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Abstract

Surface plasmon resonance (SPR) of metal-dielectric composite films formed by noble metal nanoparticles embedded in a dielectric is very sensitive to the changes in the refractive index of the dielectric induced by physical absorption or chemical reactions and is therefore exploited for gas sensing applications. In this study, Au-WO_{3-x} nanocomposite thin films were fabricated by pulsed laser deposition and the content of Au in the composite films was varied by altering the relative laser ablation time on Au and WO_3 targets. The SPR response of the Au-WO_{3-x} films in ambient atmosphere is measured for various gold percentages. The experimental results were compared to the theoretical calculations by both Maxwell-Garnett and Bruggeman effective medium theories. The SPR response of Au-WO_{3-x} films exposed to NO gas was measured. The preliminary results indicated that gas sensing using the SPR responses of metal-dielectric composite films is feasible.

1. Introduction

Surface plasmons are surface electromagnetic waves that propagate along a metal/dielectric interface [1, 2]. To excite surface plasmons in a resonant manner, a visible or infrared light beam is typically used to illuminate the metal layer from a glass prism in either Otto [3] or Kretschmann [4] configurations. Since the surface plasmon waves (SPW) are excited on the boundary of the metal layer, they are very sensitive to any change in the vicinity, such as the adsorption of molecules to the metal surface which changes the local index of refraction. By measuring the surface plasmon resonance (SPR) reflectivity, one can therefore detect molecular adsorption. When SPR is considered for the detection of gas molecules [5], however, it requires that the gas molecules interact with the metal layer itself and induce the change in its index of refraction since a monolayer of physically or chemically adsorbed gas molecules can not induce detectable changes in the local index of refraction. The most common metals used for SPR such as Au and Ag are not reactive to many gases; therefore cannot be directly used for gas sensing with a typical SPR set-up. A highly reactive metal oxide [6] or polymer thin film is usually coated on the gold or Ag metal surface, the reaction between gas molecules and the sensing metal oxide or polymer layer induces changes in the local index of refraction of the metal layer, which forms the basis of SPR gas sensing.

Nanocomposite [7] thin films formed by 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. If a highly chemically reactive metal oxide such as SnO_2 [8] and WO_3 [9] were used as the dielectric matrix in the metal-dielectric nanocomposite, we expect that the interaction between the metal oxide and gas molecules through either chemical reaction or physical adsorption may induce significant change in optical reflectivity of the composite film therefore offers the possibility to measure small concentrations of gas molecules.

In this article, the details on the fabrication of Au-WO_{3-x} composite thin films by pulsed laser deposition (PLD) technique are described. The SPR response of the Au-WO_{3-x} films in ambient atmosphere is reported for various gold percentages. The experimental results are compared to the theoretical SPR reflectivity stimulation using a general characteristic matrices method in which both Maxwell-Garnett and Bruggeman effective medium theories are used for the calculation of the effective dielectric constants of the composite films. SPR responses of Au-WO_{3-x} composite films exposed to NO gas are measured to demonstrate the feasibility of using SPR responses of the composite films for gas sensing applications.

2. Theory

The effective medium theory (EMT) [10] is employed to obtain the effective dielectric constant of the Au-WO_{3-x} nanocomposite, which is the first step to calculate the SPR response of the composite films. The most commonly used SPR setup is the Kretschmann configuration [1], [4], which consists of a glass prism, a thin noble metal film attached to the prism, and the ambient dielectric material. The SPR response is generally characterized by the reflectance of the p-polarized incident beam, i.e., R_p, which can be obtained from either direct calculation [11] or Macleod's general characteristic matrices method [12].

2.1 Effective Medium Theory

Optical properties of heterogeneous materials can be analyzed with either Maxwell Garnett effective medium theory for separated-grain structure or Bruggeman theory for aggregated structure [10]. If a composite material is composed of two mediums with dielectric constant ε_1 and ε_2, respectively, and the volume filling factor of medium 1 is f_1, then the effective permittivity of the composite is

$$\varepsilon_{eff} = \varepsilon_2 \frac{\varepsilon_1 + 2\varepsilon_2 + 2f_1(\varepsilon_1 - \varepsilon_2)}{\varepsilon_1 + 2\varepsilon_2 - f_1(\varepsilon_1 - \varepsilon_2)} \quad (1)$$

from Maxwell Garnett formulation for separated-grain structure and

$$f_1 \frac{\varepsilon_1 - \varepsilon_{eff}}{\varepsilon_1 + 2\varepsilon_{eff}} + (1 - f_1) \frac{\varepsilon_2 - \varepsilon_{eff}}{\varepsilon_2 + 2\varepsilon_{eff}} = 0 \quad (2)$$

from Bruggeman theory for more dense (interconnected) mixtures of materials.

2.2 Surface Plasmon Resonance

When using a visible or infrared light beam to excite surface plasma waves in the Kretschmann configuration, the light is shone on the wall of a prism and totally reflected. An evanescent wave penetrates through the metal film that is evaporated onto the prism to excite and interact with the plasma waves on the metal surface. Under certain conditions, free electrons respond collectively by oscillating in resonance with the incident light wave to generate surface plasmon resonance (SPR). The SPR response is generally characterized by the reflectance of the p-polarized incident beam, i.e., R_p, which can be calculated as [11], [13]

$$R_p = \left| \frac{r_{pm} + r_{md} \exp(2ik_{zm}d_m)}{1 + r_{pm}r_{md} \exp(2ik_{zm}d_m)} \right|^2 \quad (3)$$

with $r_{pm} = \dfrac{\varepsilon_p k_{zm} - \varepsilon_m k_{zp}}{\varepsilon_p k_{zm} + \varepsilon_m k_{zp}}$ and $r_{md} = \dfrac{\varepsilon_m k_{zd} - \varepsilon_d k_{zm}}{\varepsilon_m k_{zd} + \varepsilon_d k_{zm}}$. Here k is the wavenumber, d is the film thickness, and $i = \sqrt{-1}$ is the imaginary symbol. The wavenumbers along x- and z- directions are $k_x = n_p k_0 \sin\theta_p$ and $k_{zi} = \sqrt{\varepsilon_i k_0^2 - k_x^2}$, respectively. The subscripts 0, p, m, and d denote free-space, prism, metal, and dielectric (ambient or embedding material), respectively. For the calculation of R_p for metal-dielectric composite films, the effective dielectric constant ε_{ff} determined from either equation (1) or (2) is used to replace the ε_m in equation (3).

3. Experimental Details

The Au-WO_{3-x} nanocomposite films with different Au content were grown on BK7 glass substrates using the PLD technique. A pulsed laser beam generated by a KrF excimer laser at a wavelength of 248 nm and pulse

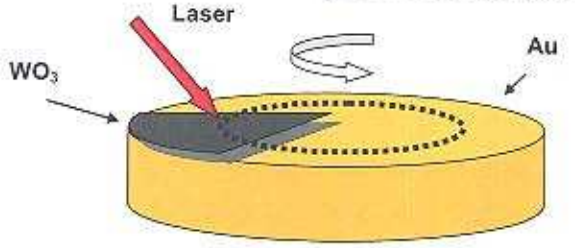

Figure 1: The laser beam subsequently ablates rotating WO_3/Au targets to produce the Au-WO_{3-x} composite film

duration of 25 ns was introduced into the deposition chamber through a quartz window and focused with optical lens onto the target surface. The laser fluence on the target was ~5 J/cm^2, while the repetition rate was fixed at 50 Hz. A 3-inch circular Tungsten oxide (WO_3) target dish was cut into pie-shaped pieces with different angles. A WO_3 target piece of selected angle was then mounted on the top of a 3-inch circular Au target dish. The laser beam was subsequently ablated on the rotating WO_3/Au targets at a speed of 18 rpm as shown in figure 1 to form composite thin films deposited directly on the 18 mm x 18 mm x 1.0 mm BK7 glass substrates. To improve the film homogeneities, the substrates were rotated along the

vertical axis at a speed of 35 rpm. All films were deposited at a room temperature of 20°C in high vacuum (< 2.0 x 10^{-6} Torr). The chemical compositions of the composite films were investigated by x-ray photoelectron spectroscope (XPS). The XPS measurements were performed using a spectrometer equipped with an Al$K\alpha$ source (λ = 1486.6 eV). The crystallographic properties of the thin films were analyzed by X-ray diffraction (XRD, Philips, X-Pert MRD) using monochromatized Cu Kα in the θ_0-2θ thin film configuration, where θ_0 was fixed at 0.5°. The diffraction photons were collected by the diffractometer from 20-70° with a 0.02° step size. A Biosuplar SPR device was used to measure the reflectivity as a function of the angle of incidence (SPR responses) of the Au-WO_{3-x} composite films using a light emitting diode at the wavelength of ~640nm in the Kretschmann configuration.

4. Results and Discussion

4.1 Structural and chemical composition analysis of Au-WO_{3-x} composite film

Figure 2 shows XRD patterns of a pure Au film, and Au-WO_{3-x} composite films deposited by laser ablation

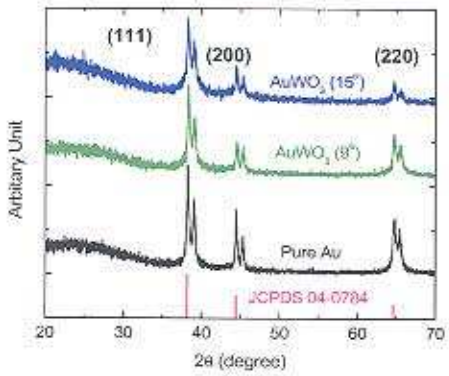

Figure 2 : XRD spectra of Au and Au-WO_{3-x} films deposited at the substrate temperature of 20 °C on BK7 glass substrates in high vacuum by laser ablation of Au/ WO_3 target with various angles of WO_3 sectors.

of the overlapped WO_3/Au targets with the pie-shaped WO_3 pieces at 9° and 15°, respectively. The diffraction patterns consist of a broad band centered at 2θ of about 25° and three main diffraction peaks at around 38°, 45° and 65°. The broad band is attributed to an amorphous-like structures for the WO_{3-x} in the composite film and the substrate (as the film is around 30~40 nm, substrate also contributes to the XRD pattern), while the three main diffraction peaks represent the (111), (200) and (220) orientations of Au particles as they match to the XRD reference JCPDS 04-0784 for Au. The results clearly illustrate that WO_{3-x} existed as an amorphous structure while Au is crystallized in the Au-WO_{3-x} composite films. All the three Au peaks are broad, which indicates that the Au particle size is very small. The appearance of dual-peak may be contributed by two types of Au particles with different lattice constants co-existing 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 [14].

Chemical compositions of the Au-WO_{3-x} composite films with various Au contents were investigated by XPS measurements. The XPS spectra were recorded

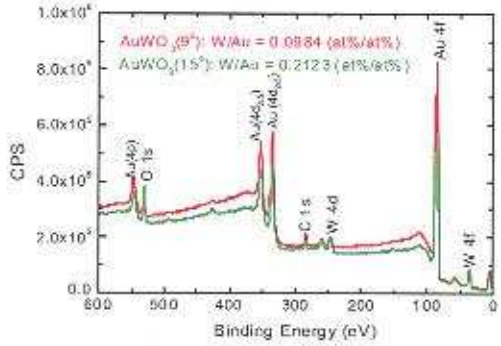

Figure 3: XPS spectra of Au-WO_{3-x} composite films deposited on BK7 glass substrates.

without Ar^+ ion etching. The recorded carbon C(1s) peak at 285.75 eV for the two investigated samples is presumably due to the atmospheric carbon surface contamination. The binding energy values of the different XPS peaks were calibrated using the C(1s) peak. The XPS peaks corresponding to Au(4f), Au(4d), Au(4p), W(4d), W(4f), and O(1s) were labeled in the figure. The W(4f) and Au(4f) peaks were used to calculate the Au/W atomic ratio. The atomic percentages for Au-WO_{3-x} composite films deposited by laser ablation of the overlapped WO_3/Au targets with 9° and 15° angles of the pie-shaped WO_3 pieces are calculated to be 90.2 % and 78.8 % of Au in Au-WO_{3-x} composite, respectively.

4.2 SPR Response of Au-WO_{3-x} nanocomposite films

SPR responses (reflectance vs. angle of incident) of PLD deposited pure Au and Au-WO_{3-x} composite films

are shown in figure 4. The reflectance almost approaches zero at an incident angle of 43.6° (resonance angle) for the 42 nm Au film. The SPR response of the PLD Au film is almost the same as that of a commercial Au films provided by MIVITEC GmbH which were prepared by d.c. sputtering. SPR

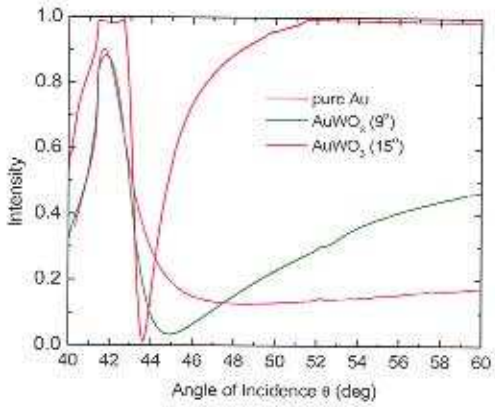

Figure 4: SPR response of a 42nm pure Au film and 30nm Au-WO_{3-x} Composites films with various Au percentages.

dips for the 30 nm Au-WO_{3-x} composite films are much broad than that of the pure Au film. The more WO_{3-x} is in the composite film, the broad the SPR response is. The angles of incidence corresponding to the minima of the reflectance also shift to higher values as the percentage of WO_{3-x} increases.

Calculations of the SPR responses of the Au-WO_{3-x} composite films at 632.8nm in the Kretschmann configuration were also carried out in order to compare with the experimental results. Effective dielectric constants of Au-WO_{3-x} composite films were calculated from both equation (1) (Maxwell-Garnett) and equation (2) (Bruggeman). The index of refraction, n, and extinction coefficient, k, used in the calculation of dielectric constant of Au were obtained from the CRC Handbook of Chemistry and Physics [13], and other literatures [2, 16-19]. The refractive index n and extinction coefficient k for Au are n = 0.16172, k = 3.21182 at the wavelength of 632.8 nm (1.9593 ev) (i.e. the wavelength of He-Ne laser). The n and k values of WO_{3-x} films used in the calculation of dielectric constant of WO_{3-x} films were measured from WO_{3-x} films deposited by the PLD. The WO_{3-x} films were deposited by ablating a 90 mm diameter rotating WO_3 (99.99% purity, from Super Conductor Materials) in high vacuum (< 10^{-6} torr) at 20°C. The resulting films are non-stoichiometric with oxygen deficiency (e.g., WO_{3-x}, where x > 0). The optical reflectance spectra of WO_{3-x} films were measured with the

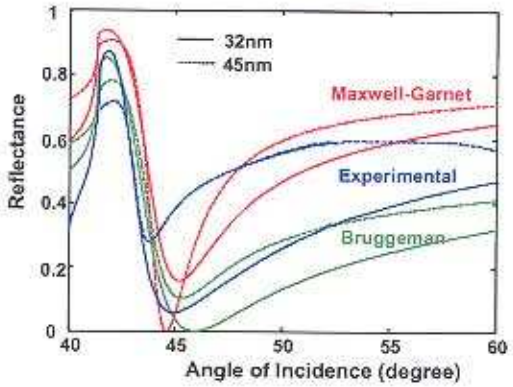

Figure 5: Experimental SPR response of a 45 nm 90.2% Au-WO_{3-x} films as comparing to theoretical simulation using both Maxwell-Garnet and Bruggeman theories for the effective dielectric constant calculation.

fiber-optic-based spectrophotometer (SCI Film TEK3000). Their n and k values were calculated from the reflectance spectra by using appropriate material model to fit the measurement data and the n and k values for WO_{3-x} films determined are 2.637 and 0.9088, respectively, at the wavelength of 632.8 nm. The n, k values of Au and WO_{3-x} were then used to calculate the effective dielectric constants of Au-WO_{3-x} composites films. After the dielectric constants were determined, the SPR response of Au-WO_{3-x} composite films was calculated using Macleod's general characteristic matrices method at 632.8nm in the Kretschmann configuration. Both the simulated and experimental results are shown in figures 5 for a 32 nm and a 45 nm Au-WO_{3-x} films with 90.2% Au. It is clear that SPR responses calculated from both Maxwell Garnett formula and Bruggeman theory do not agree well with that of experimental date indicating that both theories may be too simplify to describe the complex metal-dielectric composites deposited by the PLD. The PLD composite films can neither be described as a separated-grain structure (Maxwell-Garnett) or an aggregated structure (Bruggeman). The experimental data are sitting in between the two simulated results indicating that the structure of the PLD composite films is complicated and may posses both separated-grain and aggregated structures. More sophisticated effective medium theories should be used or developed.

4.3 SPR gas sensing using Au-WO_{3-x} composite films

It is known that WO_{3-x} [20] is one of the most interesting materials in the field of gas sensors and shows good sensitivity towards the detection of a

number of gases such as NO, CO, H_2S, and O_3. The chemical stoichiometry of WO_{3-x} thin film is strongly influenced by the presence of oxidizing or reducing gases particularly at elevated temperatures. Under oxidizing atmosphere, the WO_{3-x} approaches to the stoichiometric WO_3 structure (i.e. $x \rightarrow 0$) which has a higher electrical resistance. Under reducing conditions, the oxygen is removed by the reaction with the reducing gas species and the x in WO_{3-x} increases, as a result, the electrical resistance decreases. Similar to the electrical conductivity, the optical properties (i.e. n and k) of stoichiometric WO_3 and non-stoichiometric WO_{3-x} (with $x > 0$) are significantly different. For example, at 632.8 nm the n and k for WO_{3-x} films deposited in vacuum are 2.64 and 0.91 as comparing to 2.33 and 0.05 for WO_3 films deposited in oxygen atmosphere. The significant difference in n and k of stoichiometric WO_3 and oxygen-deficient WO_{3-x} films indicates that the SPR responses of the Au–WO_{3-x} composite films exposed to various oxidizing or reducing gas species will be significant different; therefore can be used for gas sensing applications. To demonstrate this concept, we fixed the angle of incident of the light source in the SPR device at 45 degree and monitored the reflectance also at 45 degree as the surface of a Au–WO_{3-x} composite films (with 90.2% of Au) was alternatively exposited to air and to 1000 ppm NO contained air as shown in figure 6. The intensity of

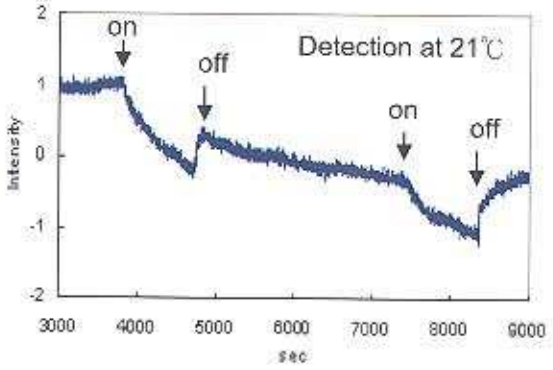

Figure 6: SPR reflectivity response at of a 90 atm.% Au-WO_{3-x} composite thin film when exposed to 1000ppm of NO gas.

reflectance decreases immediately when 1000 ppm NO is introduced into air, and the reflectance increase as NO is removed from air. However, the reflectance baseline is unstable and keeps drifting downward. In order to obtain more precise and actual data, our experimental set-up and instrumentation still need a lot improvement. The results in figure 6 is our preliminary evaluation of the feasibility of the Au–WO_{3-x} composite films for SPR gas sensing,. More detailed works in term of its sensitivity, selectivity, detection limit, temperature dependence as well as the influence of the percentage of Au and thickness is currently undergoing and will be reported in our future communications.

5. Conclusions

SPR responses of Au WO_{3-x} nanocomposite films fabricated by the PLD technique were measured in the Kretschmann configuration at the wavelength of 640 nm. The width of SPR responses of Au–WO_{3-x} composite films was much boarder than that of pure Au films, and increases as the Au percentage decreases. The angle of incidence corresponding to the minimum reflectance also shifts to a larger value as the Au percentage decreases. The SPR responses were simulated using Macleod's general characteristic matrices method, in which the effective dielectric constants of the composites were calculated by both Maxwell-Garnett and Bruggeman theories. The simulated results indicated that the composite films deposited by PLD are simply in neither a separated-grain structure nor an aggregated structure. The SPR response of the Au-WO_{3-x} films exposed to 1000 ppm NO gas was measured and our initial results demonstrated that SPR gas sensing using Au-WO_{3-x} composite films is feasible.

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