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ABSTRACT

Au-SnO_x nanocomposite thin films composed of gold nanoparticles embedded in SnO_x matrix were prepared by pulsed laser deposition technique and their crystal structure, morphology and chemical composition were evaluated by low angle X-ray diffraction, field-emission scanning electron microscopy and x-ray photoelectron spectroscopy, respectively. For the nanocomposite films with high Au percentage, the surfaces of nanocomposite films are very smooth, while for the films with low Au percentage, the surfaces consist of many Au nanoparticles with particle size of 5-20 nm embedded in the films. The XRD results revealed that Au existed as polycrystalline while SnO_x as amorphous structures in the nanocomposite films. Surface plasma resonance (SPR) responses of the Au-SnO_x nanocomposite thin films were investigated as functions of Au percentage and film thickness in the Kretschmann geometry of attenuated total reflection using a polarized light beam at 633 nm wavelength. SPR responses of Au-SnO_x nanocomposite films shifts the reflectance minimum (SPR dip) to the higher values of incident angle than that of a pure Au film and the angle shift increases with decreased in the Au percentage. The width of SPR dip also becomes broader as the Au percentage decreases. The potential use of Au-SnO_x nanocomposite films for SPR gas sensing was discussed.

INTRODUCTION

Surface plasmons are surface electromagnetic waves that propagate to and parallel along with a metal/dielectric interface. Noble metal thin films (~50 nm) such as gold (Au) are commonly used as the platform for supporting the surface plasmon waves, which can be excited in a resonant manner by a visible or infrared light beam from a glass prism in either Otto [1] or Kretschmann [2] configurations. Surface plasmon resonance (SPR) phenomena at the noble metal/dielectric interface have enabled a vast array of applications such as surface enhanced spectroscopes [3], and biological and chemical sensing [4, 5]. Nanocomposite [6] thin films formed by noble metal nanoparticles embedded in a dielectric matrix also show SPR phenomenon due to collective excitations of conduction electrons in metal nanoparticles when photons are coupled to the metal particle–dielectric interface. The metal-dielectric nanocomposites offer a high degree of flexibility, and the SPR response can be optimized for specified applications by proper choice of constituents, film thickness, metal particle concentration, size, shape, and orientation.

In this work, Au-SnO_x composite films of various Au content and thickness were prepared by pulsed laser deposition technique, and characterized by low angle X-ray diffraction (XRD), field-emission scanning electron microscopy (FE-SEM) and x-ray photoelectron spectroscopy (XPS). SPR responses of the nanocomposite films were investigated as functions of Au percentage and film thickness in the Kretschmann geometry of attenuated total reflection in order to understand the dependence of SPR response on these thin film structural and

compositional parameters. Such information is critical for the design of SPR devices (such as SPR gas sensors) based on metal-dielectric nanocomposite films.

EXPERIMENT

For the deposition of Au-SnO_x nanocomposite thin films, a pulsed laser beam generated by a KrF excimer laser (Lambda Physik, LPX-210i) at a wavelength of 248 nm and pulse duration of 25 ns was introduced into an advanced deposition chamber (PVD Inc., PLD-3000) through a quartz window, and focused with optical lenses onto the surface of a hybrid rotating (18 rpm) Au/SnO_2 target. The hybrid Au/SnO_2 target was prepared in the following way: first, a 3-inch circular Tin oxide (SnO_2) target dish was cut into pie-shaped pieces with different angles, and then a SnO_2 target piece of selected angle was mounted on the top of a 3-inch circular Au target dish. The laser beam was subsequently ablated the rotating SnO_2/Au hybrid target at a speed of 18 rpm to deposit nanocomposite thin film directly onto the 18 mm x 18 mm x 1.0 mm BK7 glass or 18 mm x 18 mm x 0.25 mm silicon (100) substrates. The laser fluence on the target was adjusted to 3 ~ 5 J/cm^2, while the repetition rate was fixed at 50 Hz. To achieve film homogeneities, the substrates were rotated along the vertical axis at a speed of 35 rpm. All films were deposited at 20 °C substrate temperature under high vacuum with base pressure of 2.0 x 10^{-6} Torr or lower. To improve the adhesion of Au-SnO_x nanocomposite films, a very thin layer of Titanium (about 1 nm thick) was deposited by PLD in vacuum on the substrates before depositing the nanocomposite films.

The cross-sectional and surface images of the nanocomposite films were taken by a Leo 440 FE-SEM. The chemical compositions of the films were analyzed by XPS using a Kratos Axis Ultra X-ray photoelectron spectrometer. The crystallographic properties of the nanocomposite films were analyzed by XRD (Philips, X-Pert MRD) using a monochromatized Cu Kα in the θo-2θ thin film configuration, where θo was fixed at 0.5°. The diffraction photons were collected by the diffractometer from 20-70° with a 0.02° step size. The SPR responses (reflectance vs. angle of incident) of Au-SnO_x nanocomposite films were measured by a Biosuplar SPR spectrometer (MIVITEC GmbH) which has the built-in the Kreschmann geometry with a retro-reflecting measurement prism installed on a rotating table. During the device operation, the back side of the BK7 substrate was glued onto the top face of the prism using immersion liquid and the Au-SnO_x nanocomposite film coated side was faced to ambient directly. To measure the SPR response, a transverse magnetic (TM) polarized light (~ 640nm) generated from a light emitting diode was used to irradiate the Au-SnO_x nanocomposite film and the reflected light were monitored as the function of incident angle.

RESULTS AND DISCUSSION

The chemical composition of Au-SnO_x nanocomposite films of various Au atomic percentages (films A, B, C and D) prepared by laser ablation of a Au/SnO_2 hybrid target was analyzed by XPS. The Au/SnO_2 hybrid target composed of a pie-shaped SnO_2 target piece of either 5°, 10°, or 20° angle mounted on the top of a 3-inch circular Au target dish. XPS survey spectra were obtained from an area of approximately 300 x 700 microns using pass energy of 160 eV. A 4 kV argon ion beam (15 mA filament current, sputter rate calculated at 1.2 nm/min based on an Al_2O_3/Al standard) was used to clean the sample surfaces before the XPS measurement. XPS probed the surface of the films to a depth of 7-10 nm and the results are presented in Table 1. The Au atomic percentages for films deposited using 5° (film A), 10° (film

B), or 20° (film C and D) angle of the pie-shaped SnO_2/Au hybrid target are 64.6%, 38.2% and 25.3%, respectively. Beside Au, Sn and O elements, there is C surface contaminations which can only be partially removed but not eliminated by the 30-second Ar sputter cleaning. The Sn/O atomic ratio is larger than 0.5 indicating than SnO_x in the naocomposite film deposited in vacuum by PLD is no-stoichiometric with $X < 2$.

Table I: XPS results of Au-SnO_x nanocomposite films

Sample	Angle of SnO_2 target	Ar Sputter Time (second)	Au (atm.%)	C (atm.%)	O (atm.%)	Sn (atm.%)
A	5	30	64.6	6.1	15.8	13.4
B	10	30	38.2	2.2	34.1	25.4
C	20	30	25.3	0.3	43.9	30.4
D	20	30	25.3	0.7	42.5	31.6

The cross-sectional FE-SEM micrographs of Au-SnO_x nanocomposite films deposited on Si(100) substrates were used to determine the film thickness. As shown in Figure 1, the thicknesses are about 55 nm, 38 nm, 40 nm and 45 nm for nanocomposite films A, B, C and D, respectively. A pure Au film was also deposited on Si(100) and BK7 substrates to compare with these nanocomposite films, and its thickness determined also by FE-SEM was ~41 nm (not show here). All the four nanocomposite films have very uniform thickness over the 14 mm X 14 mm deposition area. The surface images of all the four nanocomposite films A, B, C, and D are also shown in the inserts of Figure 1.

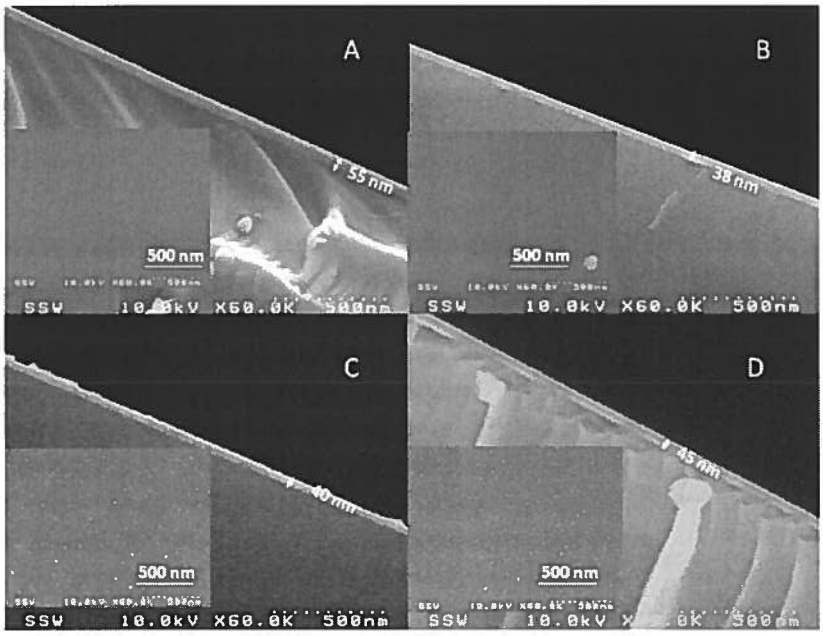

Figure 1. The cross-sectional FE-SEM micrographs of Au-SnO_x nanocomposite films of various Au percentage and film thicknesses (sample A, B, C and D). The surface images of samples are also shown in the inserts of the figure.

For nanocomposite films with high Au percentage (sample A and B), except a few embedded micro/sub-micro spherical Au particles, the surface is very smooth. For the low Au percentage films (sample C and D), the surface consists of many nanoparticles with particle size of 5-20 nm embedded in the smooth films. Those nanoparticles are very likely to be Au nanoparticles as they

appeared more brightness in SEM due to their better electron conduction. These Au nanoparticles, however, did not appear in the high Au percentage films. To further analyze the microstructures of the nanocomposite films, XRD patterns were recorded for the pure Au and Au-SnO_x nanocomposite films deposited on BK7 glass substrates and the results are shown in Figure 2.

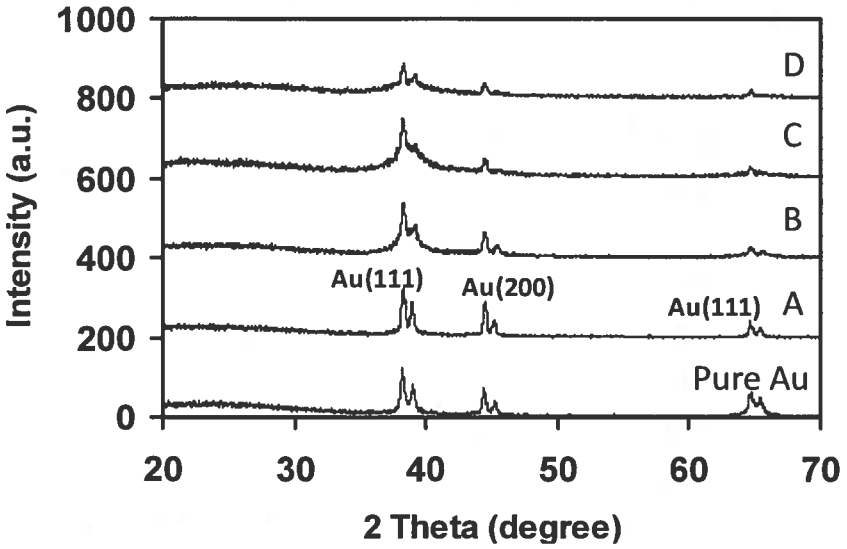

Figure 2. X-ray diffraction patterns for pure Au and Au-SnO_x nanocomposite films with various Au percentages deposited by PLD on BK7 substrates at 20°C substrate temperatures.

All the five films showed XRD peaks at angles near 38.22°, 44.43° and 64.64°, with no BK7 substrate peaks being observed. These peaks can be indexed as the diffractions from the (1 1 1), (2 0 0) and (2 2 0) planes of cubic Au [JCPDS 04-0784]. The appearance of the dual-peak feature for Au peaks in the XRD spectra could be contributed by two types of Au particles with different lattice constants co-existed in the composite films. Very likely, the dual peak originates from the Au nanoparticles in the composite film and micro or sub-micron sized Au particles embedded in the composite films. Those micro or sub-micron sized Au particles were generated during the pulsed laser ablation process [7]. No peaks were observed in the XRD patterns that are originated from the SnO_x which means that the SnO_x matrix has the amorphous structure in all the four Au-SnO_x nanocomposite films. The results clearly illustrate that Au is crystallized into polycrystalline in the pure Au and Au-SnO_x nanocomposite films while SnO_x existing in an amorphous structure. All the three Au peaks are relatively weak and broad, which indicates that the Au grain size is relative small. These peaks decreased in intensity and became broader as the Au percentage decreased indicating that the grain size of Au particles decreased with increased SnO_x content in the nanocomposite films. For high Au percentage films A and B, small amount of SnO_x very likely existed in the narrow boundary between relative large Au grains therefore they appeared to be very smooth under FE-SEM as shown in the inserts of figure 1. For low Au percentage films C and D, relative small Au nanoparticles (particle size of 5-20 nm as shown by FE-SEM) are surrounded by large amount of SnO_2 and they appeared as separated grains embedded in the smooth SnO_x matrix. The XRD results are very consistent with the FE-SEM images in figure 1.

To excite surface plasmons in a resonant manner at the Au-SnO_x nanocomposite films /air interface, a visible light beam of ~640 nm wavelength was used to illuminate the nanocomposite layer from a glass prism in the Kretschmann configurations. In order to achieve a good SPR response (sharp SPR dip and low reflectance minimum), the thickness of nanocomposite films should be controlled in the range of 30 ~ 60 nm [8]. SPR responses of the pure Au film and the Au-SnO_x nanocomposite films (sample A, B, C and D) on BK7 substrates were shown in Figure 3.

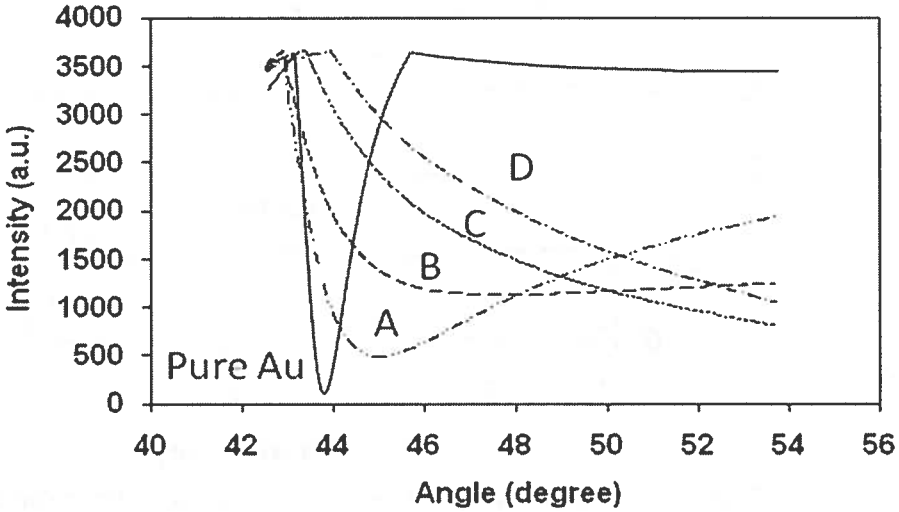

Figure 3. SPR responses of pure Au and Au-SnO_x nanocomposite films with various Au percentages and film thicknesses.

Reflectance minimum (SPR dip) of the 41 nm pure Au film almost approached zero at 43.9 degree of incident angle. The SPR response of the pure Au film fabricated by PLD is very close to that of a commercial pure Au films prepared by the sputtering technique. In comparison with the pure Au film, SPR responses of nanocomposite films shifts the reflectance minimum (SPR dip) to higher values of incident angle and the angle shift increases with reduced in the Au percentage in the nanocomposite films. The width of SPR dip also becomes broader as the Au percentage decreases. The incident angles corresponding to SPR dips of sample A (55 nm thick and 64.5% Au), and B (38 nm thick and 38.2% Au) are 44.8, and 47.5 degree respectively, while C (40 nm thick and 25.3% Au) and D (45 nm thick and 25.3% Au) have not shown any SPR minima within the incident angle investigated. Films C and D have the same Au percentage but difference film thickness, i.e. 40 nm vs. 45 nm, and they show difference SPR responses: film D always has larger reflectance than film C. Less smooth micro-feature of films C and D may also contribute to the relative high reflectance in the SPR response in addition to the low Au percentage. Figure 3 clearly shows that the SPR responses of nanocomposite films are very sensitive to film composition, thickness and microstructure which offer a high degree of flexibility to tune SPR responses for different applications.

It is well-known that SPR response of a noble metal film is very sensitive to any change in the vicinity of its surface; therefore it is widely used for biological and chemical sensing. However, a noble metal thin film cannot be directly used with a typical SPR set-up for gas sensing since noble metal like Au is not reactive to many gases. It is hard to induce any detectable change in the local index of refraction of an Au film by a monolayer of physically or

chemically adsorbed gas molecules. If a highly chemically reactive metal oxide such as SnO_2 [8] were mixed with Au metal to form the Au- SnO_x nanocomposite film, it is expected that the interaction between the reactive metal oxide and gas molecules through either chemical reaction or physical adsorption may induce significant change in optical reflectivity of the nanocomposite film. It therefore offers the possibility to measure small concentrations of gas molecules. On the other hand, the surface area available in a nanocomposite film for gas sensing reactions will also be significantly increased, which should improve the sensitivity of the SPR gas sensing. In order to use Au- SnO_x nanocomposite films for SPR gas sensing, it is critical to know how to control the metal percentage, film thickness and microstructure to achieve reasonable narrow SPR dips and desired SPR angle. SPR dip has to be reasonably narrow to warrants its practical applications for gas sensing [9, 10]. The results presented above clearly demonstrated that SPR responses can be adjusted by proper selection of these thin film structural and compositional parameters. For Au- SnO_x nanocomposite films, as an example, the suitable film thickness should be within the range of 30– 60 nm and the Au percentage should be higher than 60% in order to achieve reasonable sharp SPR dips for gas sensing application.

CONCLUSIONS

Au-SnO_x nanocomposite films which consist of polycrystalline Au nanoparticles embedded in amorphous SnO_x structure were successfully deposited by the pulsed laser deposition technique. In comparing with a pure Au film, SPR responses of the Au-SnO_x nanocomposite films are much broader and their reflectance minima (SPR dips) appeared at higher values of incident angle. The broadness of the SPR responses as well as their reflectance increases with increased in the SnO_x percentage in the nanocomposite films. When the Au percentage becomes lower than 25%, the reflectance minimum of the SPR response became undistinguishable. For SPR gas sensing using the Au-SnO_x nanocomposite films, the suitable film thickness should be within the range of 30– 60 nm and the Au percentage should be higher than 60% in order to achieve reasonable sharp SPR dips for high gas detection sensitivity.

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