Available online at www.sciencedirect.com
ScienceDirect
Ceramics International 38S (2012) S653–S656
CERAMICS INTERNATIONAL
www.elsevier.com/locate/ceramint

Work function effects of ZnO thin film for acetone gas detection

Young Soo Yoon [a], Seung Hyun Jee [a], Nitul Kakati [a], Jatindranath Maiti [a], Dong-Joo Kim [b], Seok Hee Lee [a], Hyon Hee Yoon [c,*]

[a] Department of Materials Science and Engineering, Yonsei University, 134 Shinchon-dong, Seodaemun-gu, Seoul 120-749, Republic of Korea
[b] Materials Research and Education Center, Department of Mechanical Engineering, Auburn University, AL 36849-5341, USA
[c] Department of Chemical Engineering, Kyungwon University, Sungnam 461-701, Republic of Korea

Available online 27 May 2011

Abstract

ZnO thin films were deposited on alumina substrates under various conditions and then plasma treated with the goal of fabricating ZnO sensors for acetone gas detection. The ZnO thin films were deposited using the radio frequency (RF) magnetron sputtering method with a RuO_2 micro heater and Ru electrode. In order to control the work function of the sensor, ZnO thin films were deposited under the various deposition conditions (RF power, distance from target to substrate) and then plasma treated. The sensitivity of the ZnO sensors was measured in the air or in acetone gas (500 and 1500 ppm) at a substrate temperature of 250 °C, which was heated using a RuO_2 micro-heater. The sensitivity of the ZnO sensors was dependent on the work function of the ZnO thin films. Moreover, the work function of the ZnO thin films was also dependent on the binding energy of oxygen atoms. The results of this study indicate that the work function of the as-deposited or plasma treated ZnO thin films were sufficient for these films to be used as a ZnO sensor for acetone gas detection.

Keywords: B. Surfaces; C. Electrical properties; D. ZnO; E. Sensors

1. Introduction

In recent years, zinc oxide (ZnO) nanostructures have attracted considerable attention due to their high transmittance, good electrical conductivity and high gas sensitivity [1,2]. Many recent studies have focused on ZnO thin films because it is an inexpensive n-type and wide bandgap (3.2 eV) semiconductor. These properties make the ZnO a multi-functional material that can be used as sensing material in gas sensors and a transparent electrode in optical devices [3,4]. Even though ZnO thin films show a relatively high sensitivity for acetone gas, the operation temperature and detectable minimum acetone gas concentration are still high when considering commercial application of a ZnO thin film based gas sensor [5,6]. We hypothesize that the electrons transfer from the gas to the sensing material are dependent on work function. However, the influence of the work function of the ZnO thin film on acetone gas sensitivity has not yet been reported. In this study, we investigated the relationship between the sensitivity of the ZnO sensor and the work function in the ZnO sensor for acetone gas detection by varying the work functions through different deposition conditions and plasma treatment.

2. Experimental procedure

The RF magnetron sputtering system with the Zn target was used to deposit ZnO thin films on alumina substrates through the reactive sputtering method. The sputtering gas used was a mixture of Ar–O_2 (Ar:O_2 = 9:1). The chamber had a base pressure of 5 μtorr and a working pressure of 8 mtorr. The applied RF power (P_{RF}) was 100–200 W. To investigate the effect of plasma treatment on the deposition of ZnO thin films, the distances (D_{T-S}) from the target to the substrate were maintained at 65 and 100 mm in the plasma and out of the plasma, respectively. We named ZnO films with various conditions S1(P_{RF} = 100 W, D_{T-S} = 100 mm), S2(P_{RF} = 100 W, D_{T-S} = 65 mm), S3(P_{RF} = 200 W, D_{T-S} = 100 mm), and S4(P_{RF} = 200 W, D_{T-S} = 65 mm), respectively. After deposition of the ZnO thin films, the ZnO thin films

* Corresponding author. Tel.: +82 31 750 5356; fax: +82 31 750 5363.
E-mail address: hhyoon@kyungwon.ac.kr (H.H. Yoon).

0272-8842/$36.00
doi:10.1016/j.ceramint.2011.05.128

were treated by oxygen plasma. Plasma treatment was carried out at a working pressure of 50 mtorr with a RF power of 50 W for 10 min. After plasma treatment, the patterned Ru electrodes were deposited on the sensing material using the RF magnetron sputtering system. A patterned RuO_2 heater was then deposited on the back side of the substrate by RF magnetron sputtering.The sensitivity of the sensors for acetone gas detection was calculated by measuring the resistances of the sensor in air (R_a) and in acetone gas (R_g) using a Keithley 2400, which was connected to a computer and operated using a Labview program. The sensor sensitivities were measured at a temperature of 250 °C and the acetone gas concentration in the vapor was 500 and 1500 ppm. Field-emission scanning electron microscopy (FESEM; Hitachi, S-4700, Japan) and Atomic Force Microscopy (AFM; Park Systems, XE-1500, Korea) were used to assess the surface properties of the ZnO thin films. X-ray diffraction (XRD; Rigaku, D/MAX-2200, Japan) analysis was carried out on a Rigaku X-ray diffractometer with Cu Kα radiation (λ = 1.5418 Å). X-ray Photoelectron Spectroscopy (XPS) spectra were obtained using a Thermo Electron XPS (K-Alpha, Germany). The work function of the ZnO thin films was measured using a Kelvin Probe (Mcallister, KP6500, USA).

3. Results and discussion

Fig. 1 shows cross-section and surface FESEM images of the ZnO thin films. From these images, no defects or cracks were observed in the ZnO thin films. In these FESEM images, the crystallographic planes of the ZnO with a columnar structure were clearly visible, providing strong evidence that the crystalline structure of these ZnO thin films were oriented along the *c*-axis. The thicknesses of ZnO thin films were 351, 341, 344, and 407 nm, respectively.

The sensitivity of the ZnO sensor for acetone gas detection was defined as $[(R_a - R_g)/R_a \times 100]$ where R_a is the electrical resistance of the sensor in air and R_g is the electrical resistance of the sensor in the acetone–air mixture gas. The sensor for acetone gas detection was fabricated on a alumina substrate with the Ru electrode on the topside and the RuO_2 heater on the backside. Fig. 2 shows the electrode and micro-heater design and the sensitivity of the sensors for acetone gas detection. The S2 and S4 sensor displayed a higher sensitivity. In addition, the sensitivity of the ZnO thin films with plasma treatment was higher than that of the as-deposited ZnO. Although, there were large differences in the sensitivity of the ZnO thin film fabricated under various deposition conditions, plasma treatment improved the sensitivity of all ZnO thin films.

Fig. 3 shows the XRD spectra of the ZnO thin films with the various deposition conditions, FWHM and grain size of (0 0 2) crystalline direction of the ZnO thin films, which is in good agreement with the standard data (JCPDS 36-1451) for ZnO [7]. Grain size was obtained using the Scherrer's equation [8,9]. The XRD spectra in was not affected by plasma treatment because the plasma influences only the surface of ZnO thin film. The S3 and S4 had a higher intensity in (0 0 2) the crystal direction than the other ZnO thin films. In addition, S1 had the largest grain size. On the other hand, S2 had the smallest grain size of the ZnO samples. This result demonstrated that the grain

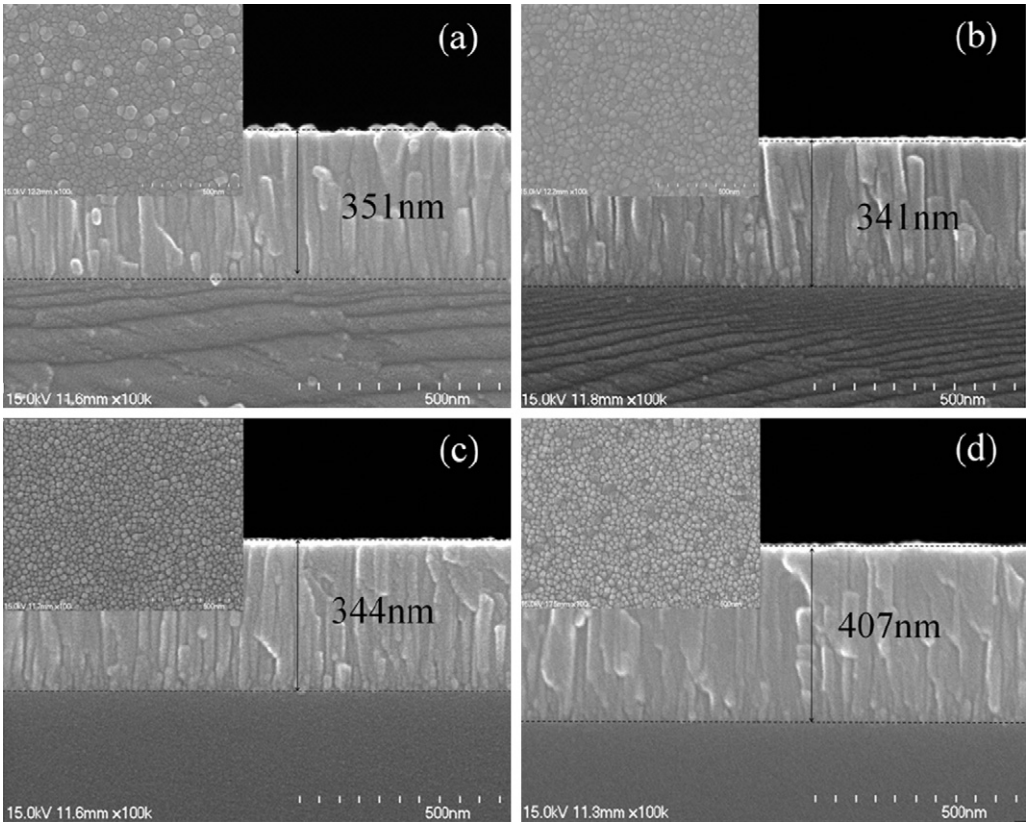

Fig. 1. . Cross-section and surface images of ZnO thin films by FESEM: (a) S1, (b) S2, (c) S3, and (d) S4.

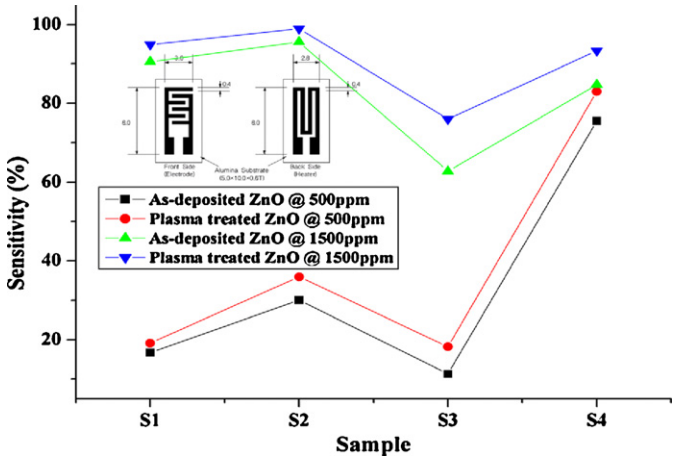

Fig. 2. . Design and sensitivity of ZnO sensors in acetone gas at acetone concentrations of 500 and 1500 ppm.

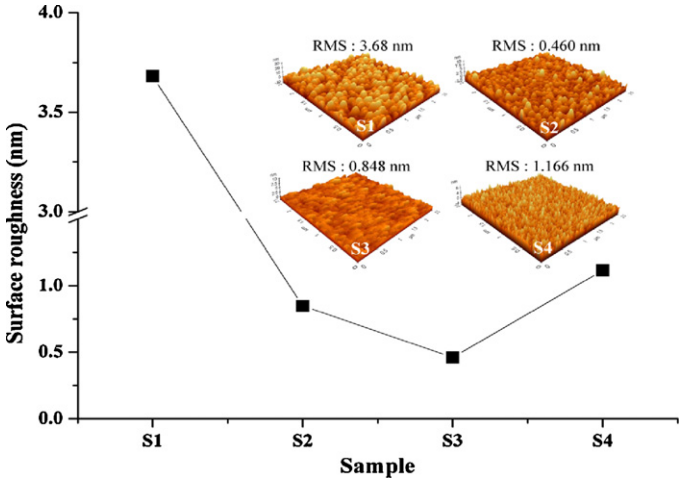

Fig. 4. . Surface images and roughness of ZnO thin film as assessed by AFM.

size of ZnO thin films had no effect on the sensitivity of the ZnO thin films in regards to acetone gas detection.

The surface roughness of the ZnO thin films were measured by AFM to vary from 0.46 to 3.68, as shown in Fig. 4. The roughness was not dependent on the deposition condition. In addition, the surface roughness did not influence on the sensitivity of the ZnO thin films.

Fig. 5 shows the work function of the as-deposited ZnO thin films and plasma treated ZnO thin films. The as-deposited ZnO thin films displayed various work functions from 4.62 to 4.75 eV, which were dependent on the deposition conditions. In addition, plasma treated ZnO thin films had a higher work function than the as-deposited ZnO thin films, which ranged from 5.15 to 5.51 eV. The error range of the work functions of ZnO thin films measured using the Kelvin probe was approximately ±0.03 eV. The ZnO thin films deposited inside the plasma had higher work function than the ZnO thin films deposited outside the plasma. Comparing with the results in Figs. 4 and 5, the Sensitivity of ZnO Sensor was dependent on the work function of the ZnO thin film.

Furthermore, the work function of the ZnO thin films was dependent on the plasma conditions, such as plasma treatment and the position of the substrate in the ZnO thin film deposited inside or outside the plasma. We demonstrated that the ZnO thin film deposited inside the plasma had a higher work function due to the positive effect of plasma treatment. Furthermore, it was demonstrated that the sensitivity of the sensors was strongly dependent on the work function of the sensing materials.

XPS spectra were used to further understand the reason for this trend in the work function. We measured binding energy peaks of oxygen atoms on the surface of the ZnO thin films by XPS. Fig. 6 shows the XPS spectra (a) and the binding energy peaks of O s1 (b). The work function of the ZnO thin films was almost entirely dependent on the binding energy of the oxygen atom. In addition, the binding energy peak of the oxygen atom in the ZnO films that had been plasma treated increased in proportion to the working function. Therefore, the change in the work function of ZnO thin films could be explained as follows: First, plasma treatment generated dangling bonds on the ZnO surface due to surface damage caused by the plasma. This means free electrons were trapped on the dangling bonds of the ZnO surface. Thus, the energy required to for free electron to escape increased. Second, the ZnO surface was oxidized by oxygen plasma. This means the binding energy of the oxygen atom was increased as shown in Fig. 5. Therefore, the bonding energy increase in the oxygen atoms on the ZnO surface

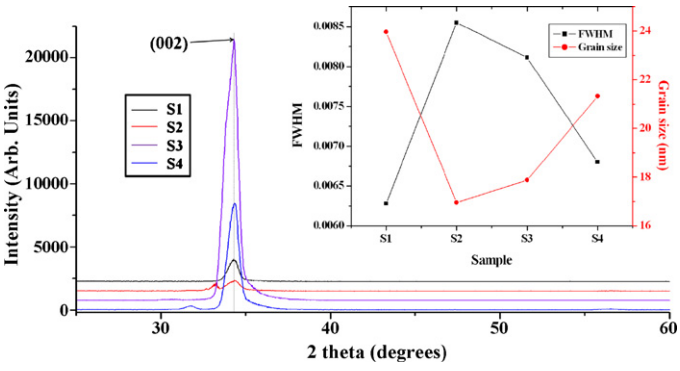

Fig. 3. . XRD spectra of ZnO thin films under various deposition conditions.

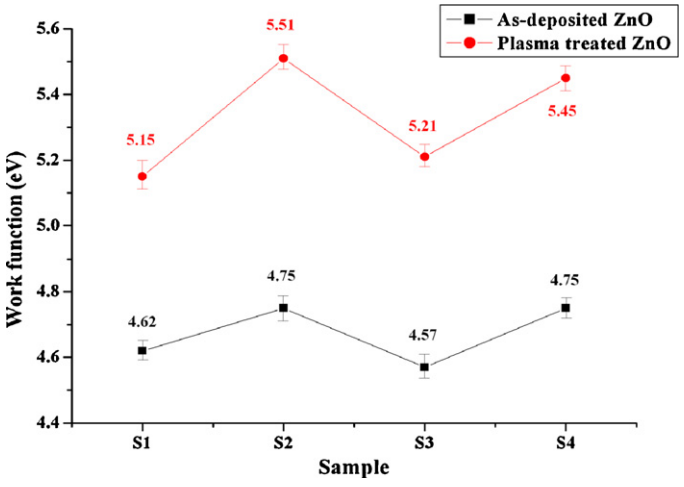

Fig. 5. . Work function of ZnO thin films fabricated under various conditions or with plasma treatment.

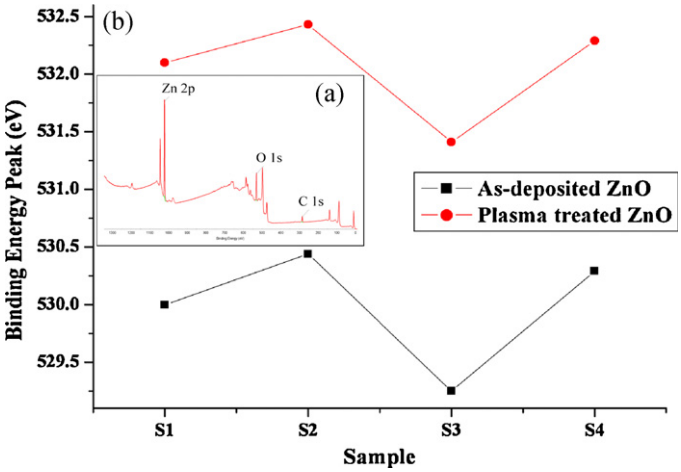

Fig. 6. . (a) XPS spectra and (b) binding energy peaks of oxygen atom in ZnO thin films.

restricts the emission of electrons and increases the work function. Based on these results, it was demonstrated that the increase in the bonding energy of oxygen atoms on ZnO with plasma treatment also increased the work function of the ZnO thin film. However, the effect of plasma treatment was dependent on treatment time. Thus, there is a need to development time-independent surface modification methods that do not alter the work function.

4. Conclusion

ZnO thin films were assembled with various work functions by RF magnetron sputtering were fabricated. Besides, the work function of ZnO thin films was increased by RF oxygen plasma treatment. The cause for the increase in structural properties and work function of the ZnO thin films were analyzed. The work function of ZnO thin films was dependent on the binding energy of the oxygen atoms on the ZnO surface. In addition, the binding energy of the oxygen atoms on the ZnO surface by plasma treatment increased in proportion with the work function of the ZnO thin films. It was expected that the increase in the work function by plasma treatment was due to the generation of the dangling bonds and an increase in the binding energy of oxygen atoms by oxidation of the ZnO surface. The sensitivity of the ZnO sensors for acetone gas detection was improved by plasma treatment. In addition, the electron swap between the ZnO surface and acetone gas was improved by increasing the work function of the sensing materials.

Acknowledgement

This work was supported by the GRRC program of Gyeonggi province (GRRC Kyungwon 2010-B06).

References

[1] R.L. Hoffman, B.J. Norris, J.F. Wager, ZnO-based transparent thin-film transistors, Applied Physics Letters 82 (2003) 733–735.
[2] N. Hongsith, C. Viriyaworasakul, P. Mangkorntong, N. Mangkorntong, S. Choopun, Ethanol sensor based on ZnO and Au-doped ZnO nanowires, Ceramics International 34 (2008) 823–826.
[3] A.K. Chawla, D. Kaur, R. Chandra, Structural and optical characterization of ZnO nanocrystalline films, Optical Materials 29 (2007) 995–998.
[4] C.Y. Tsay, K.S. Fan, Y.W. Wang, C.J. Chang, Y.K. Tseng, C.K. Lin, Transparent semiconductor zinc oxide thin films deposited on glass substrates by sol–gel process, Ceramics International 36 (2010) 1791–1795.
[5] M. Suchea, S. Christoulakis, K. Moschovis, N. Katsarakis, G. Kiriakidis, ZnO transparent thin films for gas sensor applications, Thin Solid Films 515 (2006) 551–554.
[6] A.M. Gas'kov, M.N. Rumyantseva, Nature of gas sensitivity in nanocrystalline metal oxides, Russian Journal of Applied Chemistry 74 (2001) 440–444.
[7] N. Kakati, S.H. Jee, S.H. Kim, H.-K. Lee, Y.S. Yoon, Sensitivity enhancement of ZnO nanorod gas sensors with surface modification by an InSb thin film, Japanese Journal of Applied Physics 48 (2009) 105002–105006.
[8] A. Khorsand Zak, M. Ebrahimizadeh Abrishami, W.H.A. Majid, R. Yousefi, S.M. Hosseini, Effects of annealing temperature on some structural and optical properties of ZnO nanoparticles prepared by a modified sol–gel combustion method, Ceramic International 37 (2011) 393–398.
[9] B.D. Cullity, Elements of X-ray Diffraction: A Practical Approach, Addison-Wesley Publishing Company Inc., California, 1956.