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Publisher's version / Version de l'éditeur:

<https://doi.org/10.1016/j.snb.2010.01.054>

Sensors and Actuators B: Chemical, 145, 2, pp. 832-838, 2010-03-19

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Surface Plasmon Resonance of SnO₂/Au Bi-layer Films for Gas Sensing Applications

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Abstract

Surface Plasmon resonance (SPR) sensor technology has great potential for detection and analysis of chemical and biochemical substances in many important areas including medicine, environmental monitoring, biotechnology, drug and food monitoring. Chemical sensing using SPR responses of semiconducting metal oxide films deposited on top of noble metals could offer a simple, sensitive and reliable method for the detection of low concentration of gases. In this article, ultra-thin SnO₂ films of various thicknesses were deposited by pulsed laser deposition technique on thin Au film coated BK7 glass substrates and their SPR responses were measured in the Kretschmann geometry of attenuated total reflection using a polarized light beam at 633 nm wavelength. The width of the SPR dip of the Au coated BK7 became broader with addition of the SnO₂ overcoat. As the SnO₂ layer thickness in the bi-layer films increases, the reflectance minima of the SPR response shift to larger incident angle. The SPR responses of bi-layer films were also simulated with Macleod's general characteristic matrices method to compare with experimental data. Although the simulated results show the similar trend as the experimental data in term of the dependence of SPR angle with SnO₂ layer thickness, there are discrepancy between the simulated results and experimental data, particularly, the shape of SPR response predicted by theory is much broader than the experimental results. The SPR responses of the

SnO₂/Au bi-layer films upon 50 or 100 ppm NO gas exposure were measured and the primary results indicated that gas sensing using the SPR responses of a semiconducting metal oxide deposited on top of the metal is feasible but with relatively slow response.

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1. Introduction

Thin films (~ 50 nm) of noble metal such as Gold (Au) and Silver (Ag) are capable of supporting a surface plasmon (SP) wave, which is collective oscillation of the free electrons at the boundary of a metal (or a semiconductor) and a dielectric. SP wave at the metal-dielectric interface can be excited in a resonant manner by a visible or infrared light beam when coupling with a glass prism in either Otto [1] or Kretschmann [2] configurations. In the Kretschmann configuration a light wave is totally reflected at the interface between the prism coupler and the thin metal layer (deposited on the prism surface) and excites an SPW at the outer boundary of the metal by evanescently tunneling through the thin metal layer. Since surface plasmon resonance (SPR) is very sensitive to any changes occurring in the region of the interface, presence of extremely thin gas sensing coatings on top of the metal can be used to detect gas molecules basing on a change in the plasmon resonance conditions. Gas detection by means of SPR was proposed by C. Nylander et al. as early as 1982 [3, 4] in which they used an organic oil film deposited on Ag thin film surface to reversibly absorb the anesthetic gas halothane. Due to change in the oil film thickness as well as its refractive index upon gas exposure, the SPR response (reflectance vs. incident angle) of the oil coated Ag film change. Due to requirements for more sensitive, selective, reversible, and reliable chemically active over layer for SPR gas sensors, the investigation and optimization of the active layer have become one of the centers of focus of many SPR sensor research. A better understanding of the chemistry of the sensing reaction will help to resolve questions concerning those specificity, reversibility and long-term stability. Chemically active overlayers that have been studied include phthalocyanine and porphyrin Langmuir-Blodgett (LB) films [5, 6], cobalt-phthalocyanine (Co-Pc) [7], N-methylaniline [8], Au-WO_{3-x} nanocomposite films [9, 10], nanostructured ZnO films [11], a-

WO₃ thin films [12], In₂O₃(Sn) film [13], Meso-porous membrane of noble metal [14], polyethylene glycol thin film [15], solid-phase antibody immobilized on Au surface [16], polyfluoroalkylsiloxane [17], Teflon [18] and polydimethylsiloxane films [19]. It is believed that a change in the refractive index of the overlayer of 10^{-5} may be monitored by SPR [4].

Semi-conductive metal oxide such as SnO₂ [20], WO₃ [21] and TiO₂ [22] are the most common used materials for chemoresistive gas sensors and it is worth to exploit these materials as the chemically active overlayers for SPR sensors. If these highly chemically reactive semi-conductive metal oxide such as SnO₂ and WO₃ were coated on the top of the metal, we expect that the interaction between these metal oxide overlayer and gas molecules through either chemical reaction or physical adsorption may also induce change in optical refractive index of the metal oxide thin layer therefore offers the possibility to measure small concentrations of gas molecules. In order to use these semiconductive metal oxide for SPR gas sensing application, one needs to know how does the SPR gas sensitivity and speed of response relate to the thickness of the metal oxide layer and their microstructures, how the gas selectivity can be achieved by compositional modification such as element doping, what is the optimized operating temperatures and how to achieve a stable baseline etc.

In this work, SnO₂ ultra-thin films of various thicknesses were prepared by the pulsed laser deposition technique on Au film coated BK7 glass substrates, and their SPR responses in the Kreschmann geometry were measured as the function of individual layer thickness. SPR responses of selected SnO₂/Au bi-layer films upon the NO gas exposure are measured as examples to demonstrate the feasibility of using semiconductive metal oxide chemically active overlay for SPR gas sensing applications.

2. Experimental Details

For the SnO₂/Au bi-layer film deposition, 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 surfaces of rotating (18 rpm) Au (Goodfellow, 99.99% pure) and SnO₂ (Plasmaterials, 99.9%) targets to subsequently ablate both targets to form the bi-layer thin films on the 18 mm x 18 mm x 1.0 mm BK7 glass substrates [23]. The laser fluence on the target was adjusted to 3 ~ 5 J/cm², while the repetition rate was fixed at 50 Hz. To improve the adhesion of the first Au layer on BK7 glass substrates, a very thin layer of Titanium (about 1 nm thick) was deposited by PLD on the substrates before depositing the Au film. To achieve film homogeneities, the substrates were rotated along the vertical axis at a speed of 35 rpm. Au layer was deposited at 20 °C substrate temperature under high vacuum with base pressure of 2.0 x 10⁻⁶ Torr or lower while the SnO₂ layer was deposited at 20 °C substrate temperature under oxygen atmosphere of 40 mTorr.

The cross-sectional and surface images of the films were taken by a Leo 440 field-emission scanning electron microscope (FE-SEM). The crystallographic properties of the bi-layer films were analyzed by X-ray diffraction (XRD, Philips, X-Pert MRD) using a monochromatized Cu K α in the θ_0 -2 θ 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.

The SPR responses (reflectance vs. angle of incident) of SnO₂/Au bi-layer 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 liquids and the SnO₂/Au bi-layer coated side was faced to ambient directly. To measure the SPR response, a transverse magnetic (TM) polarized light (~ 633 nm) generated from a light emitting diode was used to irradiate the SnO₂/Au bi-layer film and the reflected light were monitored as the function of incident angle. For NO gas SPR sensing measurement, a SPR-imaging system (GWC Technologies Co., America) was used to monitor the reflectance while the incident angle was fixed at a selected angle (e.g. an angle that has the one-third of maximum SPR reflectance change with incident angle). A heater embeds in the sensing chamber to increase the working temperature. After waiting 60 to 90 minutes, the baseline of reflectance under over 100 °C and by flowing with N₂ gas is approaching stabilized. Then, the SnO₂/Au bi-layer films were exposed to the pure N₂ gas and the 50 ppm NO contained N₂ gas mixture subsequently with a flow rate of 20 ml per minute during different measurement cycles. All the measurements used a light source with a wavelength of 833 nm and a BK7 triangular prism as the coupling material. The humidity in the environment was sustained at 50% RH.

4. Results and Discussions

The cross-sectional FE-SEM micrographs of pure Au (sample A) and SnO₂/Au bi-layer films (sample B, C and D) were shown in Figure 1. The thicknesses of both Au and SnO₂ layers were determined from the FE-SEM micrographs. For the pure Au film (sample A), its thickness is around 41 nm, while for the bi-layer films, the thicknesses of Au and SnO₂ layers are ~32 nm and ~17 nm for sample B, ~ 41 nm and ~32 nm for sample C and ~52 nm and ~26 nm for sample D, respectively. All the three films have very uniform thickness over the 14 mm X 14 mm

deposition area and consist of very fine grains although the Au layer in sample B and C is relatively rougher. The surface images of sample B and C are also shown in the inserts of Figure 1. Except a few embedded micro/submicro spherical Au particles, the surface of the bi-layer films is very smooth.

To further analyze the microstructures of the bi-layer films, XRD patterns were recorded for all the four samples and the results are shown in Figure 2. All the four films showed XRD peaks at angles of 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]. No peaks were observed in the XRD patterns that are originated from the SnO_2 which means that the SnO_2 top layer has amorphous structure in all the three SnO_2/Au bi-layer films. The results clearly illustrate that Au is crystallized into polycrystalline in the pure Au and SnO_2/Au bi-layer films while SnO_2 existing as an amorphous structure. All the three Au peaks are relatively weak and broad, which indicates that the Au grain size is small which is consisting with the FE-SEM images in Figure 1. The appearance of dual-peak could 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 (see insert of figure 1). Those micro or sub-micron sized Au particles were generated during the pulsed laser ablation process [24]. The intensity of all the three Au peaks for the bi-layer films decreased as the thickness of the SnO_2 layer increased since the x-ray signal from the underneath Au layer decreased when the SnO_2 layer thickness increased.

SPR responses of the pure Au film (sample A) and SnO_2/Au bi-layer films (sample B, C and D) with various SnO_2 thicknesses on BK7 substrates when excited with the 633 nm light

beam were shown in Figure 3(a). Reflectance minimum (SPR dip) of the 41 nm pure Au film almost approached zero at 43.9 degree of incident angle (figure 3(a), sample A). 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 order to achieve a good SPR response (sharp SPR dip and low reflectance minimum), the thickness of Au layer should be in the range of 30 ~ 60 nm. Therefore, the Au layer thickness in all the three SnO₂/Au bi-layer films was controlled within this 30 ~ 60 nm range. Deposition of thin SnO₂ layer on the surface of the pure Au films shifts the reflectance minimum (SPR dip) to the higher values of incident angle and the angle shift increases with the thickness of the SnO₂ top layer. The width of SPR dip also becomes broader as the SnO₂ layer thickness increases. The incident angles corresponding to SPR dips (SPR angle) of sample B, C and D are 46.1, 48.0 and 49.0 degree respectively. Figure 3 clearly shows that the SPR angle can be adjusted to a desired value by controlling the thickness of the dielectric and metal layers. This provides the great flexibility for geometry arrangement of the light source and detector in designing a SPR sensor. Calculations of the SPR responses of the SnO₂/Au bi-layer films were also carried out using Macleod's method [25] in order to compare with the experimental results. 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 [26], and other literatures [27-29]. The n and k for Au were found to be $n = 0.16172$ and $k = 3.21182$ at the wavelength of 633 nm. The n and k values used in the calculation of the dielectric constant of SnO₂ films were measured from SnO₂ films deposited by the PLD. The SnO₂ films were deposited by ablating the SnO₂ target in 40 mTorr of O₂ on Si(100) wafers at 20 °C substrate temperature. The optical reflectance spectra of SnO₂ films were measured with a fiber-optic-based spectrophotometer (SCI Film TEK3000). Their n and k values were calculated

from the reflectance spectra by using appropriate material models to fit the measurement data and the n and k values for the SnO_2 film at 633nm are: $n = 1.55321$, $k = 0$, respectively. Figure 3(b) shows the simulated data for sample A, B, C and D. It is clear that SPR responses calculated with the Macleod's method shows the similar trend as the experimental data in term of the dependence of SPR angle with SnO_2 layer thickness. The simulated SPR angles for sample A, B, C and D are 44.6, 48.5, 52.6 and 50.0 respectively. The differences between simulated and experimental SPR angles for samples A, B, C and D are 0.7, 2.4, 4.6 and 1.0 degree respectively. The simulation results predict larger SPR angles than the experimental data for all the four samples, particularly the SPR angle for sample D appeared at larger value than sample C in experimental data while it is opposite in simulated results. In addition, the shapes of SPR responses predicted by theory are much broader than the experimental results. Apparently, there are discrepancy between the simulated results and experimental data. However, when considering the complexity of the PLD bi-layer films where intermixing and roughness at the interface do exist, as well as errors in the thickness measurement by FE-SEM and the n , k measurement by spectrophotometer, the simple Macleod's method was able to approximately predict the SPR response of the bi-layer films deposited by the PLD. More sophisticated theory that could take into account for the complexity the PLD bi-layer films should be developed. SPR responses of the SnO_2/Au bi-layer film samples B and D when excited with two different wavelengths (i.e. 633 and 833 nm) of light beam were compared in Figure 4. The reflectance minimum occurred at lower incidence angles when the longer wavelength light is used. The SPR dip shifted from 46.1 degree to 41.8 degree for sample B and from 49.0 to 43.7 degree for sample D when wavelength was changed from 633 nm to 833 nm. The widths of SPR dips are also much narrower when excited with 833 nm light as comparing with 633nm light; therefore

excitation with longer wavelength light are able to achieve better sensitivity for SPR gas sensing using the SnO_2/Au bi-layer films. Experimental results as well as theoretical simulation in Figure 3 and 4 have provided critical information about the optimized film thickness and wavelength of the laser light for the design of SPR gas sensors when metal-metal oxide bi-layer films are used. Only within limited ranges of these parameters, sharp SPR response will occur and thereafter can be used for high sensitivity SPR gas sensing applications.

Surface plasma waves are collective oscillations of the free electrons at the boundary of Au and SnO_2 , the associated electric field is peaked at the SnO_2/Au interface where propagation occurs and decays exponentially into the two Au and SnO_2 media, extending into the dielectric media over a range of, typically, a few hundred nanometers [4, 30]. When one considers using SnO_2/Au bi-layer films for SPR gas sensing, the thickness of SnO_2 should be optimized. So if the SnO_2 layer is too thick, refractive index change within the surface region of SnO_2 layer upon gas exposure will have weak affect on the Surface Plasmon wave since at such distance the electric field strength is weak that is far away from the Au surface. However, if there is speed diffusion of absorbed gas molecules/ions from the SnO_2 surface region to the whole SnO_2 layer and cause the refractive index change of the whole SnO_2 layer, thick SnO_2 layer will be still suitable for the SPR sensing. Speeding up the diffusion process and reducing the response time, however, require high operating temperatures. This will increase the difficulty in designing the SPR sensor as integrating a heater into this optical device is tricky. If SnO_2 layer is too thin, on the other hand, chemical reactions/physical absorption occurred in such thin SnO_2 layer cannot cause significant change in the refractive index as the amount of material available in the dielectric media for the index change is low and it will result in low chemical sensitivity. Selection of the thickness of the chemically active overlayer in SPR gas sensor design will

depend on a number of factors such as the material properties of the semiconductive metal oxide, the operating temperatures, the wavelength of light used and the nature of the gas to be detected.

It is known that SnO_2 is one of the most common used materials in the field of gas sensors and shows good sensitivity towards the detection of large variety of gases such as NO, CO, H_2S , and H_2 . The gas sensing mechanism is: when oxidizing agent is present, it extracts electrons from SnO_2 material thereby decreasing its conductivity, while when reducing agent is present, electrons are injected into the SnO_2 material and increasing conductivity. In order to exam whether or not gas sensing using SPR response of SnO_2/Au bi-layer films is feasible, the surface of the SnO_2 layer of the bi-layer films with difference SnO_2 thicknesses was alternatively expositied to the pure N_2 and 50 or 100 ppm NO contained N_2 gas mixture at 150 °C. The angle of the 833nm incident light in the GWC SPR-imaging system was fixed at 41.5, 44.5 and 43.5 degree, for sample B, C and D, respectively, and the reflectance was monitored also at the same angles continuously when the gas flow was switched between the pure N_2 and 50 or 100 ppm NO/ N_2 mixture. Longer wavelength light was used for the SPR gas sensing to achieve better sensitivity since the SPR dips of SnO_2/Au bi-layer excited by longer wavelength light are narrower than by short wavelength light as shown in Figure 4. The SPR gas sensing responses of the three SnO_2/Au bi-layer films are shown in Figure 5. For all the three films, the intensity of reflectance increases when 50 or 100 ppm NO/ N_2 mixture is introduced, and the reflectance decreased as the NO/ N_2 mixture is switched back to pure N_2 . Second and third runs of NO injection and removal also shown reasonable good response, however, the extend of intensity increase or decrease is not as much as that of the first run indicating that portion of NO gas molecules was adsorbed irreversibly on the SnO_2 surface. The reflectance baseline is unstable and keeps drifting upward. The reasons for the baseline drift may be caused by background

refractive index variations due to temperature, humidity or pressure changes of the testing cell; particularly unstable in cell temperatures is indeed the concern. The intensity of reflectance increases more (more than 2 times) for the sample B than that for the sample C when 50 ppm NO/N₂ gas mixture was introduced. The thicknesses of both Au and SnO₂ layers in sample B are smaller than that of sample C (~32 nm Au and ~17 nm SnO₂ for sample B, ~41 nm Au and ~32 nm SnO₂ for sample C). It seems that thinner SnO₂ layer is desirable to achieve better NO gas sensing sensitivity than thicker layer. Sample C and sample D have similar thicknesses of the SnO₂ layers (i.e. 32 nm vs. 26 nm). The reflectance change when sample D was exposed to 100 ppm NO/N₂ mixture is more than 2.5 time of that of sample C when it was exposed to 50 ppm NO/N₂ mixture. Small SnO₂ layer thickness difference may contribute to the non-linearity of reflectance change vs. concentration although more experimental data are needed. The response time for 50 ppm NO/N₂ mixture was around 15 minutes while for 100 ppm NO/N₂ mixture it was reduced to around 5 minutes. The results in figure 5 are our preliminary evaluation of the feasibility of using the SnO₂/Au bi-layer films for SPR gas sensing. In order to obtain more precise and actual data, improvement with our experimental set-up and instrumentation is currently undergoing. Detailed works in term of its sensitivity, selectivity, detection limit, and temperature dependence will be reported in our future communications. The NO gas sensing experiments in figure 5 were carried out at 150°C temperature; it is well-known that the chemical reactivity of semiconductor metal oxides such as SnO₂ towards oxidizing or reducing gases increases with temperatures. Therefore it is expected that more sensitive and faster response can be achieved by SnO₂/Au bi-layer films at higher temperatures than 150°C for the NO gas sensing. However, integrating a heater into the SPR gas sensor design will face some challenges, particularly for heating up to high temperatures. The index oil that was used to glue the sample to

the prism could also evaporate and decomposed at high temperatures. Optical heating such as laser or IR lamp that provide a short heating pulse to the sample surface while the SPR responses are collected simultaneously could be the solution. Slow response of semi-conductive metal oxides for gas sensing at low operating temperature is one of the drawbacks of this series of materials and indeed makes them difficult to rapidly localize a gas source which limits their applications. Organic compounds or polymers such as phthalocyanine and polyfluoroalkylsiloxane could be more suitable for low temperature gas sensing application although sometime reversibility is an issue. Since a large variety of semiconductive metal oxides have been investigated for chemoresistive gas sensing applications and their gas sensing mechanism have been well-understood, it is nature to extend this series of material for SPR gas sensing as in most case their optical properties are changed upon different gas exposure. The main challenge is how to heat up the chemically active oxide layer to evaluated temperatures and maintain the temperatures steadily while not to damage other optical components.

5. Conclusions

SPR responses of SnO_2/Au bi-layer films were measured and simulated for various different layer thicknesses in the Kretschmann configuration. Deposition of thin SnO_2 layer on the surface of the Au films shifts the reflectance minimum (SPR dip) to the higher values of incident angle and the angle shift increases with the thickness of the SnO_2 top layer. The width of SPR dip also becomes broader as the SnO_2 layer thickness increases. The SPR responses of composite films were simulated with Macleod's general characteristic matrices method to compare with experimental data. Although the theoretical calculation shows similar trend as the experimental data in term of the dependence of SPR angle with SnO_2 layer thickness, there are discrepancy between the simulated results and experimental data, particularly, the shape of SPR response

predicted by theory is much broader than the experimental results. The SPR response of the SnO₂/Au bi-layer films exposed to 50 or 100 ppm NO gas was measured and our initial results demonstrated that SPR gas sensing using SnO₂/Au bi-layer films is feasible.

Acknowledgements

This work was supported under jointed NRC-NSC-ITRI (Canada-Taiwan) Nanotechnology Initiatives. The authors are also indebted to Mr. B. Gibson of the NRC-IMI for his technical assistant.

References

- 1 A. Otto, Excitation of nonradiative surface plasma waves in silver by the method of frustrated total reflection, *Zeitschrift fur Physik*, 216:398–410, August 1968.
- 2 E. Kretschmann and H. Raether, Radiative decay of non-radiative surface plasmons excited by light, *Zeitschrift Fur Naturforschung*, 23A:2135–2136, 1968.
- 3 C. Nylander, B. Liedbery and T. Lind, Gas detection by means of surface plasmon resonance, *Sensors and Actuators*, 3(1982/83) 79-88.
- 4 B. Liedbery, C. Nylander and I. Lundstron, Surface plasmon resonance for gas detection and biosensing, *Sensors and Actuators*, 4(1983) 299-304.
- 5 J. P. Lloyd, C. Pearson and M. C. Petty, Surface plasmon resonance studies of gas effects in phthalocyanine langmuir-blodgett films, *Thin Solid Films*, 160(1-2)(1988)431-443.
- 6 K. Kato, C. M. Dooling, K. Shinbo, Tim H. Richardson, F. Kaneko, R. Tregonning, M. O. Vysotsky and C. A. Hunter, Surface plasmon resonance properties and gas response in porphyrin Langmuir-Blodgett films, *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 198-200(2002)811-816.
- 7 A. B. El-Basaty, T. A. El-Brolossy, S. Abdalla, S. Negm R. A. Abdella and H. Talaat, Surface plasmon sensor for NO₂ gas, *Surf. Interface Anal.* 2008, 40, 1623–1626.
- 8 Samoylov AV, Mirsky VM, Qingli Hao, Swart C, Shirshov YM, Wolfbeis OS, Nanometer-thick SPR sensor for gaseous HCl, *Sensors and Actuators B (Chemical)*, 106(1)(2005)369-72.

- 9 H. Deng, D. Yang, B. Chen, C.-W. Lin, Simulation of surface plasmon resonance of Au-WO_{3-x} and Ag-WO_{3-x} nanocomposite films, *Sensors and Actuators B* 134 (2008) 502–509.
- 10 B. Chen, D. Yang and C.-W. Lin, Surface plasmon resonance response of Au-WO_{3-x} composite films, *Appl Phys A* DOI 10.1007/s00339-009-5249-4.
- 11 de Julián Fernández, M.G. Manera, G. Pellegrini, M. Bersani, G. Mattei, R. Rella, L. Vasanelli and P. Mazzoldi, Surface plasmon resonance optical gas sensing of nanostructured ZnO films, *Sensors & Actuators: B. Chemical*, 130(1)(2008)531-7.
- 12 E. Maciak, Z. Opilski, T. Pustelny, and M. Bednorz, An optical detection NH₃ gas by means of a-WO₃ thin films based on SPR technique, *Journal de Physique IV* (Proceedings), 129(2005)131-6.
- 13 V. Vaichikauskas, R. Janushkevichius, E. Radavichius, R. Antanavichius, Plasmon-type CO sensor based on In₂O₃(Sn) films, *Allerton Press. Lithuanian Physics Journal*, 37(4)(1997)253-5
- 14 T. Numata, Y. Otani, N. Umeda, Meso-porous membrane of noble metal for surface plasmon resonance gas sensors, *Mater Sci* (2007) 42:1050–1053.
- 15 T. Arakawa and S. Miwa, Selective gas detection by means of surface plasmon resonance sensors, *Thin Solid Films*, 281-282(1-2)(1996)466-468.
- 16 J. Bowen, L. J. Noe, B. P. Sullivan, K. Morris, V. Martin, and G. Donnelly, Gas-Phase Detection of Trinitrotoluene Utilizing a Solid-Phase Antibody Immobilized on a Gold Film By Means of Surface Plasmon Resonance Spectroscopy, *Applied Spectroscopy*, 57(8)(2003)906-914.
- 17 A. Abdelghani, J.M. Chovelon, N. Jaffrezic-Renault, , C. Ronot-Trioli, C. Veillas and H. Gagnaire, Surface plasmon resonance fibre-optic sensor for gas detection, *Sensors and Actuators B: Chemical*, 39(1-3)(1997)407-410.
- 18 R.P. Podgorsek, T. Sterkenburgh, J. Wolters, T. Ehrenreich, S. Nischwitz, H. Franke, Optical gas sensing by evaluating ATR leaky mode spectra, *Sensors and Actuators B* 39 (1997) 349–352.
- 19 M. Niggemann, A. Katerkamp, M. Pellmann, P. Bolsmann, J. Reinbold, K. Cammann, Remote sensing of tetrachloroethene with a micro-fibre optical gas sensor based on surface plasmon resonance spectroscopy, *Sensors and Actuators B* 34 (1996) 328–333.
- 20 R. Dolbec, M.A. El Khakani, Pulsed laser deposited platinum and gold nanoparticles as catalysts for enhancing the CO sensitivity of nanostructured SnO₂ sensors, *Sens. Lett.* 3 (3) (2005) 216–221.
- 21 K. S. Patel and H. T. Sun, Ceramic semiconductors for gas detection, *Key Engineering Materials*, 115:181–190, 1996.

- 22 N. O. Savage, S. A. Akbar, P. K. Dutta, Titanium dioxide based high temperature carbon monoxide sensors, *Sens. Actuators B* 72 (2001) 239-248.
- 23 S. Boughaba, G. I. Sproule, J. P. McCaffrey, M. Islam and M. J. Graham, Synthesis of tantalum pentoxide films by pulsed laser deposition: material characterization and scale-up, *Thin Solid Films* 358 (2000) 104-113.
- 24 B. Chrisey and G. K. Hubler, *Pulsed Laser Deposition of Thin Films*, Wiley-Interscience, 1994.
- 25 H. Angus Macleod, *Thin-Film Optical Filters*, Institute of Physics Publishing, Bristol and Philadelphia, 3rd edition, 2001.
- 26 D. R. Lide, *CRC Handbook of Chemistry and Physics*, CRC Press, 87th edition, June 2006.
- 27 D. Palik, *Handbook of Optical Constants of Solids*, Academic Press, 1998.
- 28 L. G. Schulz, The optical constants of silver, gold, copper, and aluminium. I. The absorption coefficient k , *J. Opt. Soc. Am* 44 (May (5)) (1954) 357-362.
- 29 R. A. Innes and J. R. Sambles, Optical characterisation of gold using surface plasmonpolaritons, *J. Phys. F: Met. Phys.*, 17:277-287, 1987.
- 30 H. Raether, *Physics of Thin Films*, Vol. 9 (Academic Press, New York, 1977) p. 145.

Figure Captions

- Figure 1: The cross-sectional FE-SEM micrographs of pure Au (sample A) and SnO₂/Au bi-layer films of various SnO₂ and Au layers thicknesses (sample B, C and D).
- Figure 2: X-ray diffraction patterns of pure Au (sample A) and SnO₂/Au bi-layer films of various SnO₂ layer thicknesses (sample B, C and D).
- Figure 3: Experimental and Simulated SPR responses of pure Au (sample A) and SnO₂/Au bi-layer films of various SnO₂ layer thicknesses (sample B, C and D) when excited by 633 nm light beam.
- Figure 4: Experimental SPR response of SnO₂/Au bi-layer films of various SnO₂ layer thicknesses (sample B and D) when excited by 633 nm and 833 nm light beams.
- Figure 5: Experimental SPR response of SnO₂/Au bi-layer films of various SnO₂ and Au layer thicknesses (sample B, C and D) when they were alternatively exposed to the pure N₂ gas and 100 or 50 ppm NO contained N₂ gas mixture.

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5