International Journal of Modern Physics B
Vol. 23, Nos. 6 & 7 (2009) 1904–1909

World Scientific
www.worldscientific.com

INFLUENCE OF THE GROWTH TEMPERATURE ON THE PROPERTIES OF Mn-DOPED SnO_2 THIN FILMS GROWN BY PULSED LASER DEPOSITION

YANXUE CHEN and JUN JIAO*

School of Physics and National Key Laboratory of Crystal Materials, Shandong University, Jinan, 250100, Shandong, China
Department of Physics, Portland State University, P.O. Box 751, Portland OR, 97207, U.S.A.
**jiaoj@pdx.edu*

Mn-Doped SnO_2 thin films were grown on sapphire (012) substrates by pulsed laser deposition. The influence of substrate temperature on the film properties was investigated. X-ray diffraction patterns show that the thin films grown at lower substrate temperatures were amorphous, while those grown at higher temperatures had only a single (101) orientation. Atomic force microscopy results indicate that the films grown at low temperature were extremely flat and they became rougher as substrate temperature (T_s) increased. Optical transmission spectra reveal that the absorption edge shifts towards the blue side and becomes steeper at increasing T_s. High-resolution transmission electron microscopy analysis clearly indicates that the samples have a well-arranged tetragonal structure without any detectable secondary phase. Inhomogeneous incorporation of Mn atoms into the SnO_2 lattice was also observed.

Keywords: Mn-doped SnO_2; thin film; pulsed laser deposition; magnetic semiconductor.

1. Introduction

Owing to its unique electrical, optical and electrochemical properties and high chemical stability, tin dioxide (SnO_2), has a variety of applications in many fields. Triggered by a prediction of room temperature ferromagnetism in P-type ZnO doped with 5% Mn,[1] oxide based diluted ferromagnetic semiconductors have attracted much attention in the last few years. In such materials, electrical conductivity combines with ferromagnetism and optical transparency. This leads to promising uses in a class of multifunctional devices, such as spin-valve transistors, spin light-emitting diodes, non-volatile memories, ultra-fast optical switches, and so on. Soon after the experimental reports of high temperature ferromagnetism in TiO_2[2] and ZnO based magnetic oxide semiconductors,[3] several research groups started to explore SnO_2-based dilute magnetic semiconductors.[4-8] The reported results for Mn-doped SnO_2 are rather controversial: some published papers reported observation of room-temperature ferromagnetism in Mn-doped SnO_2.[6] Low-temperature ferromagnetism with a Curie temperature below 27K[9] was also reported and others reported only paramagnetic behavior.[10] This discrepancy may be caused by the different microstructures of the samples grown by different research groups. This suggests that it is important to investigate the influence of experimental parameters on the properties of Mn-doped SnO_2.

In this paper, we report the growth of 5 at. % Mn-doped SnO_2 films on sapphire (012) substrates by pulsed laser deposition, and the effect of the growth temperature on the electrical conductance, the crystal structure, the surface morphology and the optical property of Mn-doped SnO_2. It is found that the substrate temperature strongly affects the film properties, which may provide an explanation for the discrepancies in Mn-doped SnO_2 magnetic properties.

2. Experimental Details

The Mn-doped SnO_2 thin films were deposited on sapphire (012) substrates by pulsed laser deposition. A $Sn_{0.95}Mn_{0.05}O_2$ target was sintered in air at 1300°C for ten hours using high purified SnO_2 (99.99%) and MnO_2 (99.99%) powders. Sapphire (012) slips were cleaned by an Ar^+ sputtering gun and then annealed at 640°C for 10 minutes before deposition. To determine the influence of substrate temperature on the film properties, the substrate was heated by a resistive heater at different T_s ranging from 280 to 580°C in 60°C steps. All other parameters were kept identical during deposition. The target was ablated by a KrF excimer laser operating at 248 nm and 5 Hz. The energy density on the target was ~2 J/cm^2, and the base pressure of the growth chamber was 1×10^{-5} Pa. Next, pure oxygen (99.999%) was introduced and pressure was kept at 5×10^{-4} Pa during the deposition. The distance between the target and the substrate was ten cm. After deposition the sample was cooled in the same oxygen atmosphere at a rate of 20°C/min.

The microstructure analysis and phase identification of the Mn-doped SnO_2 thin films were carried out by X-ray diffraction (XRD) (CuK_α radiation) and high-resolution transmission electron microscopy (TEM). Diffractograms were recorded from 20° to 75° with a step increment of 0.02°. Surface conductance of the films was measured at room temperature using a four-point probe method. The surface morphology of the samples was studied by CSPM4000 atomic force microscopy (from Being Nano-instruments Ltd) in tapping mode. The optical transmission spectra were obtained in wavelengths from 190 to 800nm with a V570 spectrophotometer.

3. Results and Discussion

All of the as-grown films were transparent with smooth mirror-like surfaces showing no indication of pinholes, and their color changed from yellow to white when the growth temperature was increased from 280 to 580°C. Four-point conductance measurements showed that the conductance increased dramatically as the growth temperature increased. The film grown at 280°C was insulating, while the resistivity of film grown at 580°C was only 0.02Ω·cm. The obvious change in color and conductance indicates that the microstructure and phase composition undergo some transformation when the substrate temperature varies. This is confirmed by the XRD results. The X-ray diffraction results for the films deposited at: (a) 340°C, (b) 460°C, (c) 520°C, (d) 580°C are presented in Fig. 1. As shown in Fig. 1a, only peaks from substrate Al_2O_3 (012), (024) are observed and there is no peak from the deposited film. There is a broad peak centered around

$2\theta = 29.8°$, which indicates that film grown at 340°C is amorphous Mn-doped SnO. Our result is different than that reported by Dolbec et al, who observed a SnO_2 phase in film grown at 20°C.[11] This can be explained by considering the higher on-target laser fluence and repetition rate used in their experiments. Under their experimental conditions, the ionization degree and kinetic energy of the species reaching the substrate were high. This causes the surface temperature to be quite high during deposition, so the deposited SnO_2 will crystallize even though the backside of the substrate is kept at a low temperature. As T_s is increased above 460°C, peaks from SnO, SnO_2 and Sn appear in the XRD patterns (Fig. 1b), which means the film is a mixture of Sn, SnO and polycrystalline SnO_2. Upon further increasing T_s to 520°C, the Sn (200) peak and the SnO_2 (002) and (112) peaks disappear. The SnO_2 (101) and (202) peaks increase distinctly and the SnO (101) peak is still visible (Fig. 1c). It can be seen that although the T_s is not high enough to get a pure SnO_2 film, the growth mechanism of SnO_2 has changed. For the film deposited at 580°C, only the (101) family of the SnO_2 rutile phase and the peak from the Al_2O_3 (012) substrate could be seen. The diffraction patterns indicate that $Sn_{1-x}Mn_xO_2$ films have a single phase of (101) preferred orientation. The full width at half-maximum of the SnO_2 (101) peak is 0.17 degree, which indicates an excellent crystalline quality. The average crystal size calculated using the Scherrer formula is 48.3 nm. No traces of manganese clusters, manganese oxides or any binary tin manganese phases were observed in the detection limit of the X-ray diffractometer.

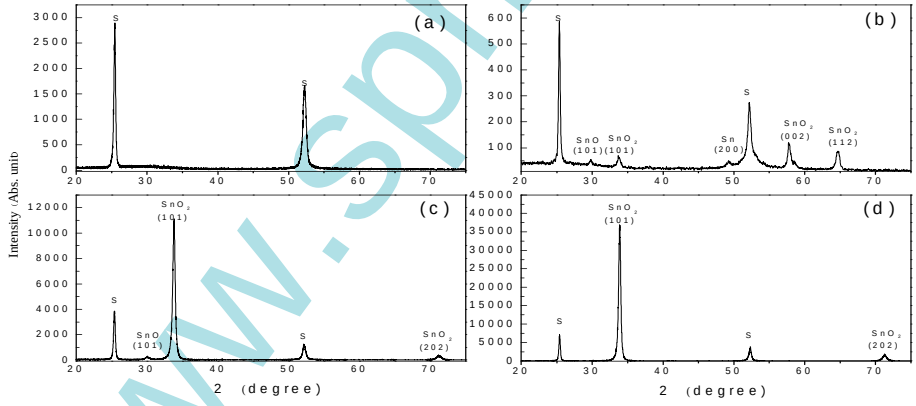

Fig. 1. X-ray diffraction patterns of the Mn-doped SnO_2 films grown on sapphire (012) substrates by pulsed laser deposition at (a) 340°C, (b) 460°C, (c) 520°C and (d) 580°C.

The surface morphology and roughness of the same films were investigated with atomic force microscopy. As shown in Fig. 2b, the film deposited at 280°C appears to be smooth without any distinct grain or porous structures, indicating a planar growth mode. Images over a $0.8\times0.8\ \mu m^2$ area have a rms roughness of 1.6 nm. A clear departure from a smooth, featureless film is observed for the film fabricated at 580°C (Fig. 2b). Under this condition, the film has a rough surface with an rms roughness of 3.66 nm and a

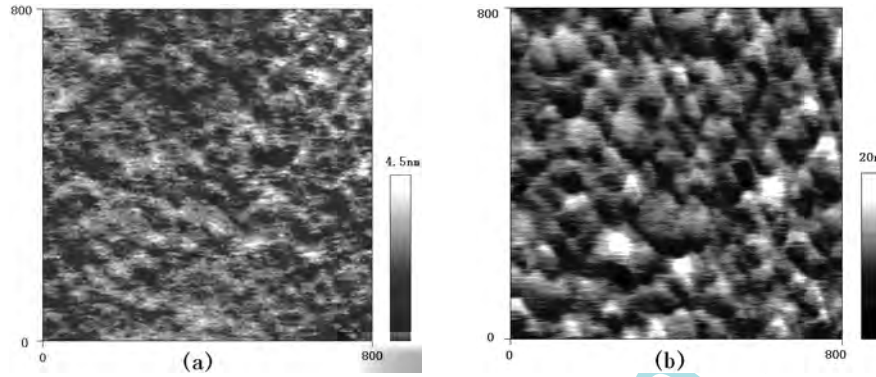

Fig. 2. Atomic force microscopy images of the surface of the Mn-doped SnO_2 films grown on sapphire (012) substrates at (a) 280 and (b) 580°C.

grainy structure with an average lateral size of several tens of nanometers. These measurements show that although the film shows single orientation with epitaxial relationship SnO_2 (101) on (012) sapphire, it is not single-crystal epitaxy. The experimental parameters need to be optimized further to grow smooth and dense Mn-doped SnO_2 with single-crystalline properties.

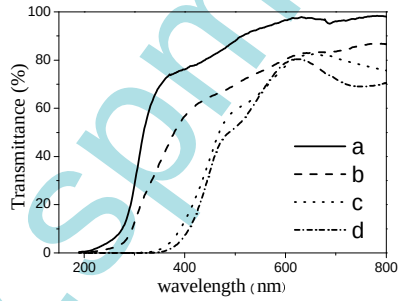

Fig. 3. Optical transmission spectra of the Mn-doped SnO_2 films grown on sapphire (012) substrates at (a) 580°C, (b) 520°C, (c) 460°C and (d) 280°C.

The optical transmission spectra of the Mn-doped SnO_2 films deposited at different T_s values were shown in Fig. 3. As illustrated in Fig. 3, the optical transmittance of the Mn-doped films is sensitive to the variation of the deposition temperature. By increasing the substrate temperature from 280°C to 580°C, the onset of stronger absorption shifts towards the blue side and the slope of the absorption edge becomes steeper. As a first approximation, the optical band gap of the Mn-doped SnO_2 can be obtained from the optical transmission spectra by using the relation E_g (eV)=1241.5/λ_c (nm), where λ_c is the critical wavelength defined as the inflexion point of the UV absorption edge. For the films grown at 280°C and 340°C, the absorption edges are identical and the optical band gaps are 2.80 eV. As T_s increases, the SnO_2 phase begins to form and the optical band gap increases at the same time. For the film deposited at 580°C, a single SnO_2 phase is

achieved. The mean optical transmittance is enhanced to ~90% and the optical band gap significantly increases to 4.05eV, which corresponds quite well with high quality SnO_2 films. No change of the optical band gap was observed when the substrate temperature was increased further, resulting in larger grains. This indicates that the optical band gap of the Mn-doped SnO_2 films is very sensitive to the phase structure variation.

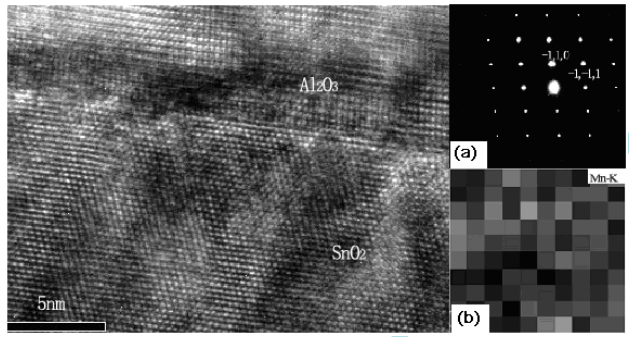

Fig. 4. High-resolution TEM image of Mn-dopd SnO_2 grown on sapphire (012) substrates at 580°C.

A high-resolution TEM image for the film deposited at 580°C is shown in Fig. 4, from which we can see that in a nanometer scale, the film is uniform with a well-arranged tetragonal structure. Inset (a) is the corresponding selected-area electron diffraction (SAED) pattern. Being consistent with the XRD pattern, only diffraction dots of SnO_2 can be seen. The lattice distances along [-1, 1, 0] and [-1, -1, 1] are 3.575Å and 2.623Å, respectively, while the corresponding parameter of pure SnO_2 is 3.350Å and 2.308Å. This change indicates that Mn atoms are incorporated and dilate the SnO_2 lattice. Fig. 4b is a Mn-K mapping of a 20nm×20nm area which indicates the distribution of Mn element in the sample. Different colors denote different ratios of Mn/(Mn+Sn). The brighter the color is, the bigger the ratio it represents. In the brightest area, the ratio is 19%, while in the darkest area it is only 6.6%. This concentration was much higher than in the ceramic target due to the evaporation of Sn during deposition at high substrate temperature. Since the average crystal size measured by XRD pattern is 48.3nm, the Mn-k mapping presented here should be of a single grain. Even though no inhomogeneous sections in the high-resolution patterns could be seen, the Mn element, in fact, does not distribute uniformly. There is random distribution of Mn-rich and Mn-depleted areas in the SnO_2 lattice.

4. Conclusion

The influence of the growth temperature (in the range from 280°C to 580°C) on the electrical conductance, the crystal structure, the surface morphology and the optical property of Mn-doped SnO_2 was investigated. The measurements indicate that the growth temperature plays an influential role in the properties of the deposited films. When T_s is low, a yellowish smooth amorphous Mn-doped SnO film is fabricated. Its resistivity is

very high and the optical band gap is narrow. At moderate substrate temperature, the depositions are a mixture of polycrystal SnO_2, SnO and Sn. The absorption edge shifts towards the blue side because of the formation of the SnO_2 phase. As T_s is increased to 520°C, a strong (101) preference growth of the SnO_2 phase is observed. Single rutile phase epitaxial Mn-doped SnO_2 film is fabricated at T_s=580°C. It is conductive and highly transparent with a band gap of ~4.05eV. Inhomogeneous incorporation of Mn atoms into the SnO_2 lattice was also observed.

Acknowledgments

This work was supported by the NSF of China (No. 50572053) and Key Laboratory for Magnetism and Magnetic Materials of the MOE.

References

1. T. Dietl, H. Ohno, F. matsukura, J. Cibert, D. Ferrand, *Science* **287**, 1019 (2000).
2. Y. Matsumoto, M. Murakami, T. Shono, T. Hasegava, T. Fukumura, M. Kawasaki, P. Ahmet, T. Chikyow, S. Koshihara, and H. Koinuma, *Science* **291**, 854 (2001).
3. K. Ueda, H. Tabata, and T. Kawai, *Appl. Phys. Lett.* **79**, 988 (2001).
4. N. H. Hong, A. Ruyter, W. Prellier, J. Sakai and N. T. Huong, *J. Phys.: Condens. Matter* **17**, 6533 (2005).
5. N. H. Hong, J. Sakai, W. Prellier and A. Hassini, *J. Phys.: Condens. Matter* **17**, 1697 (2005).
6. C. B. Fitzgerald, M. Venkatesan, A. P. Douvalis, S. Huber, and J. M. D. Coey, *J. Appl. Phys.* **95**, 7390 (2004).
7. J. M. D. Coey, A. P. Douvalis, C. B. Fitzgerald, and M. Venkatesan, *Appl. Phys. Lett.* **84**, 1332 (2004).
8. S. B. Ogale, R. J. Choudhary, J. P. Buban, S. E. Lofland, S. R. Shinde, S. N. Kale, V. N. Kulkarni, J. Higgins, C. Lanci, J. R. Simpson, N. D. Browning, S. Das Sarma, H. D. Drew, R. L. Greene, and T. Venkatesan, *Phys. Rev. Lett.* **91**, 077205 (2003).
9. K. H. Gao, Z. Q. Li, X. J. Liu, W. Song, H. Liu, E. Y. Jiang, *Solid State Communications* **138**, 175 (2006).
10. H. Kimura, T. Fukumura, M. Kawasak, K. Inaba, T. Hasegawa, H. Koinuma, *Appl. Phys. Lett.* **80**, 94 (2002).
11. R. Dolbec, M. A. El Khakani, A. M. Serventi, M. Trudeau and R. G. Saint-Jacques, *Thin Solid Films* **419**, 230 (2002).