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Carbon Monoxide Gas Sensor Based on Titanium Dioxide Nanocrystalline with a Langasite Substrate

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Abstract—Titanium dioxide (TiO_2) and gold doped TiO_2 (Au- TiO_2) thin films on langasite (LGS) substrates were employed for carbon monoxide (CO) sensing. These two types of sensors have interdigital electrodes with Ti, Ni and Au metallization film. Thin films of TiO_2 were deposited using the radio frequency (RF) magnetron sputtering method. Both TiO_2 and Au- TiO_2 based gas sensors were exposed to low concentrations of CO gas in synthetic air at a temperature range between 230°C and 320°C and their electrical conductivity were measured. It has been observed that the device sensitivity is much greater for the Au- TiO_2 based gas sensor. The response time of the sensor is shorter than that of commercial conductometric CO sensors.

I. INTRODUCTION

Due to the rapid growth in industries and population, environmental health hazards are a growing concern for our society today. There is a need to monitor and reduce harmful gases e.g. carbon monoxide, nitrogen oxides and hydrocarbons from power plants and automobiles using reliable and low-cost methods. Solid-state gas sensors offer a low-cost and practical alternative to conventional analytic equipment. Particularly, metal-oxide gas sensors are of interest due to their high sensitivity and small dimension.

Titanium dioxide (TiO_2) is one of the semiconductor metal oxides suitable for development of conductometric gas sensors. Being one of the most investigated materials, TiO_2 has been extensively used in gas sensing experiments [1-5]. TiO_2 has also found itself to be commercially viable in photocatalytic products e.g. air cleaners and air conditioners and self-cleaning surfaces [6].

TiO_2 has three polymorphs namely anatase, rutile and brookite. These different polymorphs influence the sensing properties. The anatase phase is preferred over rutile in gas sensing due to its higher photocatalytic activity [7]. Anatase and brookite are thermodynamically metastable forms of TiO_2 which irreversibly convert to rutile at high temperatures. This anatase-to-rutile transition has a severe

effect on the sensor's sensitivity. Therefore, it is essential to maintain the nanostructure in anatase phase to increase the device's sensitivity in gas sensing [8].

The addition of dopants to metal oxide semiconductors is the most common approach to control the selectivity and sensitivity in gas sensing experiments. Recently, gold has earned its reputation as an excellent catalyst in gas sensing performances. Much literature have reported that the ultra fine particles of gold resulted in a higher catalytic oxidation of CO [9, 10]. This catalytic activity is also affected by the anatase phase of TiO_2 . Takaoka et al. [11] have revealed that the anatase phase has more oxygen vacancies than the rutile phase of TiO_2 which lead to more Ti^{3+} states. Therefore, the catalytic oxidation of CO is enhanced when gold was supported on the anatase phase.

Langasite (LGS) is a material which has excellent stability at high temperature and, to best of the authors' knowledge, has not previously been used as a conductometric substrate for gas sensing applications.

In this paper, we use the radio frequency (RF) magnetron sputtering method for the fabrication of nanocrystallite thin films of TiO_2 on a LGS substrate. Microstructural characterization of the films was carried out by means of scanning electron microscopy (SEM) and X-ray diffraction (XRD). Electrical responses of both sputtered TiO_2 and gold doped TiO_2 (Au- TiO_2) films towards CO at a temperature range between 230°C and 320°C have been measured.

II. EXPERIMENTAL

A. Fabrication

Two types of sensor were fabricated on a LGS substrate using photolithography. Sensors have interdigital electrodes with Ti, Ni and Au (in order of deposition) metallization film thicknesses of 20 nm, 30 nm and 50 nm, respectively. Each sensor consists of 113 electrode pairs, aperture width of $5600\ \mu\text{m}$ and an electrode width of $8.5\ \mu\text{m}$. TiO_2 films were prepared using a 99.9% pure Ti target by RF magnetron

sputtering in an Ar (60%) and O₂ (40%) mixture for 40 minutes at room temperature. A chamber pressure of 1×10^{-2} Torr by RF magnetron sputtering in an Ar (60%) and O₂ (40%) mixture for 40 minutes at room temperature. A chamber pressure of 1×10^{-2} Torr and RF power of 140 W were used for sputtering. The sputtered films have a thickness of ~100 nm. On one type of sensor, a thin layer of Au was sputtered for 10 seconds.

B. Morphological and Structural Characterization

For SEM characterization, a thin layer of Au was sputtered on the TiO₂ films. The TiO₂ films were deposited for 7 hours and 40 minutes. This was conducted to obtain a sufficiently thick layer for XRD measurements. Both nonannealed and annealed (at 500°C) bare LGS substrates with TiO₂ films are shown in Fig. 1 and Fig. 2 respectively. Fig. 1 shows a denser amorphous TiO₂ film and consists of pyramidal shaped grains. Significant grain coarsening, less elongated and edge rounded shaped grains are shown in Fig. 2.

Both nonannealed and annealed (at 500°C) LGS with Ti, Ni and Au metallization film (LGS-TiNiAu) substrates are shown in Fig. 3 and Fig. 4 respectively. Fig. 3 consists of a compact and homogeneous polycrystalline nanostructure and the grain size is approximately 100nm. Fig. 4 shows that the anatase structure is changed after annealing at 500°C. Slight grain coalescence occurred during annealing. There is the presence of spherical particles surrounded by larger grains. There is no significant grain growth in the spherical particles. Guidi et al. [12] reported that the grain coalescence is almost certainly due to the anatase-to-rutile transition and that the small particles of the cluster were TiO₂ anatase and the larger grains were TiO₂ rutile.

Figure 1. SEM image of a TiO₂ film on nonannealed bare LGS substrate.

Figure 2. SEM image of a TiO₂ film on annealed (at 500°C) bare LGS substrate.

Figure 3. SEM image of a TiO₂ film on nonannealed LGS-TiNiAu substrate.

Figure 4. SEM image of a TiO₂ film on annealed (at 500°C) LGS-TiNiAu substrate.

The XRD patterns of TiO₂ films were obtained using a Bruker D8 Advance XRD with a CuK α source. The analysis was performed to understand the growth of TiO₂ films on the nonannealed LGS substrates. The XRD patterns of both bare LGS and LGS-TiNiAu substrates are shown in Fig. 5 and Fig. 6 respectively. Both substrates have a TiO₂ film deposited for 7 hours and 40 minutes.

The XRD pattern in Fig. 5 shows several anatase peaks for the bare LGS substrate. For the LGS-TiNiAu substrate, there is an increase number of anatase peaks in Fig. 6 as compared with Fig. 5. The anatase peaks in Fig. 6 are observed to be slightly broader. An intense peak due to anatase (112) was observed in the 2θ range at 38.5° . This significant increase of the intensity is accompanied by the decrease of anatase (101). Similar anatase phases i.e. (101), (112), (200) and (211) were also reported in [13]. The other peaks in Fig. 6 correspond to the gold electrodes and LGS substrate.

Figure 5. XRD pattern of the anatase (A) peaks from a bare LGS substrate.

Figure 6. XRD pattern of the anatase (A) peaks from a LGS-TiNiAu substrate.

C. Gas Sensing Measurements

Both TiO_2 and Au-TiO_2 thin films on LGS-TiNiAu substrates were tested separately. Each conductometric sensor was mounted on an alumina microheater. The microheater was controlled by a regulated DC power supply providing different operating temperatures. The output resistance as a function of time across the conductometric sensor during CO exposure was measured using a multimeter (Keithley 2001). A computerized gas calibration system, with mass flow controllers, was used to expose the sensor to different concentrations of CO gas. The total flow rate was

kept constant at 200 sccm and synthetic air was used as the reference gas.

III. RESULTS AND DISCUSSION

The change in conductance of TiO_2 and Au-TiO_2 thin films on LGS-TiNiAu substrates were examined in 60 and 125 ppm of CO in synthetic air at a temperature range between 230°C and 320°C . It has been observed that the device sensitivity is much greater for the Au-TiO_2 based gas sensor.

The response of the sensor is defined as a ratio of resistance in synthetic air to the resistance when exposed to the target gas. In Fig. 7, the Au-TiO_2 sensor showed fast response and recovery time of less than 20 seconds towards 60 and 125 ppm of CO at 318°C , respectively. The Au-TiO_2 sensor also had a good repeatability in Fig. 8. The Au-TiO_2 sensor exhibited the largest response towards 125 ppm of CO at 230°C as shown in Fig. 9. The Au-TiO_2 sensor response was 3 to 5 times larger than that of the TiO_2 sensor, with the ratio varying with temperature. It is observed in Fig. 10 that by increasing the operational temperature, the Au-TiO_2 sensor response becomes smaller for both 60 and 125 ppm of CO.

Figure 7. Response and recovery times of Au-TiO_2 sensor towards 60 and 125 ppm of CO for different temperatures.

Figure 8. Response of Au-TiO_2 sensor towards 60 and 125 ppm of CO at 230°C .

Figure 9. Comparison of responses for TiO₂ and Au-TiO₂ sensors towards 60 and 125 ppm of CO at 230°C.

Figure 10. Response of Au-TiO₂ sensor towards 60 and 125 ppm of CO from 230°C to 320°C.

IV. CONCLUSION

Thin films of anatase TiO₂ have been deposited on LGS-TiNiAu substrates using the RF magnetron sputtering method and successfully used as conductometric CO sensors. The SEM images show the compactness and homogeneous polycrystalline nanostructure for the as deposited TiO₂ film on the LGS-TiNiAu substrate. A grain size of approximately 100nm was achieved. The XRD patterns also depict the nanostructure of the as deposited TiO₂ film with a slight broadening of the anatase peaks. The Au-TiO₂ sensor has shown to enhance its sensitivity by 3 to 5 times as compared to the TiO₂ sensor. The Au-TiO₂ sensor also demonstrated the largest response towards 125 ppm of CO at 230°C. The increase in sensitivity of the sensor towards CO gas can be attributed to the addition of gold on the surface of TiO₂ which acts as a catalyst. As compared to other metal types of doping on TiO₂ films, our work has shown that the Au-TiO₂ sensor displayed a relatively fast response and recovery time of less than 20 seconds towards 60 and 125ppm of CO at 318°C.

REFERENCES

- [1] L. Sun, H. Zhao, S. Gao, and J. Zhao, "Preparation and gas-sensing property of a nanosized titania thin film towards alcohol gases," *Sens. Actuators, B*, vol. 114, pp. 387-391, 2006.
- [2] F. H. Babaei, M. Keshmiri, M. Kakavand, and T. Troczynski, "A resistive gas sensor based on undoped p-type anatase," *Sens. Actuators, B*, vol. 110, pp. 28-35, 2005.
- [3] O. K. Varghese, D. Gong, M. Paulose, K. G. Ong, and C. A. Grimes, "Hydrogen sensing using titania nanotubes," *Sens. Actuators, B*, vol. 93, pp. 338-344, 2003.
- [4] M. L. Frank, M. D. Fulkerson, B. R. Patton, and P. K. Dutta, "TiO₂-based sensor arrays modeled with nonlinear regression analysis for simultaneously determining CO and O₂ concentrations at high temperatures," *Sens. Actuators, B*, vol. 87, pp. 471-479, 2002.
- [5] A. Rothschild, F. Edelman, Y. Komem, and F. Cosandey, "Sensing behavior of TiO₂ thin films exposed to air at low temperatures," *Sens. Actuators, B*, vol. 67, pp. 282-289, 2000.
- [6] A. Fujishima and X. Zhang, "Titanium dioxide photocatalysis: present situation and future approaches," *C. R. Chimie*, vol. 9, pp. 750-760, 2006.
- [7] N. Ruzicki, G. S. Herman, L. A. Boatner, and U. Diebold, "Scanning tunneling microscopy study of the anatase (1 0 0) surface," *Surf. Sci.*, vol. 529, pp. 239-244, 2003.
- [8] M. C. Carotta et al., "Gas sensors based on semiconductor oxides: basic aspects onto materials and working principles," *Mater. Res. Soc. Symp. Proc.*, vol. 828, pp. A4.6.1-A4.6.11, 2005.
- [9] L. Fan, N. Ichikuni, S. Shimazu, and T. Uematsu, "Preparation of Au/TiO₂ catalysts by suspension spray reaction method and their catalytic property for CO oxidation," *Appl. Catal., A*, vol. 246, pp. 87-95, 2003.
- [10] T. V. Choudhary and D. W. Goodman, "Oxidation catalysis by supported gold nano-clusters," *Top. Catal.*, vol. 21, 2002.
- [11] G. H. Takaoka, T. Hamano, K. Fukushima, J. Matsuo, and I. Yamada, "Preparation and catalytic activity of nano-scale Au islands supported on TiO₂," *Nucl. Instrum. Methods Phys. Res., Sect. B*, vol. 121, pp. 503-506, 1997.
- [12] V. Guidi, M. C. Carotta, M. Ferroni, G. Martinelli, and M. Sacerdoti, "Effect of dopants on grain coalescence and oxygen mobility in nanostructured titania anatase and rutile," *J. Phys. Chem. B*, vol. 107, pp. 120-124, 2003.
- [13] T. Y. Yang, H. M. Lin, B. Y. Wei, C. Y. Wu, and C. K. Lin, "UV enhancement of the gas sensing properties of nano-TiO₂," *Rev. Adv. Mater. Sci.*, vol. 4, pp. 48-54, 2003.