IMPROVEMENT OF OZONE DETECTION WITH WO_3 ORIENTED FILMS

Julien OLLITRAULT[1], Nicolas MARTIN[1 *], Jean-Yves RAUCH[1], Jean-Baptiste SANCHEZ[2], Franck BERGER[2]

[1]Institut FEMTO-ST, UMR 6174, Université de Franche-Comté, CNRS, ENSMM, UTBM, 15B, Avenue des montboucons, 25030 Besançon Cedex, France

[2]Laboratoire de Chrono-Environnement, UMR 6249, Université de Franche-Comté, CNRS, UFR ST La Bouloie, 16, Route de Gray, 25030 Besançon Cedex, France

Abstract

Tungsten oxide WO_3 thin films were prepared by dc reactive magnetron sputtering. The GLancing Angle Deposition (GLAD) technique was implemented to transform the typical dense microstructure into an inclined columnar and porous architecture. The incident angle α of the sputtered particles was 0 and 70° leading to a column tilt angle β of 0 and 40°, respectively. Conventional and inclined WO_3 films were sputter deposited on a commercial hotplate system. Ozone gas was periodically injected from 0 to 220 ppb and the variation of resistance of the system was measured vs. time at 250°C. The conventional WO_3 films exhibited a significant change of conductance as a function of the ozone injection. GLAD WO_3 films with a columnar angle β = 40° were even more sensitive to the ozone pulses and the time of response or recovery was significantly enhanced. This ozone detection improvement was mainly attributed to the more porous structure of WO_3 films produced by the GLAD method.

Keywords: GLancing Angle Deposition; WO_3 thin films, porosity, ozone detection.

1. Introduction

Enhancement of the gas detection requires the development of novel materials and thin films in which the surface interactions with gaseous species have to be investigated. Small size, easy use and flexibility in fabrication are the main advantages of chemoresistive-type semiconductor sensors based on metal oxide compounds. Among such compounds, tungsten trioxide (WO_3) appears as an interesting material for the gas detection since it is an indirect

* Corresponding author: nicolas.martin@femto-st.fr; Tel.: +33 (0)3 63 08 24 31; Fax: +33 03 81 66 67 01

band gap n-type semiconductor sensitive to very low concentrations of toxic gases like Cl_2, SO_2, CH_4 or O_3 [1-3]. When gases interacts with tungsten trioxide, surface conductivity changes take place mainly due to variations of the free electron concentration occurring by charge exchange with adsorbed species. It is commonly admitted that the sensitivity of the metal oxide to ozone is mainly due to the presence of surface oxygen vacancies [4]. Several doping strategies were developed in order to favor this type of vacancies and improve the gas sensor performances [5-8]. Another approach consists in tuning the structure of thin films in order to produce porous architectures at the micro and nanoscales [9, 10]. To this aim, the GLAD method (GLancing Angle Deposition) is an elegant way for growing films exhibiting original and porous structures (inclined columns, zigzags, helices …) using physical vapor deposition processes such as magnetron sputtering [11].

In this letter, we show that sensors utilizing WO_3 thin films sputter deposited by GLAD strongly improve the detection of ozone. A classical WO_3 film produced with a normal incidence of the particle flux is compared to an inclined columnar WO_3 GLAD film. Both materials are similarly tested as gas sensors in an ozone environment. Response and recovery times, repeatability and sensitivity of these systems are compared taking into account the difference of architectures produced by conventional and GLAD sputtering.

2. Material and methods

Films were deposited by reactive dc magnetron sputtering. A stainless-steel home made vacuum reactor (volume of 40 L) was equipped with a circular planar and water cooled magnetron sputtering source. It was evacuated with a turbomolecular pump, backed by a mechanical pump, in order to reach an ultimate pressure of 10^{-5} Pa. A tungsten target (purity 99.9 at. %, 51 mm diameter) was dc sputtered using a constant current I = 50 mA. The pumping speed was set constant at S = 13 Ls^{-1}. Argon flow rate was kept at 2.4 sccm and oxygen flow rate was maintained at 2 sccm, corresponding to argon and oxygen partial pressures of 3×10^{-1} and 3×10^{-2} Pa, respectively. Substrates, introduced through a 1 L airlock, were glass microscope slides and (100) silicon wafers (p-type, ρ = 1-30 Ωcm). Before each run, all substrates were cleaned with acetone and alcohol, and the target was pre-sputtered in a pure argon atmosphere for five minutes before injecting oxygen, in order to remove the target surface contamination layer. Afterwards, oxygen gas was introduced and the process was stabilized for 10 minutes. The target to substrate distance was kept at 50 mm in all runs. Substrates were grounded and all depositions were carried out at room temperature. The deposition time was adjusted in order to obtain a thickness close to 1 µm. Morphological features

of the samples were probed by scanning electron microscopy (SEM) at 15 keV. Films produced on (100) Si were used to observe architecture and cross-section morphology. WO_3 thin films were sputter deposited on a commercial MSP769 Heraeus sensor. Such a device allows a simultaneous heating, temperature and resistance measurements vs. time during the gas test. The later was performed at 250°C (optimized temperature not shown) according to a procedure further described in [12]. O_3 was periodically supplied by means of UV irradiation of a dry air flow (200 $mLmin^{-1}$ at 0.2 % of relative humidity) combined with a dilution bench leading to an accurate injection of 220 ppb following a rectangular signal. The conductance change of the coated device was measured as a function of time.

3. Results and discussion

Films deposited with a conventional incident angle (α = 0°) exhibit a poorly defined cross-section morphology (Fig. 1a). A dense packed structure can be distinguished with major fracture directions, which are perpendicular to the film/substrate interface. This kind of feature is typical of amorphous oxides prepared by reactive sputtering at room temperature. Some better defined columns are clearly observed for WO_3 films produced with an incident angle α = 70° (Fig. 1b). An inclined columnar architecture is achieved with narrow columns (a few tens of nanometers) and a column angle β = 40°. As usually reported with the GLAD process, this column angle β is systematically lower than the incident angle α [13]. It is dependent upon many factors including the type of sputtered materials, growth temperature, composition, energy of particles, shadowing effect, etc. Several analytical equations have been proposed in the literature providing different predictive relationships between α and β [14]. They systematically lead to the conclusion that the column inclination angle (β) always lies between the film normal and the vapor incidence angle and strongly varies with the deposition conditions. It is worth noting that the SEM cross-section of GLAD WO_3 films also displays a more voided structure. As shadowing is enhanced for larger incident angles (α > 70° is considered as the beginning of extreme shadowing regime), it results in formation of more isolated columns and thus a more porous material. The relationship between α and film density can be made via geometric analysis of oblique deposition [15]. Density models and experimental measurements all show a significant drop of the film density as α reaches 60°. For our WO_3 films prepared with α = 70° and taking into account a simple geometric approach from Tait *et al.* [16], one can assume a normalized film density of 51 %. It means that nearly half part of the GLAD films

is occupied by void regions, which correlates with the important intercolumnar spacing previously noticed from the SEM cross-section observations (Fig. 1b).

The dynamic sensing transients of the conventional (α = 0° and β = 0°) and GLAD (α = 70° and β = 40°) WO_3 thin film sensors towards pulses of 220 ppb of O_3 at 250°C are reported in Fig. 2. Ozone was periodically injected using a constant flow for 1200 s and stopped for 1800 s. The normalized sensor conductance $\Delta G/G_{air}$ vs. time t was plotted setting G_{air} as the conductance in dry air and $\Delta G = G_{air} - G_{oz}$ where G_{oz} is the conductance in the presence of ozone. Since WO_3 is an n-type semiconductor and ozone is an oxidizing gas, the conductance of the both type of sensors (β = 0 and 40°) decreases when exposed to ozone (reduction mechanism of O_3 molecules). For both WO_3 films, a drift of the $\Delta G/G_{air}$ signal can be noticed as the number of ozone injections increases. It tends to become negligible after a few periodic injections, which means that the sensors tend to be stable. For conventional WO_3 sensor (β = 0°), $\Delta G/G_{air}$ drops from 1 down to 0.12 at the end of ozone exposure (after 1200 s). By stopping the ozone injection, $\Delta G/G_{air}$ rapidly restores to 1 before the next pulse. A cyclic gas injection correlates with periodic and repeatable responses of the sensor following exponential signals, which are typical of performant systems exhibiting adsorption and desorption mechanisms vs. time.

Sensors coated with the WO_3 GLAD film (α = 70° and β = 40°) also show a clear response when ozone is periodically supplied (Fig. 2). Exponential growth and decay of the normalize variation of conductance as a function of time is similarly measured. It is worth noticing the more pronounced and rapid evolution of the sensor signal as ozone is injected or stopped. Following the same pulsing procedure as previously implemented for conventional samples, $\Delta G/G_{air}$ is lower than 0.06 at the end of the first ozone injection and tends to be null after a couple of cycles. This extended variation of the signal corresponds to enhanced sensitivity of the WO_3 GLAD sensor. In addition, the time required to reach a nearly stable conductance ratio is also improved as especially recorded on the third ozone pulse. Last but not least, response time as well as recovery time are both boosted. They can be quantitatively estimated from the slope of the curve when ozone is injected and stopped, respectively. Taking into account the beginning of the ozone injection, $\left|\partial(\Delta G/G_{air})/\partial t\right| = 2.5\times10^{-3}$ s^{-1} for WO_3 films with β = 0° whereas it is more than 3.6×10^{-3} s^{-1} for β = 40°. On the other hand, when ozone is stopped, the return to the background signal is also more defined for WO_3 GLAD film since $\partial(\Delta G/G_{air})/\partial t = 5.0\times10^{-3}$ s^{-1} whereas it reaches only 2.3×10^{-3} s^{-1} for conventional WO_3 film. It is commonly admitted that performances of sensors based-on WO_3 compounds (or other

oxides) are directly connected to the atomic defects in the films, especially oxygen deficiencies. Zhang *et al.* [17] have reported that WO_{3-y} films exhibit a metallic appearance for $y > 0.5$ and become transparent for $y < 0.3$. In our films, both samples (conventional with $\alpha = 0°$ and GLAD with $\alpha = 70°$) are transparent and the oxygen flow rate used during the deposition is high enough to deposit stoichiometric WO_3 compound. So, the improvement of the ozone detection cannot be only assigned to oxygen deficiencies but has to be correlated with the architecture, i.e. strongly dependent on the voided structure favored by the GLAD process. In addition, it was previously shown that GLAD films become strongly porous for $\alpha > 60°$ (due to extreme shadowing). Oxidation of the film is also enhanced when heated at 250°C [18]. Thus oxygen deficiencies are strongly reduced and cannot be considered as the main criterion influencing the sensor performances. Inclined columnar structure is also kept in spite of the temperature rising as previously shown for similar compounds [19] or for more reactive systems based on titanium oxide [20]. As a result, we can claim that stoichiometric GLAD WO_3 films are produced and the improvement of the ozone detection is mainly attributed to the increase of the specific surface in GLAD films. Our results are in agreement with a few investigations focused on the detection of NO_2, water vapor or other gaseous species implementing WO_3 GLAD thin films [9, 10, 19]. This enhanced response of the GLAD sensors was mainly assigned to the porous nanostructure with high surface-to-volume ratio (more than several order of magnitudes higher specific area than dense planar film). In addition to high sensitivity, long-term reliability, short response and recovery times and based-on changes of conductance reported in figure 2, one can expect that the detection limit reached by such nanostructured WO_3 films should be below the sub-ppb level [10].

4. Conclusions

Ozone sensors were fabricated by coating commercial Heraeus devices with WO_3 thin films. Reactive dc magnetron sputtering was implemented to deposit these tungsten oxide films. A conventional process was used to prepare dense and poorly structured thin films whereas the GLancing Angle Deposition method (GLAD) was developed to produce oriented and well defined columnar architectures. The GLAD WO_3 films were produced by means of an incident angle of the particle flux $\alpha = 70°$ leading to a column tilt angle $\beta = 40°$. The conductance response of the sensors maintained at 250°C was measured vs. time when they were submitted to a pulsed and periodic injection of ozone. It was shown that both type of films were sensitive to this gas. However the WO_3 GLAD films exhibited a stronger effect on the shape of the response curve. These oritented films showed superior ozone sensing

performances especially highest and fastest responses and recovery times towards ozone at an operating temperature of 250°C. This enhanced sensing characteristics were mainly attributed to the large surface area favored by the GLAD process. A more porous and voided structure was produced by GLAD giving rise to more active surface sites. The open and porous microstructure emphasized by this approach makes these films ideal candidates for sensing applications. Gaseous species can readily interact with the high-surface area peculiar to the inclined columnar architectures. Future experiments require dilution tests and other inclinations of the columnar structure. Other architectures will also be explored in next works.

Acknowledgements

This work was supported by the Region of Franche-Comté (FIMICAP and MATECO projects) and performed in cooperation with the Labex ACTION program (contract ANR-11-LABX-01-01).

References

[1] G.F. Fin, L.M. Cavanagh, A. Afonja, R. Binions, Sensors, 10 (2010) 5469-5502.

[2] K. Wetchakun, T. Samerjai, N. Tamaekong, C. Liewhiran, C. Siriwong, V. Kruefu, A. Wisitsoraat, A. Tuantranont, S. Phanichphant, Sens. Actuators B, 160 (2011) 580-591.

[3] S.M. Kanan, O.M. El-Kadri, I.A. Abu-Yousef, M.C. Kanan, Sensors, 9 (2009) 8158-8196.

[4] S.R. Utembe, G.M. Hansford, M.G. Sanderson, R.A. Freshwater, K.F.E. Pratt, D.E. Williams, R.A. Cox, R.L. Jones, Sens. Actuators B, 114 (2006) 507-512.

[5] E. Rossignyol, A. Prim, E. Pellicer, J. Arbiol, F. Hernandez-Ramirez, F. Peiro, A. Cornet, J.R. Morante, L.A. Solovyov, B. Tian, T. Bo, D. Zhao, Adv. Funct. Mater., 17 (2007) 1801-1806.

[6] B.T. Marquis, J.F. Vetelino, Sens. Actuators B, 77 (2001) 100-110.

[7] A. Hoel, L.F. Reyes, P. Heszler, V. Lantto, C.G. Granqvist, Current Applied Physics, 4 (2004) 547-553.

[8] S. Zhu, X. Liu, Z. Chen, C. Liu, C. Feng, J. Gu, Q. Liu, D. Zhang, J. Mater. Chem., 20 (2010) 9126-9132.

[9] J.J. Steele, M.T. Taschuk, M.J. Brett, Sens. Actuators B, 140 (2009) 610-615.

[10] H.G. Moon, Y.S. Shim, D.H. Kim, H.Y. Jeong, M. Jeong, J.Y. Jung, S.M. Han, J.K. Kim, J.S. Kim, H.H. Park, J.H. Lee, H.L. Tuller, S.J. Yoon, H.W. Jang, Scientific Reports, 2(588) (2012) 1-7.

[11] M.W. Hawkeye, M.T. Taschuk, M.J. Brett, “Glancing Angle Deposition of Thin Films”, John Wiley & Sons, Ltd, Chichester, 2014.

[12] A. Gaddari, F. Berger, M. Amjoud, J.B. Sanchez, M. Lahcini, B. Rhouta, D. Mezzane, C. Mavon, E. Beche, V. Flaud, Sens. Actuators B, 176 (2013) 811-817.

[13] K. Robbie, J.C. Sit, M.J. Brett, J. Vac. Sci. technol., B16(3) (1998) 1115-1122.

[14] R. Alvarez, L. Gonzalez-Garcia, P. Romero-Gomez, V. Rico, J. Cotrino, A.R. Gonzalez-Elipe, A. Palmero, J. Phys. D: Appl. Phys., 44 (2011) 385302-7.

[15] C. Buzea, K. Robbie, J. Optoelectron. Adv. Mater., 6(4) (2004) 1089-1097.

[16] R.N. Tait, T. Smy, M.J. Brett, Thin Solid Films, 226 (1993) 196-201.

[17] J.G. Zhang, D.K. Benson, C.E. Tracy, S.K. Deb, A.W. Czanderna, C. Bechinger, J. Electrochem. Soc., 144 (1997) 2022-2026.

[18] A. Besnard, N. Martin, F. Sthal, L. Carpentier, J.Y. Rauch, Funct. Mater. Lett., 6(1) (2013) 1210051-5.

[19] M. Horprathum, K. Limwichean, A. Wisitsoraat, P. Eiamchai, K. Aiempanakit, P. Limnonthakul, N. Nuntawong, V. Pattantsetakul, A. Tuantranont, P. Chindaudom, Sens. Actuators B, 176 (2013) 685-691.

[20] N. Martin, J. Sauget, T. Nyberg, Mater. Lett., 105 (2013) 20-23.

Figure captions

Fig. 1. SEM cross-section micrographs of WO_3 thin films prepared a) with a normal incidence (α = 0° and β = 0°); b) by GLAD (α = 70° and β = 40°)

Fig. 2. Ozone injection profile and corresponding normalized conductance $\Delta G/G_{air}$ vs. time t of WO_3 thin films with normal incidence (α = 0° and β = 0°) and by GLAD (α = 70° and β = 40°).

Figure 1

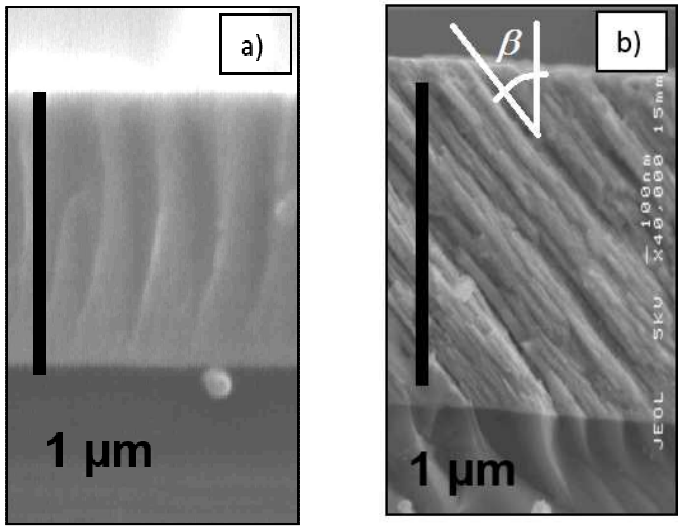

Figure 2