Multilayer Surface Plasmon Resonance Device to Detect Film Surface Configuration and Film Thickness from the Backside

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Abstract: We propose detection of the Surface plasmon resonance (SPR) can be applied to estimate the thickness of the amorphous carbon (α-C:H) films and protein adsorption on their film surfaces. To detect changes using SPR, devices with an α-C:H/Au structure were fabricated. The SPR angle was shifted from 44.24 to 58.44 deg. after deposition of 45 nm thick α-C:H, and from 59.10 to 59.57 deg. by the protein adsorption on the film surface. The film thickness and surface condition could be detected by this SPR system from backside.

Keywords: Surface plasmon resonance, Multilayer device, Detection from backside.

1. Introduction

Surface plasmon resonance (SPR) is the resonance between a surface plasmon wave and an evanescent wave on a metal surface[1-4]. At a metal film on a prism glass block, the light is illuminated from the glass and an evanescent wave penetrates through the metal film. Plasmon waves are also excited at the outer side of the film. When the wave numbers of these waves are close, the SPR phenomenon occurs. As a result, the laser irradiates the back side of the metal film, and the reflection intensity of the laser from the back side of the metal film reduces rapidly at the SPR angle. A plasmon wave depends on the reflective index on the metal surface. Hence, the reflective index is changed by the configuration change on the metal surface, leading to a shift in the SPR angle. SPR has been applied to the detection of biomolecules adsorption on a metal surface under a liquid[5-7]. The SPR sensing technique offers several distinctive features, such as high sensitivity and real time analysis[8-10]. The basic setup of SPR measurement consists of a laser diode, a goniometer, an optical prism coated with a metal film and an optical power detector. These parts are inexpensive and easily obtainable.

When Au is used as a metal layer, the sensing area using the SPR phenomenon is generally 200 nm above the metal. When multilayer structure of thin films on Au films is constructed into this 200 nm, the interactions between film and incrustation on the films can be detected by SPR phenomenon[11]. And the film thickness deposited on Au films is going to be estimated using this multilayer structure. As the beginning on the study, the hydrogenated amorphous carbon (α-C:H) / the Au multilayer structure was fabricated to realize multilayer SPR device for the detection of film thickness on the Au films. And relationship between SPR phenomenon and film thickness of α-C:H films are described in this report. Furthermore, a flow cell attached on the α-C:H layer to detect adsorption of dissolved proteins in the buffer liquids at the α-C:H surface. When total thickness between the α-C:H layer and proteins are less than 200 nm, this adsorption also may be able to detect by SPR detection with this multilayer device.

In this study, we attempted to determine the change in film thickness of an α-C:H film and the protein adsorption on film surface by the detection of SPR on the α-C:H/Au multilayer structure, as shown in Fig. 1. To check the precision of SPR detection, these results for film thickness determinations were compared with the film thickness determined by XRR.

Fig. 1. Schematic illustration of SPR measurement device of α-C:H/Au multilayer structure.

2. Experimental

BK7 and S-TIH-11 optical glasses with refractive indexes of 1.515 and 1.778 were chosen as the substrate, respectively. Au layer was prepared on the glass by sputtering. The α-C:H films were synthesized on this Au/glass substrate by sputtering and electron cyclotron resonance chemical vapor deposition (ECR-CVD). The α-C:H films
were also deposited on silicon substrates under the same conditions. In the sputtering method, \( a\)-C:H films were deposited by radio-frequency (13.56 MHz) sputtering from a graphite target in the presence of argon plasma. In the ECR-CVD method, microwaves with frequency of 2.45 GHz were guided through a rectangular waveguide and introduced into the ECR magnetron excitation chamber. Methane gas (\( CH_4, 99.99\% \)) was distributed in the vacuum chamber using a gas shower. These deposition durations for the \( a\)-C:H film layer were less than 30 min, because these films should be less than 200 nm which was limit of detection for SPR measurement.

In the XRR technique, reflection intensity was measured using X-ray diffraction apparatus (M03XHF MXP3: MacScience Co.) with a Cu lamp with an electric power of 1.6 kW. Information on the density and film thickness is obtained by modeling the reflections; XRR can be used to obtain the density and thickness of carbon films with high precision (0.05 g/cm\(^3\) and 0.1 nm, respectively)[12]. The \( a\)-C:H film thickness and true density were obtained from the XRR profiles using a fitting program (GXRR: Rigaku Co.). The film thickness and density were extracted from the fringe pattern and the total-reflection angle, respectively. In the SPR measurement, the laser beam and the device are set in the Kretschmann-Raether arrangement[13]. Figure 1 shows the SPR measurement setup using the fabricated device. The laser beam passed through a high-refractive-index glass substrate and was monitored by an optical power meter. The wavelength of the laser from the laser diode was 635 nm. The angle of incidence of the laser and the optical power meter were controlled by a goniometer.

The flow cell (volume is approximately 0.5 ml) was attached to the multilayer SPR device to investigate the adsorption of proteins for the films. phosphate buffer (PB) is usually used as the buffer solution for proteins. The PB was mixture of \( Na_2HPO_4\cdot 12H_2O \) and \( NaH_2PO_4\cdot 2H_2O \), and the phosphate coordinated at 0.2 M. Human serum albumin(HSA) was use as protein. HSA containing PB solutions were coordinated at 0.01 in HAS concentrations. These solutions were adjusted to pH 7.

### 3. Results and Discussions

Figure 2 shows that typical XRR curves for \( a\)-C:H films deposited by ECR-CVD and sputtering. These XRR profiles showed good agreement with the calculated profiles simulated using single layer model. So, the densities of the \( a\)-C:H films have uniform density with their thickness. All curves exhibited the fringe patterns. The \( a\)-C:H film thickness varied from 11 nm to 45 nm depending on the deposition time. The film thicknesses of the films fabricated by ECR-CVD were determined to be 26 and 45 nm, and those of \( a\)-C:H films deposited by sputtering were 11, 21 and 31 nm. The critical angle for \( a\)-C:H films depends on only the deposition method. The densities of the films deposited by ECR-CVD and sputtering were obtained to be 1.4 g/cm\(^3\) and 1.6 g/cm\(^3\), respectively.

![Fig. 2. XRR curves of \( a\)-C:H films deposited by ECR-CVD and Sputtering method.](image)

The SPR spectra of the \( a\)-C:H layer deposited by sputtering on a Au layer on optical glass are shown in Fig. 3(a). From the attenuation of the reflected light, the SPR angle was determined to be 44.90 degree for the device consisting of only Au film. The SPR angle was shifted from 44.90 degree to 47.05 degree by the deposition of 11 nm thick \( a\)-C:H film on the Au film. Upon the deposition of thicker layer, the SPR angle shifted 50.48 and 57.44 degrees for film thicknesses of 21 and 31 nm, respectively. The SPR spectra of the \( a\)-C:H layer deposited by ECR-CVD on a Au layer on optical glass are shown in Fig. 3(b). The SPR angle was shifted from 44.24 degree to 49.18 degree by the deposition of 26 nm thick \( a\)-C:H film on the Au film, and the angle reached 58.44 degrees for an \( a\)-C:H film thickness of 45 nm. From these results, the SPR angle shift increased with increasing the film thickness.

![Fig. 3. Reflectance profiles measured for device of the Au and the multilayer device of \( a\)-C:H/Au.](image)

Figure 4 shows the relationship between the SPR angle shift and the \( a\)-C:H film thickness obtained by XRR techniques. The SPR angle shift indicated a change in the di-
electric constant due to deposition of a-C:H film on Au. The SPR angle shift increases with the a-C:H film thickness. The rate of change of the SPR angle with increasing film thickness was different for the two methods of deposition. The reflective index of the laminated material on the Au film has a marked effect on the SPR angle. It is well known that the reflective index of an a-C:H film depend on its density[14,15]. The solid line in Fig. 4 were obtained by calculation and represent reflective index of 1.95 and 1.65 for films deposited by sputtering and ECR-CVD, respectively. Both calculated lines were constructed from more than three plots, because these plots contained the 0 nm thick at 0 degree in the shift of the SPR-angle. The plots obtained by measurement are good agreement with the calculated lines. The reflective indexes have a margin of error of 0.02. However, this margin of error was smaller than difference of the reflective indexes for both films. These differences suggested difference of the true densities measured by XRR. These results indicated that the film thickness can be determined using the a-C:H/Au SPR device with an a-C:H film of the density.

Fig. 4. SPR angle shift varied on film thickness measured by XRR and calculated line of SPR angle shift with the film thickness for a-C:H layer deposited by sputtering and ECR-CVD.

Next, we show you the result of protein adsorption evaluation by SPR analysis. The SPR profiles on protein adsorption evaluation of the a-C:H deposited by sputtering layer on a Au layer are shown in Fig. 5. The profile of (1) was PB placed on the a-C:H layer. The profiles of (2) was PB with 0.01 mM of HSA replaced from (1). The profiles of (3) was replaced from (2) to remove non-adsorbed proteins on the a-C:H layer surface. From the attenuation of the reflected light, the SPR angle was determined to 59.10 degree from profile of (1). The SPR angle was shifted from 59.10 degree to 59.74 degree at the profile of (2) by introduction of protein to a-C:H surface. After remove non-adsorption proteins on profile of (3), the SPR angle shifted to 59.57 degree. The difference of SPR angles between (1) and (3) was 0.47 degree from comparison of SPR angle, and SPR angle of (3) did not back to first profile of (1) which was placed PB without HSA on a-C:H surface. Thus, this angle shift of 0.47 degree indicated protein adsorption on the a-C:H film surface. Thus, it was indicated that a-C:H/Au multilayer devices can detect the protein adsorptions on film surfaces from backside of devices.

Fig. 5. Reflectance profiles measured for device of the multilayer device of a-C:H/Au on protein adsorption tests. (1) was PB placed on the a-C:H layer. The profiles of (2) was PB with 0.01 mM of HSA replaced from (1). The profiles of (3) was replaced from (2) to remove non-adsorbed proteins on the a-C:H layer surface.

4. Conclusion
SPR detection using a-C:H/Au multilayer device was developed to determine film thickness and to detect protein adsorption. The a-C:H/Au device showed an SPR angle shift, which depended on the film thickness and adsorption. These detections were investigated from backside of the films. On film thickness determinations, the rate of SPR angle shift depended on the reflective index, which is related to the a-C:H film density. These results indicate that the thickness of an a-C:H film can be determined by the SPR angle shift on an a-C:H/Au device with an a-C:H film of same density. On protein adsorption detection, SPR angle shift indicated clearly difference compared with non-adsorption. The detection from the backside to estimate film surface configuration and film thickness were realized by means of these multilayer SPR devices.

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References