INTRODUCTION

Surface Plasmons (SPs), also known as surface plasmon polaritons or surface plasma waves, are essentially collective oscillation of free electrons that are trapped on the interface between a metal and a dielectric (Barnes et al., 2003). A visible or infrared light beam can cause excitation of the SPs at the metal-dielectric interface by a glass prism coupler in either Otto (1968) or Kretschmann and Raether (1968) configurations. The so-called surface plasmon resonance based on the Attenuated Total Reflection (ATR) method phenomenon occurs when the momentum of the SPs matches the parallel component of the incident TM light wave vector. As SPR is very sensitive to any change taking place at the outer boundary of the metal, SPR-based sensor technology has great potential for many fields, such as biomedical science, measurement of biomolecular interactions (Campbell and Kin, 2007), quantification of proteins (Mullett et al., 2000) and measurement of DNA (Brockman et al., 2000), detection of hazardous gases and analysis of mercuric ions, as well as the integrated optics and so forth. In the SPR sensor, gold and silver are the optimal options for the metal film. Because of its high chemical stability, gold is a more ideal choice for SPR-based sensor techniques. However, the adhesive strength between the glass prism and gold film is very poor. The weak adhesive strength reduces the stability of the sensor, also decreases the overall performance of the SPR-based sensor. Nonetheless, there has been a little attention on how to improve the adhesive strength between the glass prism and gold film under such condition. On the other hand, because of its peculiar properties such as wide band gap, higher refracting index, non-toxic, super visible and infrared light transmittance, bismuth oxide (Bi$_2$O$_3$) has been widely used in various domains. Adding an additional bismuth oxide film is a promising method for improving the adhesive strength between gold film and glass prism. Thus in this study, we investigated the adhesive improvement between gold and glass using bismuth oxide.

In this study, Au/Bi$_2$O$_3$ bilayer films with various thicknesses of bismuth oxide layer were grown on BK7 prisms by thermal evaporation deposition technique and then undergone heat treatment on the air ambience. The influence of the thickness of layer and post annealing temperature on the adhesive strength of Au/Bi$_2$O$_3$ and Bi$_2$O$_3$/prism was investigated. Also the SPR responses (reflectance vs. incident angle) in the Kretschmann geometry were measured as the function of the thickness of Bi$_2$O$_3$ layer under the ethanol (AR, from Alfa Aesar) dielectric.

EXPERIMENTAL DETAILS

Bi$_2$O$_3$ films and Au films were deposited sequentially on BK7 prism substrates by using thermal...
evaporation technology. High-purity Bi$_2$O$_3$ (99.99%) powder was pressed into a tablet and used for the Bi$_2$O$_3$ ceramic target. And the Au used gold bar (99.99%). Prior to the Bi$_2$O$_3$ growth, the chamber was evacuated down to a base pressure of about 5.0×10$^{-7}$ Pa. During the Bi$_2$O$_3$ film deposition, the working pressure increment was kept at about 1.0×10$^{-3}$ Pa and the deposition time changed from 0 to 1.5 min at an interval of 30 sec while the deposition current was fixed at 180 A. Then, the samples with Bi$_2$O$_3$/prism structure were annealed at 275 Celsius degree for 1 h and then let it cool to room temperature. When the Au films were grown, the working pressure increment was kept at about 5.0×10$^{-3}$ Pa. The Au films covering deposition time of 5 min were grown with fixed current of 240 A. The samples with Au/Bi$_2$O$_3$/prism structure were undergone a heat treatment process at 275 Celsius degree for 2 h.

Field Emission Scanning Electron Microscopy (FESEM) was applied to calibrate the thickness. The adhesive strength between Au and Bi$_2$O$_3$ as well as Bi$_2$O$_3$ and prism of all the samples was measured by Pull-Off Adhesion Tester (PosiTest-AT-A Automatic, DeFelsko). The surface plasmon resonance responses of the samples with the relationship between reflectance and incident angle were tested in the Kretschmann configuration using a polarized light beam at 633 nm wavelength. Figure 1 shows the structure of SPR responses test instrument using Kretschmann configuration.

**EXPERIMENTAL RESULTS AND DISCUSSION**

**Thickness calibration of Bi$_2$O$_3$ and Au film:** When employing Au/Bi$_2$O$_3$ bilayer films for SPR sensing, the thickness of Bi$_2$O$_3$ layer must be taken into account and should be optimized. If the Bi$_2$O$_3$ layer is too thick, the evanescent wave based upon the attenuated total reflection method can not enter into the Au film. The electric field strength of the evanescent wave decreases when it goes through such Bi$_2$O$_3$ layer and then weakens its effect on surface plasmon wave. If the Bi$_2$O$_3$ layer is too thin, on the other hand, both adhesive strength between Au and Bi$_2$O$_3$ as well as Bi$_2$O$_3$ and prism are loose and will lead to Au film desquamate easily.

**Adhesion of Bi$_2$O$_3$ and Au/Bi$_2$O$_3$ film on BK7 glass:** Figure 3a illustrates the adhesive strength of single Bi$_2$O$_3$ films and Au/Bi$_2$O$_3$ bilayer films on the BK7 glass substrate with various Bi$_2$O$_3$ film thicknesses. Both the adhesive strength of single Bi$_2$O$_3$ film and Au/Bi$_2$O$_3$ bilayer film enhances with the Bi$_2$O$_3$ film thickness increasing as shown in Fig. 3a. The least value, 0.26 MPa, of the adhesive strength as the thickness of Bi$_2$O$_3$ film is zero, i.e., the monolayer Au film, has been observed in Fig. 3a. It demonstrates that the adhesive strength between Au and BK7 prism can be improved more than triple times by introducing the Bi$_2$O$_3$ buffer layer.
However, Fig. 3a presents the discrepancy in the adhesive strength between single Bi$_2$O$_3$ film and Au/Bi$_2$O$_3$ bilayer film in the same Bi$_2$O$_3$ layer thickness, such as about 6 nm. All of the adhesive strength of Au/Bi$_2$O$_3$ bilayer films is greater than that of single Bi$_2$O$_3$ film. It can be inferred that the annealing duration has influence on the adhesive strength because the monolayer Bi$_2$O$_3$ only annealed for 1 hour and yet the bilayer film annealed for 2 hours at the same annealed temperature 275 Celsius degree. And the alternative explanation is that the gold film enhances the adhesive fracture energy between Au/Bi$_2$O$_3$ film and prism, which defined as the difference between the total potential energy of the material-connected state and that of the material-separated state.

On the other hand, in Fig. 3b, the line shows how the annealed temperature affects the adhesive strength of Au/Bi$_2$O$_3$ bilayer film, which thickness is fixed at about 90 nm and 6 nm. It indicates that the adhesive strength boosts with the increasing annealed temperature at the range of 175 Celsius degree to 275 Celsius degree.

**The influence of Bi$_2$O$_3$ thickness on SPR response:**

Figure 4 shows the SPR spectra of monolayer Au sample and bilayer Au/Bi$_2$O$_3$ with different Bi$_2$O$_3$ thicknesses samples. The thicknesses of all gold films are about 90 nm. And the thicknesses of Bi$_2$O$_3$ films are 6 nm and 13 nm, respectively.

From Fig. 4, it is seen that SPR sensor based on the Au/Bi$_2$O$_3$ bilayer can occur SPR effect. However, the height of SPR dip with about 6 nm Bi$_2$O$_3$ layer is quadruple or so weaker than that of the monolayer Au with the width (FWHM) broadens from 9° to 11°. Another phenomenon is that the resonant angle is greater than that of the sensor based on the monolayer Au. It is well known that the SP resonance condition of prism coupler can be expressed by:

$$n_\text{p} \sin \theta_\text{p} = \text{Re} \left\{ \frac{\varepsilon_\text{d}\varepsilon_\text{m}}{\varepsilon_\text{d} + \varepsilon_\text{m}} \right\} $$

(1)

where $n_\text{p}$ is the refractive index of the prism or the bismuth oxide for monolayer Au structure or Au/Bi$_2$O$_3$ bilayer structure respectively, $\theta_\text{p}$ is the resonant angle, Re{[} corresponds to the real part and $\varepsilon_\text{d}$, $\varepsilon_\text{m}$ represent the dielectric constants of dielectric, i.e., ethanol and metal, i.e., gold respectively. From (1), it can be considered that the resonant angle excursion may arise from the introduction of the Bi$_2$O$_3$, that is, the difference of refractive index between prism, 1.51 and Bi$_2$O$_3$ thin film.

Refractive indices of Bi$_2$O$_3$ films with 275 Celsius degree annealing temperature and 1 hour annealing duration subjected to various thicknesses of Bi$_2$O$_3$ film were measured by Spectroscopic Ellipsometer (M2000, J. A. Wollam) and illustrated in Fig. 5a. According to the Fig. 5a, the variation of refractive index of Bi$_2$O$_3$ films at wavelength $\lambda = 633$nm as a function of thickness of Bi$_2$O$_3$ film was plotted in Fig. 5b and the solid line was to fit the experimental data with a cubic polynomial form to a curve. The refractivity of Bi$_2$O$_3$ film at $\lambda = 633$nm gains with its thickness increasing. The variation tendency in refractivity of Bi$_2$O$_3$ films possessed fixed annealing temperature and duration with thickness. In contrast, the relationship between refractivity of Bi$_2$O$_3$ film and the resonant angle was obtained by solving (1) numerically, as illustrated in Fig. 5c. Because of the higher refractivity on the basis...
Fig. 5: (a) Refractivity of Bi$_2$O$_3$ film with various thicknesses; (b) Refractivity of Bi$_2$O$_3$ film with various thicknesses at $\lambda=633$ nm, the inset is the transmittance of about 48nm and 72nm Bi$_2$O$_3$ films; (c) Numerical simulation of the relationship between refractivity of Bi$_2$O$_3$ and Resonant angle of Fig. 5b, when the refractivity of Bi$_2$O$_3$ film increases, the resonant angle decreases, i.e. the SPR curve with thicker Bi$_2$O$_3$ film shifts left in Fig. 4. From Fig. 5c, it can be seen that the Bi$_2$O$_3$ refractivity of 1.47 corresponding to resonant angle is 80°. In our experiment, at about 5.62nm Bi$_2$O$_3$ film thickness, the refractive index is approximately 1.468 (Fig. 5b). Meanwhile, the SPR resonant angle with approximately 6nm Bi$_2$O$_3$ bilayer structure is about 80° (Fig. 4). The experimental result gives a good support for the theoretical data and also the tendency of resonant angle shifting with Bi$_2$O$_3$ film thickness is conformed to the numerical simulation.

On the other hand, the inset in Fig. 5b shows the transmittance of Bi$_2$O$_3$ films with different thicknesses. It is seen that Bi$_2$O$_3$ film has strong absorption in the ultraviolet band (300-370 nm), however, its transmittance exceeds 60 and 70% with the thickness of about 72 nm and 48 nm, respectively for the visible light (e.g., 633 nm). The high transmittance property has been investigated by B. L. Zhu, R. B. Patil and T. P. Gujar. Thus it confirms that the SPR dip is not the result of the absorption of Bi$_2$O$_3$ film. And it is reasonable to consider that SPR dip is still due to the surface plasmon resonance effect.

The results demonstrate that the feasibility of using Bi$_2$O$_3$ buffer layer for SPR sensors.

**CONCLUSION**

From the above results, the adhesive strength between Au and prism in conventional sensors can be mended by introducing a buffer layer of Bi$_2$O$_3$ film. The enhancement effect can be adjusted through altering the Bi$_2$O$_3$ layer thickness. The adhesive strength can be enhanced more than 3 times by introducing about 6 nm Bi$_2$O$_3$ layer. The SPR responses based on the Au/Bi$_2$O$_3$ bilayer films indicate that the viability of exploiting Bi$_2$O$_3$ buffer layer for SPR sensors although the width and height of SPR dips, i.e. in the sensitivity, of those are weaker than those of monolayer Au.

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