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Measurement of optical anisotropy in ultrathin films using surface plasmon resonance

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The optical phenomenon, surface plasmon resonance (SPR) is employed for the measurement of optical anisotropy in the ultrathin films fabricated through Langmuir–Blodgett (LB) and self-assembled monolayer (SAM) techniques onto 50 nm gold film supported on BK7 glass substrates. The resonance angle (RA) is measured using a home built setup in Kretschmann configuration. The LB films and SAM can provide a single layer of highly ordered and organized molecules on the two dimensional surface. If the film forming molecules are anisotropic, their organization in the LB films and SAM can yield an anisotropic film due to tilt of the molecules with respect to the surface normal. The SPR spectra are recorded for the two orthogonal directions of the film with respect to the plane of incidence. The spectra are simulated by modeling the Fresnel's reflection from 4-layers viz., prism, gold, ultrathin films and air; and the real and imaginary parts of refractive index are estimated. Our study shows the metallic and dielectric nature of the LB films of bundles of single walled carbon nanotubes (SWCNTs) when the long axis of SWCNTs are aligned parallel and perpendicular to plane of incidence, respectively. The optical anisotropy was estimated from the change in real part of refractive index (Δn_r) of the ultrathin films measured in the orthogonal directions. In addition, we have also studied such optical anisotropy in the LB film of cadmium-stearate and self-assembled monolayer of octadecanethiol.

1. Introduction

Surface plasmon resonance (SPR) is an optical phenomenon which is being potentially used for the detection of molecular specific interaction [1]. Such phenomenon resulted in the development of biological, chemical and gas sensors [2]. SPR technique is label free and non-destructive and hence exhibits numerous advantages over the conventional sensing technology. In the Kretschmann configuration [3], the surface plasmon is excited in 50 nm gold film deposited onto glass substrate which is coupled to a prism with a refractive index (RI) matching fluid. For an incident p-polarized light of fixed wavelength, the SPR occurs at a unique angle of incidence also known as resonance angle (RA). The RA is extremely sensitive to the dielectric layer adsorbed onto the gold surface. Any change in the dielectric layer causes a shift in the RA with respect to the reference. The dielectric (hence optical) properties of the adsorbed material can be estimated by modeling the reflection from different interfaces involved during the process by employing the Fresnel's equation [4]. Wang has demonstrated the condition for the SPR can be altered by altering the dielectrics of a liquid crystal on the metal surface due to the application of electric field [5]. The optical anisotropy in a stable ultrathin film at the air–water interface (known as Langmuir monolayer) has been observed and studied extensively using Brewster angle microscope (BAM) [6–8]. Such anisotropy in Langmuir monolayer arises due to tilt of the molecules with respect to the surface normal [9–12]. In Brewster angle microscopy, the reflected intensity from the air–water interface is extremely sensitive to a change in refractive index at the interface. The refractive index changes due to change in the surface density or tilt variation of the molecules. Therefore, any change in the RI due to tilt variation of the molecules in a given phase of the Langmuir monolayer, changes the reflectivity significantly resulting in variation in grayshades in the visible region of

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the BAM images [10,13,14].

In this paper, we report the measurement of optical parameters (refractive index) in the orthogonal directions of the ultrathin films of well organized bundles of single-walled carbon nanotubes (SWCNTs), octadecanethiol (ODT) and cadmium stearate (CdSA) using a SPR instrument. The ultrathin films of SWCNTs and CdSA are fabricated through Langmuir–Blodgett (LB) technique whereas that of ODT through self assembly on the gold surface. Such ultrathin films offer a well organized and orientationally ordered single layer of the molecules [15,16], which exhibits anisotropy due to the alignment of the molecules (or SWCNTs) in a preferential direction on the substrate. The anisotropy in the films depends on the shape anisotropy of the molecules and their tilt orientation on the substrate with respect to the surface normal [6].

The SPR spectra of the fabricated ultrathin films are recorded in the orthogonal directions of the film i.e., parallel (0°) and perpendicular (90°) with respect to the plane of incidence. We aligned the long axis of SWCNTs along the direction of dipping during the LB film fabrication process [17]. The SPR spectra of LB film of SWCNTs show very interesting result. The film of SWCNTs behaves metal-like and insulating dielectric layer when the long axis of SWCNTs is aligned parallel and perpendicular to the plane of incidence, respectively. The ultrathin films of structurally similar molecules viz., ODT and stearic acid on the gold surface differ with respect to the orientational tilt of the molecules in the single layer. ODT in SAM and CdSA in LB are known to tilt ~30° and ~10° with respect to the surface normal, respectively [18,19]. Therefore, there is a different degree of anisotropy in SAM of ODT as compared to that of LB film of CdSA. We found the optical anisotropy as a change in the real part of refractive index (Δn_r) of SAM of ODT and LB film of CdSA to be 0.24 and 0.10, respectively.

2. Experimental section

The SPR setup in Kretschmann configuration was built in the laboratory (Fig. 1).The material of semi-cylindrical prism was BK7 having the refractive index of 1.51. The 50 nm gold film was deposited onto BK7 substrates by electron beam deposition technique. The thickness of deposited gold layer was monitored in-situ during evaporation process by employing quartz crystal based digital thickness monitor. The substrate and the prism are optically coupled by using refractive index matching fluid (Cargille). The ultrathin films of CdSA and SWCNT were fabricated by LB technique using a teflon trough (Apex Instruments). The stearic acid (SA) was obtained from Sigma–Aldrich. A chloroform solution of the SA having a concentration of 3.5 mM was spread onto an aqueous subphase of 1×10^{-5} M of cadmium chloride ($CdCl_2$) in ultrapure ion-free water (MilliQ, DQ5). A single layer of LB film of CdSA is deposited on the gold substrate at a target surface pressure of 30 mN/m. The tilt of the chains of the molecules in the LB films was reported to be around 10° with respect the surface normal [19]. An isotropic thin film of SA is deposited onto the gold substrate by spin coating technique. A 5 μl of the chloroform solution of SA is spread onto gold substrate rotated at a speed of 7000 rotations per minute. In order to obtain isotropy and homogeneity in the film, it is annealed at a temperature of about 80 °C for 15 min. A uniformly dispersed solution of 9×10^{-3} mg/ml of SWCNTs (Carbon Solutions, P2-SWNT) was obtained by dissolving the nanotubes in dimethylformamide solvent and ultrasonicating the dispersion for about 1 h. The Langmuir film of SWCNTs is found to be stable with a collapse surface pressure of 11 mN/m. The LB films of SWCNTs are deposited onto solid substrates at 2 mN/m and the surface morphology were studied using atomic force microscope (Solver-Pro, NTMDT). We found that the long axis of SWCNTs oriented along the direction of deposition of the film [17]. Such morphology can yield exceptionally high anisotropy in the electrical and optical properties when measured in orthogonal directions. The SAM of ODT was prepared by immersing the gold substrates into the 1 mM solution of ODT in absolute ethanol for about 12 h. The ODT deposited gold substrates were rinsed thoroughly by absolute ethanol followed by HPLC grade chloroform before mounting on the scanning stage of the SPR instrument. The SPR spectra were collected by changing the angle of incidence at a step of $21.2 \times 10^{-3\circ}$ and recording the reflected intensity simultaneously. The reported SPR spectra of the ultrathin films are little broader at the minimum because of low resolution of the data acquisition card (12-bit, National Instruments). In order to check the reproducibility of the data, the SPR spectra were collected from different locations of the films, and from the films deposited in different batches. The RA for the gold film (gold–air interface) was found to be 44°. The average shift in RA ($\Delta\theta$) for the ultrathin films of different materials were estimated with reference to that of RA for the gold film (i.e. 44°). The standard deviation of the RA was found to be in the range of 0.01°–0.02°.

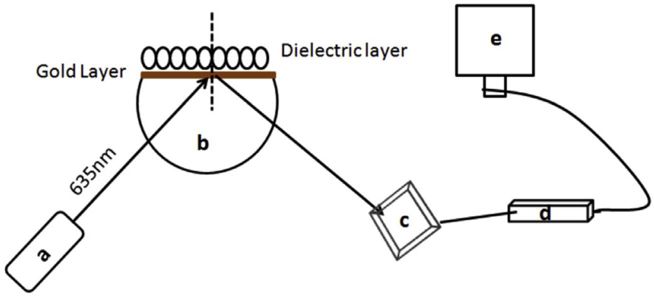

Fig. 1. The schematic of the SPR instrument setup. (a) laser, 635 nm, Newport, (b) semi-cylindrical prism of material BK7, (c) photodiode, OSI-Optoelectronics, (d)Data acquisition card, 12-bit, National Instruments, and (e) computer.

3. Modeling

The SPR spectra are simulated by modeling reflection of light from a 4-layer system viz., prism, gold, dielectric layer, air. In the 4-layer system, the final Fresnel's equation is obtained by considering the reflection from three interfaces viz., prism-gold, gold-dielectric film and dielectric film-air [4]. The final Fresnel's equation of reflectance R_p for the p-polarized light is given by

$$R_p = \left| r_p^2 \right| \tag{1}$$

where r_p is the reflection coefficient for p-polarized wave.

$$r_p = \frac{(M_{11} + M_{12}q_4)q_1 - (M_{21} + M_{22}q_4)}{(M_{11} + M_{12}q_4)q_1 + (M_{21} + M_{22}q_4)} \tag{2}$$

$$M_{ij} = \left(\prod_{k=2}^{3} M_k \right)_{ij} \quad , i,j = 1,2 \tag{3}$$

For the k^{th} layer,

$$M_k = \begin{bmatrix} cos\beta_k & -isin\beta_k/q_k \\ -iq_k sin\beta_k & cos\beta_k \end{bmatrix} \tag{4}$$

Here,