

Hydrogen-doped high conductivity ZnO films deposited by radio-frequency magnetron sputtering

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Hydrogen-doped zinc oxide (ZnO:H) films were deposited by rf magnetron sputtering as transparent conductive films. The resistivity of ZnO:H film was significantly reduced by the addition of H₂ in Ar during rf sputtering. The electrical resistivity of ZnO:H films reached $2 \times 10^{-4} \Omega \text{ cm}$. The carrier concentration increased with increasing H₂ concentration during deposition. X-ray diffraction results showed that the d_{0002} interplanar spacing increased with increasing H₂ concentrations. The carrier concentration was significantly reduced in two orders of magnitude by increasing the substrate temperature from 150 to 250 °C during deposition. Both results suggested that the increase of carrier concentration by adding H₂ during sputtering was due to the hydrogen donor rather than the oxygen vacancies in ZnO films, consistent with the theoretical predictions by Van de Walle. UV-visible spectroscopy further showed that the transmittance is high up to 100% in the visible range. The band gap determined by optical absorption increased with increasing H₂ composition. The phenomenon is interpreted as the filling of conduction band by electrons in *n*-type semiconductor. © 2004 American Institute of Physics. [DOI: 10.1063/1.1835991]

Zinc oxide (ZnO) is a wide-band-gap semiconductor with many technological applications, including piezoelectric transducers, gas sensor, phosphors, and transparent conducting electrodes of optoelectronic devices.¹⁻³ In serving as the transparent electrode of optoelectronic devices, ZnO film owns several advantages including high transmittance in low-wavelength region, abundance in natural resource, and amorphous structure. However, it remains difficult to grow ZnO films with stable and sufficiently high conductivity. Furthermore, although all experimental results have shown that the undoped ZnO is *n*-type, whether the donor is zinc interstitial (Zn_i) or oxygen vacancy (V_O) remains controversial.^{4,5}

Recently, using first-principles calculation based on the density functional theory, Van de Walle^{6,7} has found strong evidence that hydrogen acts as a source of conductivity for ZnO. H⁺ is the stable and the lowest-energy state for all Fermi-level positions and can be incorporated in high concentrations as a shallow donor in ZnO. This behavior is very different from hydrogen in other semiconductors, in which it only acts as a compensating center and always counteracts the conductivity. The above-noted prediction was experimentally confirmed by Cox *et al.*⁸ and Hofmann *et al.*⁹ using muon spin rotation and electron paramagnetic resonance technique, respectively. The molecular structure was further confirmed by infrared spectroscopy.¹⁰ Kiliç *et al.*¹¹ generalized the hydrogen doping behavior in various oxides recognizing that there exists a “hydrogen pinning level” at about $3.0 \pm 0.4 \text{ eV}$ below vacuum for all oxides. Van de Walle⁷ further suggested the existence of a universal alignment for the hydrogen energy level in various semiconductors, insulators, and even aqueous solutions.

Various post-treatment methods have been reported on the fabrication of hydrogen-doped ZnO films. Baik *et al.*¹² treated the ZnO films deposited by metalorganic chemical vapor deposition in H₂ under UV illumination in a mercury-sensitized photo chemical vapor deposition system. The resistivity of the H₂-treated film decreased from 1×10^{-2} to $2 \times 10^{-3} \Omega \text{ cm}$. Ip *et al.*¹³ investigated the electrical conductivity of hydrogen in ZnO finding that exposure of ZnO to H₂ plasma caused an increase in donor concentration. The effect was attributed to hydrogen passivation of acceptor impurities present in the as-grown ZnO layers.^{13,14} Kohiki *et al.* enhanced the conductivity of ZnO film through hydrogen doping by ion implantation.¹⁵ The resistivity decreased from $1 \times 10^7 \Omega \text{ cm}$ for the as-grown ZnO to $1.8 \times 10^{-3} \Omega \text{ cm}$ for a hydrogen doping level of $1 \times 10^{17} \text{ cm}^{-2}$.

In this study, hydrogen-doped ZnO thin films (ZnO:H) were deposited directly in a rf magnetron sputtering system

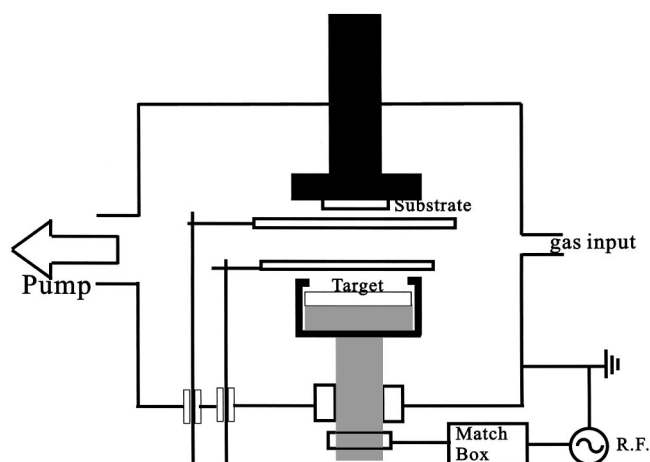


FIG. 1. A schematic diagram of rf magnetron sputtering system.

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TABLE I. Conditions for the deposition of ZnO:H thin films.

Target	ZnO powder
Sputtering gas	H ₂ /Ar
Pressure	5 × 10 ⁻³ Torr
rf power	55–100 W
Substrate	Si (100), fused silica
Substrate temperature	150, 250 °C

by incorporating H₂ in the sputtering gas, Ar. Figure 1 shows the schematic diagram of the sputtering system employed. The film deposition conditions are listed in Table I. The electrical resistivity, Hall mobility, and carrier concentration were measured at room temperature using the van der Pauw method. The crystal orientation and surface morphology were inspected by x-ray diffraction (XRD, Rigaku) and scanning electron microscopy Hitachi F4200), respectively. The optical transmittance was measured using an UV/visible spectrometer in a spectral range of 200–900 nm.

The electrical properties of ZnO:H films as a function of H₂ compositions (in Ar) are shown in Fig. 2. The ZnO:H films are *n*-type with carrier concentration increased with increasing H₂ composition during film deposition. The increase of carrier concentration can be due to the incorporation of hydrogen donor of ZnO crystals by hydrogen radicals in plasma or due to the formation of oxygen vacancy by ZnO reduction with hydrogen plasma. The maximum mobility value is 40 cm²/V s, where the carrier concentration remains high around 6 × 10²⁰ cm⁻³. Hall mobility increases first with increasing H₂ composition up to 40%, and then starts to decrease upon further increasing H₂ composition above 40%. The decrease of mobility is likely due to the increase of the density of electron scattering centers. However, the reason for the increase of mobility for a semiconductor material is that the resistivity is inversely proportional to the carrier concentration and the carrier mobility. Thus, the lowest resistivity, 2 × 10⁻⁴ Ω cm, was obtained at a H₂ composition of 40%, where the mobility is at the maximum value, 39 cm²/V s, and the carrier concentration is high around 6 × 10²⁰ cm⁻³.

XRD results in Fig. 3 show all ZnO films prepared at various H₂ compositions. From the inset of Fig. 3, the XRD

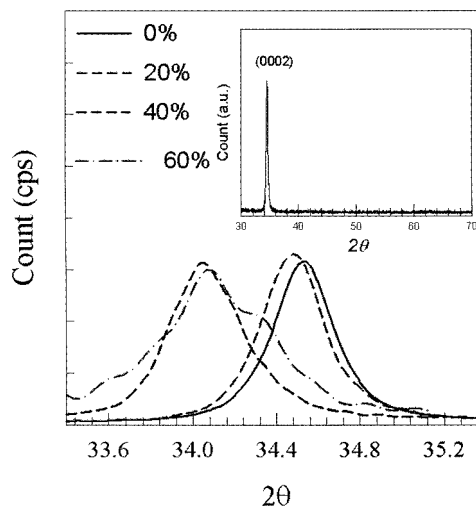


FIG. 3. X-ray diffraction patterns of ZnO:H films deposited at 150 °C substrate, 5 mTorr, and various H₂ compositions. The inset shows the ZnO:H thin film crystallite with preferred orientation along *c* axis.

spectrum has only one peak around 34°. The results confirm that the ZnO:H films consisted of crystallites with preferred orientation along the *c* axis. The ZnO grain size is reduced by increasing H₂ composition during deposition, as indicated by the increase of the full width at half maximum of the peak. Besides, the (0002) peak is shifted to a lower 2θ value, indicating an increase of interplanar distance, *d*₀₀₀₂, with the increase of H₂ composition. Previously we mentioned that the increase of carrier concentration in ZnO with increasing H₂ during deposition was either due to the presence of hydrogen donor or due to the formation of oxygen vacancy. Furthermore, Lee *et al.* reported that the *d*₀₀₀₂ spacing decreased with increasing oxygen vacancy in ZnO films.¹⁶ Therefore, the observed increase of *d*₀₀₀₂ spacing with increasing H₂ composition in Fig. 3 suggests that the increase of carrier concentration must result from the increase of H donor rather than the increase of oxygen vacancy. Our results are consistent with those reported by Van de Walle, who performed extensive calculations to conclude that the H donor is a shallow donor in ZnO.⁶

The effect of substrate temperature on the conductivity of ZnO:H thin films was also studied to investigate the behavior of hydrogen in ZnO. Figure 4 shows the Hall measurement results for the ZnO:H films deposited at 150 and

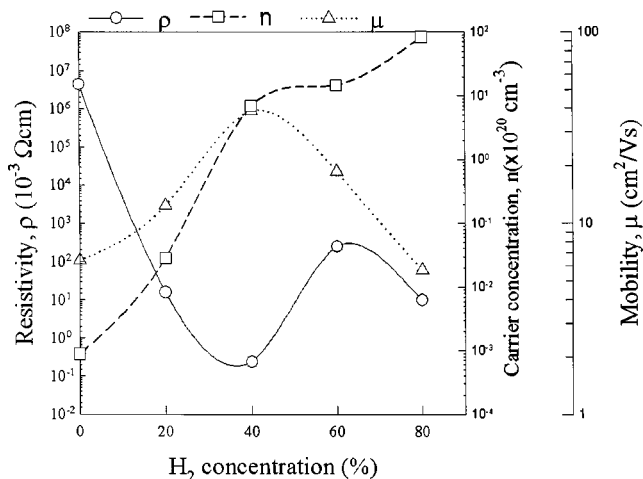


FIG. 2. The electrical properties of ZnO:H films varied with H₂ composition in Ar.

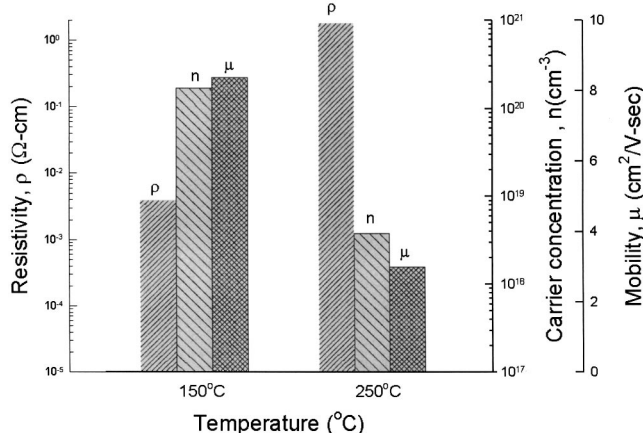


FIG. 4. The electrical properties of ZnO:H films deposited at 150 and 250 °C by Hall measurements.

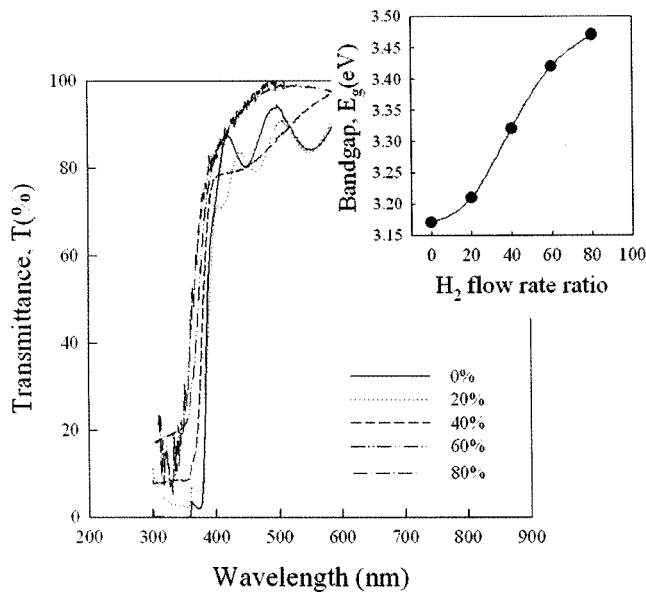


FIG. 5. Optical transmittance spectra of the ZnO:H films deposited at various H₂ compositions. The inset shows the optical band gaps, determined from the transmittance spectra, vs H₂ composition.

250 °C. The carrier concentration is significantly higher for the film deposited at 150 °C than that at 250 °C by almost two orders of magnitude. For the film deposited at a high substrate temperature, hydrogen tends to be desorbed from the ZnO:H film inducing the increase of the resistivity. On the other hand, at a high substrate temperature oxygen might be desorbed or removed by reaction with hydrogen, forming oxygen vacancies and decreasing the resistivity of ZnO. Since the resistivity of ZnO film is observed to decrease with increasing the substrate temperature during deposition, the formation of oxygen vacancies should not be the major factor in enhancing the conductivity of ZnO:H films. Therefore, our results show that hydrogen donor is responsible for the increase of carrier concentration in ZnO, as theoretically suggested by Van de Walle and experimentally confirmed by S Cox *et al.*^{9(a)} and Hofmann *et al.*^{9(b)}

In the study, UV–visible spectroscopy was also employed to measure the optical transmittance of ZnO films deposited at various H₂ compositions. As shown in Fig. 5, the transmittance of the as-grown ZnO film fell off steeply with decreasing wavelength around $\lambda=380$ nm, characteristic of high quality ZnO crystallites. The films are highly transparent with the transmittance in the visible region over 80%. When H₂ composition increases, the transmittance can be further increased up to 100%. In addition, the transmittance edge shifts to a lower wavelength with increasing H₂ composition. The phenomenon might be due to the Burstein–Moss effect,^{17,18} pointing out that the Fermi level inside the conduction band moves upward with increasing donor concentration due to the filling of conduction band by the increase of electron carriers. The increase of carrier concentrations in the ZnO:H films with increasing H₂ composition as

measured by UV–visible spectroscopy is consistent with the electrical properties by Hall measurements.

In summary, the resistivity of ZnO film is significantly reduced by the addition of H₂ in Ar during rf sputtering, likely due to the hydrogen donor of ZnO. The resistivity reaches $2 \times 10^{-4} \Omega \text{ cm}$ when H₂ composition is around 40%. The corresponding carrier concentration and Hall mobility are $6 \times 10^{20} \text{ cm}^{-3}$ and $38.9 \text{ cm}^2/\text{V s}$, respectively. XRD results show that the d_{0002} spacing increases with increasing H₂ composition due to the increasing amount of hydrogen donor in ZnO crystallites. The carrier concentration in ZnO is greatly reduced by increasing the substrate temperature from 150 to 250 °C. Both results suggest that the hydrogen donor, instead of oxygen vacancies, is responsible for the increase of carrier concentrations by increasing H₂ concentration during deposition. They are consistent with the theoretical predictions proposed by Van de Walle.^{6,7} The optical transmittance of the hydrogen-doped ZnO film is high up to 100% in the visible range. Furthermore, the transmittance edge shifts toward the lower wavelength with increasing H₂ composition during deposition, likely due to the Burstein–Moss effect.^{17,18}

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- ¹Y. P. Wang, W. I. Lee, and T. Y. Tseng, *Appl. Phys. Lett.* **69**, 1807 (1996).
- ²D. C. Reynolds, D. C. Look, and B. Jogai, *Solid State Commun.* **99**, 873 (1996).
- ³D. M. Bagnall, Y. F. Chen, Z. Zhu, T. Yao, S. Koyama, M. Y. Shen, and T. Goto, *Appl. Phys. Lett.* **70**, 2230 (1997).
- ⁴P. Kasai, *Phys. Rev.* **130**, 989 (1963).
- ⁵K. Vanheusden, C. H. Seager, W. L. Warren, D. R. Tallant, and J. A. Voigt, *Appl. Phys. Lett.* **68**, 403 (1996).
- ⁶C. G. Van de Walle, *Phys. Rev. Lett.* **85**, 1012 (2000).
- ⁷(a) C. G. Van de Walle, *Physica B* **308–310**, 899 (2001); (b) C. G. Van de Walle and J. Neugebauer, *Nature (London)* **423**, 626 (2003).
- ⁸K. Shimonura, K. Nishiyama, and R. Kasono, *Phys. Rev. Lett.* **89**, 255505 (2002).
- ⁹(a) S. F. J. Cox, E. A. Davis, S. P. Cottrell, P. J. C. King, J. S. Lord, J. M. Gil, H. V. Alberto, R. C. Vilão, J. Poroto Duarte, N. Ayres de Campos, A. Weidinger, R. L. Lichti, and S. J. C. Irvine, *Phys. Rev. Lett.* **86**, 2601 (2001); (b) D. M. Hofmann, Al. Hofstaetter, F. Leiter, H. Zhou, F. Henecher, B. K. Meyer, S. B. Orlinskii, J. Schmidt, and P. G. Baraov, *ibid.* **88**, 045504 (2002).
- ¹⁰E. V. Lavrov, J. Weber, F. Börnert, C. G. Van de Walle, and R. Helbig, *Phys. Rev. B* **66**, 165205 (2002).
- ¹¹Ç. Kiliç and A. Zunger, *Appl. Phys. Lett.* **81**, 73 (2002).
- ¹²S. Jae Baik, J. Hoon Jang, C. Hyun Lee, W. Yeong Cho, and K. Su Lim, *Appl. Phys. Lett.* **70**, 3516 (1997).
- ¹³K. Ip, M. E. Overberg, Y. W. Heo, D. P. Norton, S. J. Pearton, C. E. Stutz, B. Luo, F. Ren, D. C. Look, and J. M. Zavada, *Appl. Phys. Lett.* **82**, 385 (2003).
- ¹⁴(a) B. Theys, V. Sallet, F. Jomard, A. Lusson, J. -F. Rommeluere, and Z. Teukam, *J. Appl. Phys.* **91**, 3922 (2002); (b) C. H. Seager and S. M. Myers, *ibid.* **94**, 2888 (2003).
- ¹⁵S. Kohiki, M. Nishitani, T. Wada, and T. Hirao, *Appl. Phys. Lett.* **64**, 2878 (1994).
- ¹⁶Y. Eui Lee, J. Bin Lee, Y. Jin Kim, H. Kook Yang, J. Chul Park, and H. Joon Kim, *J. Vac. Sci. Technol. A* **14**, 1943 (1996).
- ¹⁷M. K. Hudait, P. Modak, and S. B. Krupanidhi, *Mater. Sci. Eng., B* **56**, 1 (1999).
- ¹⁸N. Y. Lee, K.-J. Lee, C. Lee, J.-E. Kim, H. Y. Park, D.-H. Kwak, and H.-C. Lee, and H. Lim, *J. Appl. Phys.* **78**, 3367 (1995).