Preparation and characterization of ZnO thin films on shape memory alloy substrates prepared by sol-gel method

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ZnO thin film has been successfully prepared on shape memory alloy (SMA) substrate by sol-gel method. The thin films are characterized by X-ray diffraction (XRD), photoluminescence (PL), X-ray photoelectron spectroscopy (XPS) and optical reflection. Results show that (002)-oriented polycrystalline film is deposited on the SMA substrate. The successful formation of ZnO films on SMA substrate implies that it may be possible to use the SMA transformation to adjust the electro-optical properties of the ZnO film.

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1. Introduction

ZnO is a direct wide bandgap II-VI semiconductor (3.36 eV) that is suitable for short wavelength optoelectronic applications [1]. ZnO thin films have also been used for piezoelectric devices, such as surface acoustic wave (SAW) devices and bulk acoustic wave devices [2]. For the realization of these devices based on ZnO, it is necessary to grow high quality ZnO thin films. Many deposition techniques have been developed to prepare ZnO thin films, such as radio frequency sputtering [3], direct current (DC) sputtering [4], electron cyclotron resonance sputtering [5], plasma-assisted molecular beam epitaxy (MBE) [6], and pulsed laser deposition [7]. However, these techniques require sophisticated instruments. ZnO thin films also can be prepared by sol-gel deposition [8,9]. The sol-gel chemical deposition technique is very attractive as it can be implemented easily in a laboratory for the deposition of semiconducting thin films. In addition, the efficiency of deposition technique and the non-alkoxide route make the sol-gel ZnO films very interesting in the semiconductor oxide thin films field. ZnO film has been successfully deposited on many kinds of substrates, such as organic substrates [10-12], oxide substrates [13,14], and metal substrates [15]. However, there is no report on the ZnO film deposited on intermetallic substrate. Shape memory alloys (SMAs) are new kinds of smart materials which have unique shape memory effect (SME) and superelastic (SE) behavior. It may be possible to use the SMA transformation to adjust the electro-optical properties of the ZnO film. In this study, ZnO thin films deposited on the shape memory alloy (SMAs) substrate were investigated with an aim to investigate whether ZnO can be deposited on the SMAs intermetallic substrates.

2. Experimental

The substrate used in this study was a TiNi thin film. TiNi thin film with a thickness 4.5μm were prepared by co-sputtering of a TiNi target and a Ti target on (100) silicon wafers using a magnetron sputtering equipment. Chemical composition of the films was investigated by energy dispersive X-ray spectrometry (EDX). Measurements were done on 5 different regions on the sample, and the average value is Ti-49.8at.%Ni. The detailed preparation and characterization of this film can be found in Ref [16].

ZnO thin films were prepared by the sol–gel technique. Zinc acetate dihydrate ($Zn(CH_3COO)_2 \cdot 2H_2O$) was added in a mixture of 2-methoxyethanol and monoethanolamine (MEA) at room temperature. The molar ratio of MEA to zinc acetate ($Zn(CH_3COO)_2$) was maintained at 1.0 and the final molarity of zinc acetate was chosen to be 0.4 M. The role of MEA is as sol stabilizer. The solution was stirred at 60□ for 2 h to yield a clear and homogeneous solution that was aged for 2 days at room temperature in the dark, prior to deposition. The solution was deposited onto the SMA film substrates, which were rotated at 3000 rpm for 30 s. After deposition the films were dried at 100 ^{o}C for 10 min over a hot plate to evaporate the solvent and remove organic residuals. The above process of deposition and heating was repeated 12 times to increase the thickness of the films. The films were annealed at 550 ^{o}C for 1h at air atmosphere.

The crystalline structure of the resulting ZnO thin films was studied using a Bede D1 type x-ray diffractometer and the Cu Kα line at 1.54056Å. Reflection spectroscopy of the film was measured using a Shimadzu UV-2550 double beam spectrophotometer in the wavelength range of 190-1010nm. Photoluminescence was recorded on a Shimadzu RF-5301PC fluorometer employing a 150 W Xe lamp as the light source. The transformation behavior of the samples had been measured using Differential Scanning Calorimetry (DSC131, Setaram Company, France) with a scanning rate of 10□/min. The chemical composition of the ZnO film was analyzed by XPS using a XSAM 800 Flexo electron spectrometer with monochromatic Mg K-alpha X-ray radiation.

3. Results and discussion

The XPS results on the chemical composition are presented in Fig. 1. Fig. 1(a) shows the XPS survey spectra between binding energies of 0-1000 eV for the as deposited film. The dominant signals correspond to C, O, and Zn. High-resolution XPS collections of the O_{1s}, and Zn_{2p} binding energy regions are shown in Fig. 1 (b) and (c), respectively. The XPS results show that ZnO if formed on the SMA substrate, with peaks at 1022.451, 1045.548 and 531.242 eV corresponding to the binding energies of Zn $_{2p3/2}$, Zn $_{2p1/2}$ and O_{1s}, respectively.

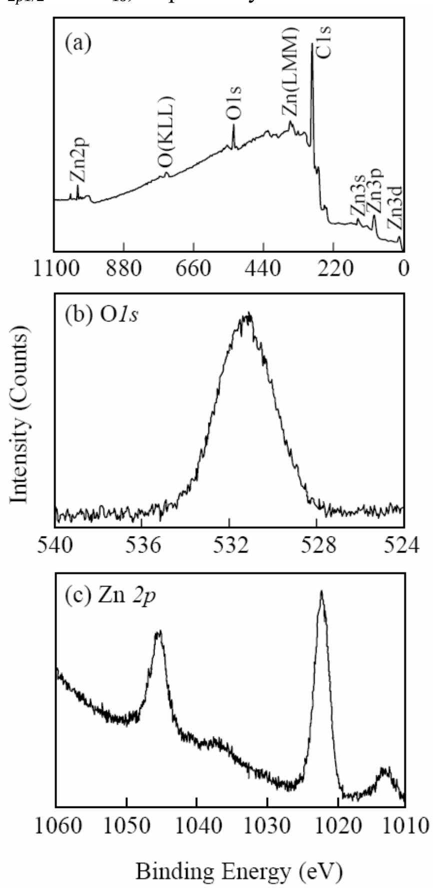

Fig. 1. The XPS survey spectra in the binding energy range of 0-100 eV (a) and high-resolution XPS collections of the O_{1s} (b) and Zn_{2p} (c) binding energyfor ZnO film deposited on SMA substrate.

The XRD patterns of the SMA substrate and ZnO thin film deposited on the substrate are shown in Fig.2. A peak at 2θ=34.5° can be clearly observed after the deposition, which is attributed to the ZnO (002) plane. This indicates that the deposited film has a good orientation along the *c*-axis. Peaks related to the SMA substrate can also be seen.

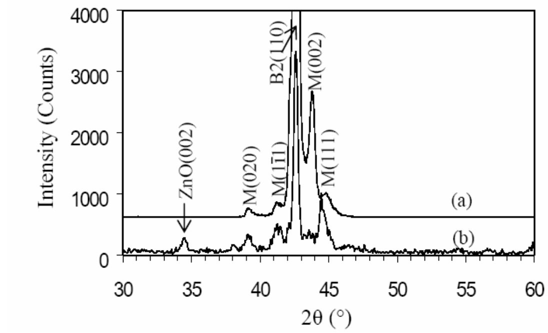

Fig. 2. The XRD pattern of (a) the substrate and (b) the ZnO film.

The phase transformation behaviors of the TiNi substrate before and after the ZnO film deposition are shown in Fig. 3. Upon heating, a one-stage transformation is observed, namely from the martensite (M) to parent phase (B2) transformation. Upon cooling, there is a one-stage transformation, corresponding to transformations between the B2 and M phase. The ZnO deposition has no effect on the shape memory effect of the SMAs substrate, except for the transformation M-B2 shift to lower temperature. The decreasing of the transformation temperatures of M to B2 phase transformation should be related to the annealing at 550□. There are many dislocations in the deposited SMA films, associated internal stress generated from the dislocations restrict the specimen transform martensite to austenite. Annealing induces the decrease of the dislocation density and internal stress, which leads to decrease of transformation temperatures [17].

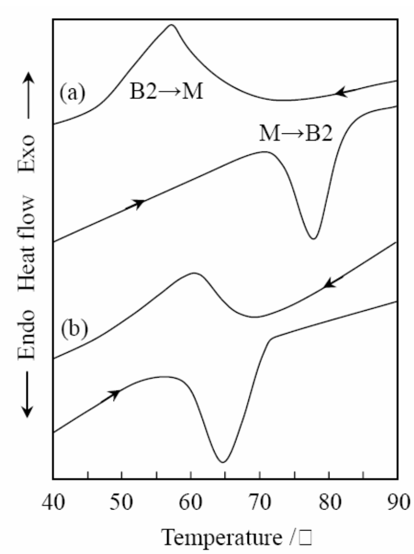

Fig. 3. DSC results of (a) the SMAs substrate and (b) ZnO film deposited SMAs.

Fig. 4 shows the photoluminescence spectra of ZnO film exited by different wavelengths at room temperature. A UV emission at wavelength about 388 nm can be observed. There's no obvious shift of the position of the luminescence peak with excitation wavelength, although the intensity of the peak does vary. The UV luminescence is produced by exciton annihilation [18,19].

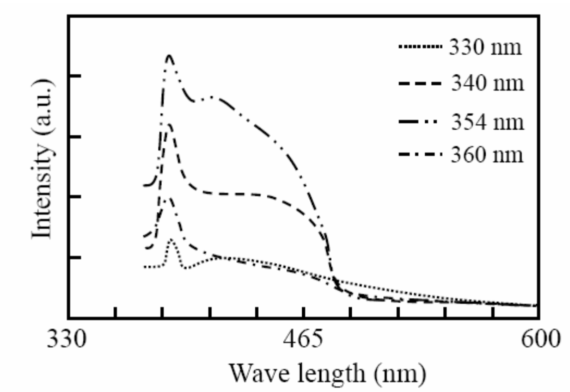

Fig. 4. Room temperature photoluminescence of ZnO film deposited on SMAs substrate.

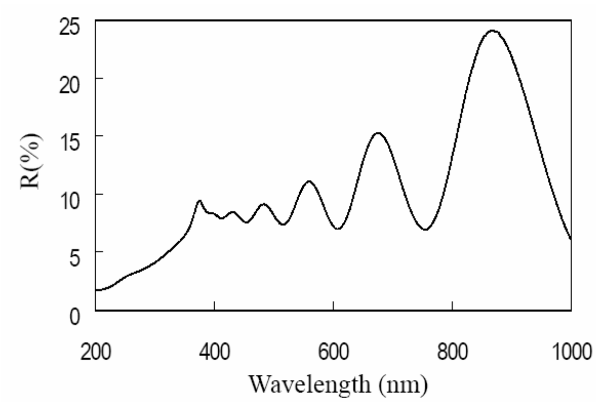

Fig. 5. The optical reflectance of the ZnO films deposited on SMAs substrate at room temperature.

Fig. 5 shows the optical reflectance R as a function of wavelength below 1000 nm. The R curve shows interference fringes with deep valleys and tall crests, indicating a smooth surface film was deposited on the SMA substrate.

4. Conclusions

The results presented in this study show the sol-gel process to be feasible for the deposition of oriented ZnO films. X-ray diffraction, X-ray photoelectron spectroscopy, photoluminescence and optical reflection have been used to characterize the ZnO film. (002)-oriented polycrystalline film is deposited on the shape memory alloy substrate. The film is shown to be of high crystalline and optical quality. The successful formation of ZnO films on SMA substrate implies that it may be possible to use the SMA transformation to adjust the electro-optical properties of the ZnO film.

References

[1] T. Gruber, C. Kirchner, K. Thonke, R. Sauer, A. Waag, Phys. Status Solidi A **192**, 166 (2002).
[2] T. Yamamoto, T. Shiosaki, W. Kawabata, J. Appl. Phys. **51**, 3113 (1980).
[3] Y. Yoshino, T. Makino, Y. Katayama, T. Hata, Vaccum. **59**, 538 (2000).
[4] J. J. Chen, F. Zen, D. M. Li, J. B. Niu, F. Pan, Thin Solid Films. **485**, 257 (2005).
[5] M. Kadota, T. Miura, M. Minakata, J. Cryst. Growth **237**, 523 (2002).
[6] K. Kiroyuki, S. Michihiro, M. Kazuhiro, Y. Takafumi, J. Crystal Growth **275**, 2459 (2005).
[7] F. K. Shan, G.. X. Liu, W. J. Lee, G. H. Lee, I. S. Kim, B. C. Shin, Y. C. Kim, J. Crystal Growth **277**, 284 (2005).
[8] L. Liu, W. J. Weng, W. H. Ding, K. Cheng, P. Y. Du, G. Shen, G.. R. Han, Surf. Coat. Technol. **198**, 274 (2005).
[9] W. F. Shen, Y. Zhao, C. B. Zhang, Thin Solid Films **483**, 382 (2005).
[10] D. H. Zhang, T. L. Yang, J. Ma, Q. P. Wang, R.W. Gao, H.L. Ma, Appl. Surf. Sci. **158**, 43 (2000).
[11] E. Fortunato, P. Nunes, A. Marques, D. Costa, H. Aguas, I. Ferreira, M. E. V. Costa, M. H. Godinho, P. L. Almeida, J. P. Borges, R. Martins, Surf. Coat. Technol. **151-152**, 247 (2002).
[12] A. W. Ott, R. P. H. Chang, Mater. Chem. Phys. **58**, 132 (1999).
[13] H. W. Liang, Y. M. Lu, D. Z. Shen, J. F. Yan, B. H. Li, J. Y. Zhang, Y. C. Liu, X. W. Fan, J. Crys. Growth **278**, 305 (2005).
[14] H. L. Porter, C. Mion, A. L. Cai, X. Zhang, J. F. Muth, Mater. Sci. Eng. B. **119**, 210 (2005).
[15] Y. Yoshino, K. Inoue, M. Takeuchi, T. Makino, Y. Katayama, T. Hata, Vaccum. **59**, 403 (2000).
[16] Y. Q. Fu, H. J. Du, S. Zhang, Thin Solid Films **444**, 85 (2003).
[17] Z. G. Wang, X. T. Zu, X. D. Feng, S. Zhu, J. M. Zhou, L. M. Wang, Physica B **253**, 9 (2004).
[18] T. Minami, H. Nanto, S. Takata, Thin Solid Films **109**, 379 (1983).
[19] H. Heck, E. Moliwo, Solid State Commun. **105**, 399 (1998).

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