m, respectively [20, 21]. The molecules in a single layer of LB films of CdSA and 8CB were tilted by \( \sim 10 \) and \( 60^\circ \) with...
respect to the substrate normal [22, 23]. Hence, they can offer anisotropy in the refractive indices and therefore can exhibit nonzero values of $\Delta n$. The thickness of the LB films was obtained from X-ray reflectivity measurement (Fig. 5). The experimental curve was fitted using Parrat’s formulation [27], and the thickness of the film was estimated therefrom. The thickness of gold film deposited over the glass plate, LB films of CdSA and 8CB deposited over such gold substrates was estimated as 49, 2.4 and 2.0 nm, respectively.

The LB films of CdSA and 8CB were scanned using the SPR instrument. The change in RA along the such orthogonal directions ($\Delta \theta$) was found to be 24 and 71 millidegree, respectively. Such nonzero values suggest the anisotropy in the ultrathin films. The values of thickness and $\Delta \theta$ were substituted in the calibration surface, and $\Delta n$ of the ultrathin films of CdSA and 8CB were estimated as 0.012 and 0.022, respectively.

Our analysis gives a strong foundation for the measurement of in-plane birefringence of ultrathin films of organic molecules. Such information is essential for the development of optical devices.
Conclusion

The measurement of physical properties at a lower dimension is challenging due to large dependencies of the properties on other parameters, e.g., thickness of the thin film, aspect ratio of nanomaterials, morphology, etc. In this article, we simulated the SPR phenomenon in Kretschmann configuration to measure the in-plane birefringence of thin organic film. The thin film consists of rod-shaped organic molecules tilted on the gold surface and thus exhibited in-plane nematic ordering. We performed simulation to obtain a calibration surface showing the variation of $\Delta n$ as a function of $\Delta \theta$ and thickness of the film. Such calibration surface was employed for the estimation of $\Delta n$ in single layer of LB films of CdSA and 8CB. This study provides a vital methodology for the measurement of very small value of $\Delta n$ even in case of a single layer of ultrathin organic film. Further studies involve the role of percolation in quasi-two-dimensional film on the optical properties.

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Author Contributions Simulation and part of experiments were done by Amrit Kumar. Conceptualization, data analysis and manuscript preparation were done by Raj Kumar Gupta. Data analysis and manuscript preparation were done by Manjuladevi. SPR measurements and part of experiments were done by Ashutosh Joshi.

Data Availability Statement The datasets generated during and/or analyzed during the current study are available from the corresponding author on reasonable request.

Code Availability Lumerical is GUI-based commercial simulation package. As such code availability is not applicable. However, some scripts can be made available on reasonable request to corresponding author.

Compliance with Ethical Standards

Conflict of Interest There are no conflicts of interest/competing interests to declare.

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