Research Journal of Applied Sciences, Engineering and Technology 5(23): 5391-5395, 2013
DOI:10.19026/rjaset.5.4206
ISSN: 2040-7459; e-ISSN: 2040-7467

Submitted: November 12, 2012 Accepted: January 17, 2013 Published: May 28, 2013

Research Article

Enhanced Stability in Surface Plasmon Resonance Sensor Using Prism Coupler Based on Au/Bi2O3 Bilayer Film

Chenghua Sui, Zhong Lu, Bo Yan and Gaoyao Wei
College of Science, Zhejiang University of Technology, Hangzhou 310023, China

Abstract: Surface Plasmon Resonance (SPR) sensing has become a comprehensive utilized technology for detection, measurement and analysis in a wide spectrum of fields, ranging from biotechnology, environmental monitoring to food and drug monitoring. In this study, Au/Bi_2O_3 bilayer films with various layer thicknesses were deposited by thermal evaporation method on BK7 prism substrates and then post-annealing was conducted under ambient conditions. The adhesive strength of Au/Bi_2O_3 and Bi_2O_3/prism was measured with different layer thicknesses. Also, the SPR responses (reflectance vs. incident angle) were investigated as a function of the thickness of Bi_2O_3 layer in the Kretschmann geometry using ethanol as dielectric. The results indicate that the adhesive strength between Au and prism was improved more than 3 times by introducing the Bi_2O_3 as buffer layer. And the SPR dips also demonstrate that SPR sensor based on Au/Bi_2O_3 bilayer films is practical, although the height of SPR dip with about 6nm Bi_2O_3 is approximately 4 times weaker than that of monolayer Au and the width (defined as FWHM) broadens from 9° to 11°.

Keywords: Adhesive strength, Au/Bi_2O_3 bilayer film, Kretschman geometry, SPR sensor

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_2O_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_2O_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_2O_3 and Bi_2O_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_2O_3 layer under the ethanol (AR, from *Alfa Aesar*) dielectric.

EXPERIMENTAL DETAILS

Bi_2O_3 films and Au films were deposited sequentially on BK7 prism substrates by using thermal

Corresponding Author: Zhong Lu, College of Science, Zhejiang University of Technology, Hangzhou 310023, China

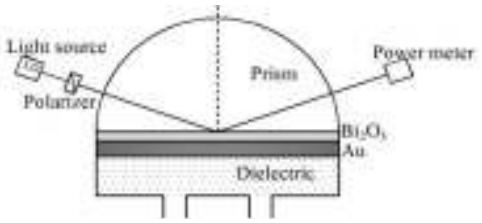

Fig. 1: The structure of SPR responses test instrument using Kretschmann configuration

evaporation technology. High-purity Bi_2O_3 (99.99%) powder was pressed into a tablet and used for the Bi_2O_3 ceramic target. And the Au used gold bar (99.99%). Prior to the Bi_2O_3 growth, the chamber was evacuated down to a base pressure of about 5.0×10^{-3}Pa. During the Bi_2O_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 180A. Then, the samples with Bi_2O_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 240A. The samples with Au/Bi_2O_3/prism structure were undergone a heat treatment process at 275 Celsius degree for 2h.

Field Emission Scanning Electron Microscopy (FESEM) was applied to calibrate the thickness. The adhesive strength between Au and Bi_2O_3 as well as Bi_2O_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_2O_3 and Au film: When employing Au/Bi_2O_3 bilayer films for SPR sensing, the thickness of Bi_2O_3 layer must be taken into account and should be optimized. If the Bi_2O_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_2O_3 layer and then weakens its effect on surface plasmon wave. If the Bi_2O_3 layer is too thin, on the other hand, both adhesive strength between Au and Bi_2O_3 as well as Bi_2O_3 and prism are loose and will lead to Au film desquamate easily.

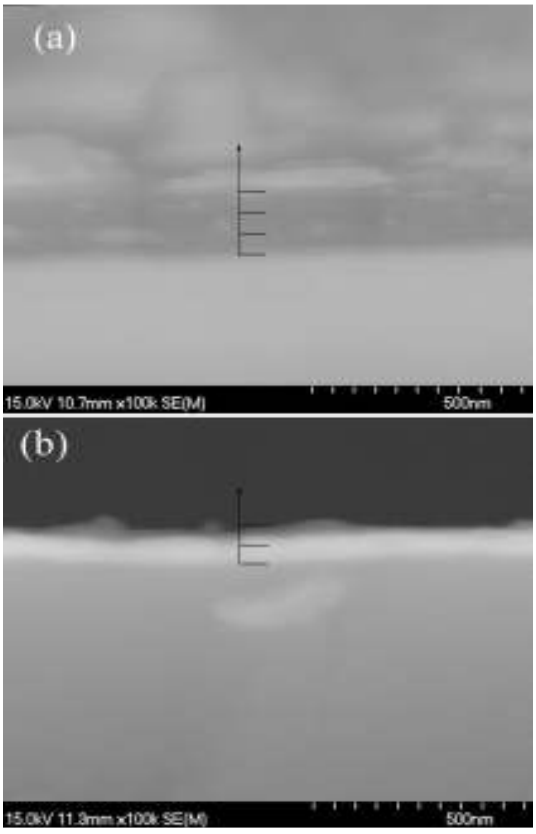

Fig. 2: The typical SEM cross profile images of; (a) Bi2O3 and; (b) Au film on the BK7 glass slide substrate

Figure 2a and b show the typical SEM cross profile images of Bi_2O_3 film with 15 min deposition time and Au film with 5 min growth time on the BK7 glass slide substrate in order to confirm the relationship between deposition time and thickness of Bi_2O_3 layer and Au film, respectively. As shown in Fig. 2, the thicknesses of Bi_2O_3 film and Au film are 200 nm and 90 nm or so, respectively. Thus the deposition rates of Bi_2O_3 and Au film are approximately 13 nm/min and 18 nm/min. And the thicknesses of Bi_2O_3 film with 0, 0.5, 1.0 and 1.5 min deposition time are about, other conditions being equal, 0, 6, 13 and 19 nm.

Adhesion of Bi_2O_3 and Au/Bi_2O_3 film on BK7 glass: Figure 3a illustrates the adhesive strength of single Bi_2O_3 films and Au/Bi_2O_3 bilayer films on the BK7 glass substrate with various Bi_2O_3 film thicknesses. Both the adhesive strength of single Bi_2O_3 film and Au/Bi_2O_3 bilayer film enhances with the Bi_2O_3 film thickness increasing as shown in Fig. 3a. The least value, 0.26MPa, of the adhesive strength as the thickness of Bi_2O_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_2O_3 buffer layer.

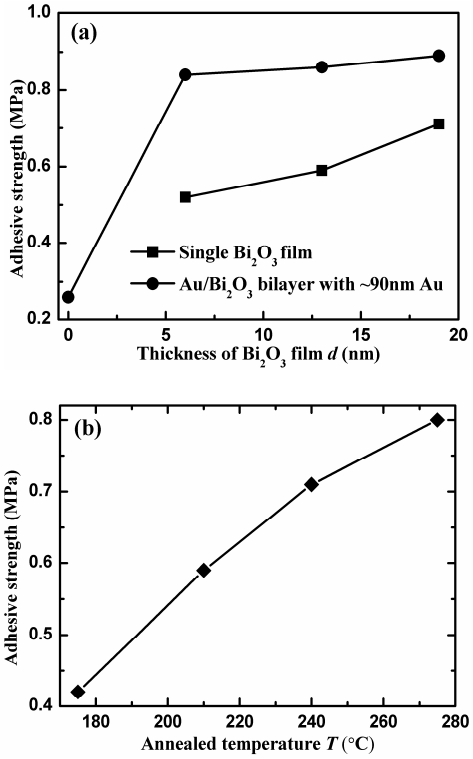

Fig. 3: The relationship between adhesive strength and; (a) thickness of Bi2O3 layer; (b) annealed temperature

However, Fig. 3a presents the discrepancy in the adhesive strength between single Bi_2O_3 film and Au/Bi_2O_3 bilayer film in the same Bi_2O_3 layer thickness, such as about 6 nm. All of the adhesive strength of Au/ Bi_2O_3 bilayer films is greater than that of single Bi_2O_3 film. It can be inferred that the annealing duration has influence on the adhesive strength because the monolayer Bi_2O_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_2O_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_2O_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_2O_3 thickness on SPR response: Figure 4 shows the SPR spectra of monolayer Au sample and bilayer Au/Bi_2O_3 with different Bi_2O_3 thicknesses samples. The thicknesses of all gold films are about 90 nm. And the thicknesses of Bi_2O_3 films are 6 nm and 13 nm, respectively.

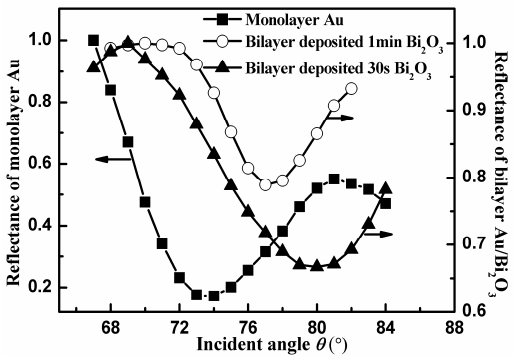

Fig. 4: SPR spectra for monolayer Au and bilayer Au/Bi2O3 with various Bi2O3 thicknesses under ethanol dielectric using Kretschmann configuration

From Fig. 4, it is seen that SPR sensor based on the Au/Bi_2O_3 bilayer can occur SPR effect. However, the height of SPR dip with about 6 nm Bi_2O_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:

$$n_x \sin\theta_{sp} = \mathrm{Re}\left\{\sqrt{\frac{\varepsilon_d \varepsilon_m}{\varepsilon_d + \varepsilon_m}}\right\} \quad (1)$$

where n_x is the refractive index of the prism or the bismuth oxide for monolayer Au structure or Au/Bi_2O_3 bilayer structure respectively, θ_{sp} is the resonant angle, Re{} corresponds to the real part and ε_d, ε_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_2O_3, that is, the difference of refractive index between prism, 1.51 and Bi_2O_3 thin film.

Refractive indices of Bi_2O_3 films with 275 Celsius degree annealing temperature and 1 hour annealing duration subjected to various thicknesses of Bi_2O_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_2O_3 films at wavelength λ = 633nm as a function of thickness of Bi_2O_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_2O_3 film at λ = 633nm gains with its thickness increasing. The variation tendency in refractivity of Bi_2O_3 films possessed fixed annealing temperature and duration with thickness. In contrast, the relationship between refractivity of Bi_2O_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

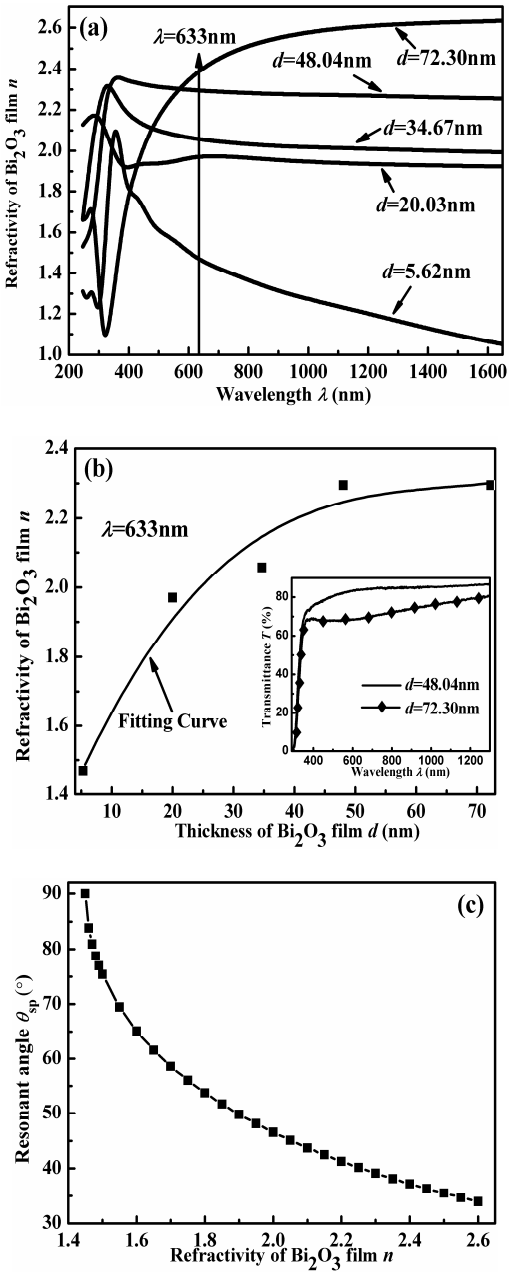

Fig. 5: (a) Refractivity of Bi2O3 film with various thicknesses; (b) Refractivity of Bi2O3 film with various thicknesses at λ=633nm, the inset is the transmittance of about 48nm and 72nm Bi2O3 films; (c) Numerical simulation of the relationship between refractivity of Bi2O3 and Resonant angle

of Fig. 5b, when the refractivity of Bi_2O_3 film increases, the resonant angle decreases, i.e. the SPR curve with thicker Bi_2O_3 film shifts left in Fig. 4. From Fig. 5c, it can be seen that the Bi_2O_3 refractivity of 1.47 corresponding to resonant angle is 80°. In our experiment, at about 5.62nm Bi_2O_3 film thickness, the refractive index is approximately 1.468 (Fig. 5b). Meanwhile, the SPR resonant angle with approximately 6nm Bi_2O_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_2O_3 film thickness is conformed to the numerical simulation.

On the other hand, the inset in Fig. 5b shows the transmittance of Bi_2O_3 films with different thicknesses. It is seen that Bi_2O_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_2O_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_2O_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_2O_3 film. The enhancement effect can be adjusted through altering the Bi_2O_3 layer thickness. The adhesive strength can be enhanced more than 3 times by introducing about 6 nm Bi_2O_3 layer. The SPR responses based on the Au/Bi_2O_3 bilayer films indicate that the viability of exploiting Bi_2O_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.

ACKNOWLEDGMENT

The authors wish to thank the helpful comments and suggestions from the teachers and colleagues in College of Science, Zhejiang University of Technology. This study is supported by the Foundation of Education Bureau of Zhejiang Province (Z201018276) and the Natural Science Foundation of Zhejiang Province (LY12F05006).

REFERENCES

Barnes, W.L., A. Dereux and T.W. Ebbesen, 2003. Surface plasmon subwavelength optics. Nature, 424: 824-830.

Brockman, J.M., B.P. Nelson and R.M. Corn, 2000. Surface plasmon resonance imaging measurement of ultra thin organic films. Ann. Rev. Phys. Chem., 51: 41-63.

Campbell, C.T. and G. Kin, 2007. SPR microscopy and its applications to high-through put analyses of biomolecular binding events and their kinetics. Biomaterials, 15: 2380-2392.

Kretschmann, E. and H. Raether, 1968. Radiative decay of non-radiative surface plasmons excited by light. J. Nature Res., 23A: 2135-2136.

Mullett, W.M., E.P.C. Lai and J.M. Yeung, 2000. Surface plasmon resonance- based immunoassays. Methods, 22: 77-91.

Otto, A., 1968. Excitation of nonradiative surface plasma waves in silver by method of frustrated total reflection. J. Phys., 216: 398-410.