Epitaxial growth and properties of $Zn_{1-x}V_xO$ diluted magnetic semiconductor thin films

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Here we report systematic studies on the epitaxial growth and properties of $Zn_{1-x}V_xO$[x=0.001-0.2] thin films deposited onto sapphire *c*-plane single crystals. The thin films were deposited using pulsed laser deposition technique and were found to be epitaxial in nature. X-ray diffraction and high resolution transmission electron microscopy were employed to study the epitaxial relations of $Zn_{1-x}V_xO$ with the sapphire substrate and electron energy loss spectroscopy was used to establish the bonding characteristics and oxidation states of vanadium inside the ZnO host. The main emphasis is on the magnetic properties of this system taking into consideration the phase purity and microstructural characteristics of these films. Our results show that the $Zn_{1-x}V_xO$ system, with V in zinc substitutional sites, does not exhibit any signature of ferromagnetism, both at room temperature as well as at lower temperatures down to 10 K. © *2005 American Institute of Physics*.
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Recent interest in spintronic devices, which utilize the spin degree of freedom of the electron, has attracted widespread attention. There are various novel device concepts, which have been proposed that are based on this technology, and a few (e.g., read heads for magnetic recorders and nonvolatile memory components) that have already found practical applications.[1] Diluted magnetic semiconductors (DMS), obtained by incorporating magnetic impurities into host semiconductors, have been shown to be promising candidate materials for such applications. But owing to the low T_c of the early DMS (e.g., Mn-doped GaAs has a Tc below 180 K) the initial demonstrations were only possible at low temperatures.[2] Practical applications will require ferromagnetism in these systems to extend above room temperature. Following the theoretical works of Dietl *et al.*,[3] and Kazunori *et al.*[4], there have been experimental reports confirming the presence of room temperature ferromagnetism (RTFM) in III-V and II-VI semiconductors. Both GaN and ZnO have been studied as potential systems and a variety of dopants have been studied with mixed results. For example, several works on Co doped ZnO[5] and Mn doped GaN have reported RTFM in these systems. Ueda *et al.* studied various transition metal doped ZnO systems and found that particular compositions of Co in ZnO resulted in RTFM.[6] Also, there are contradicting reports on Mn doped ZnO where a few have ruled out the possibility of RTFM at higher concentrations[7] but a more recent report has found RTFM in Mn doped ZnO at relatively low concentrations.[8] It appears that the presence or absence of ferromagnetism is fundamentally tied to the exact microstructure of these materials[9] and that careful microstructural characterization of the systems is required to understand their magnetic properties.

In the sparsely studied V-doped ZnO system, ferromagnetism was observed by Saeki *et al.*,[10] and Venkatesan *et al.*[11] but there has been no microstructural characterization done in this system so far, to confirm whether the properties were due to dopants in substitutional sites or precipitates/clusters of a second phase. Hence, we have performed a systematic study of the vanadium doped ZnO thin films for concentrations of 1% to 20%, prepared using pulsed laser deposition technique. Special emphasis has been placed on the correlation of microstructural and optical characteristics of the films with their magnetic properties. We have probed this aspect to conclusively provide evidence for the absence of ferromagnetism in this system using various techniques including high resolution transmission electron microscopy (HRTEM) and electron energy loss spectroscopy (EELS).

$Zn_{1-x}V_xO$ (x=0.01–0.2, nominal composition of the target) thin films were grown on the *c*-plane of sapphire single crystal substrates, by pulsed-laser deposition. The targets were prepared by the conventional solid-state reaction technique. A pulsed KrF excimer laser with a wavelength of 248 nm was used for the deposition. The energy density and the repetition rate of the laser beam were 2–4 J/cm^2 and 10 Hz, respectively. Thin film growth was carried out over a temperature range of 400–600 °C and at a pressure of 10^{-6} Torr, for 15–20 min yielding films about 0.2–0.4 microns in thickness. X-ray diffraction measurements on the grown films were performed using a Rigaku x-ray Diffractomer with Cu-K_α radiation and a Ni filter. Magnetic measurements were carried out using a quantum design (SQUID) magnetometer over a temperature range of 10–300 K. Microstructural and epitaxial characterization including atomic structure and chemistry investigations were conducted using high resolution TEM and EELS in a JEOL-2010 field emission transmission electron microscope equipped with a GIF (Gatan Image Filter) tuning attachment. It should be pointed out that x-ray diffraction (θ–2θ) investigations reveal axial alignment only in the direction perpendicular to the film / substrate interface, whereas, cross section TEM provides information on the alignment in all of the three axes, thus confirming epitaxial growth or single crystal growth of thin films. Optical measurements (absorption/transmission) were made using a Hitachi Spectrophotometer.

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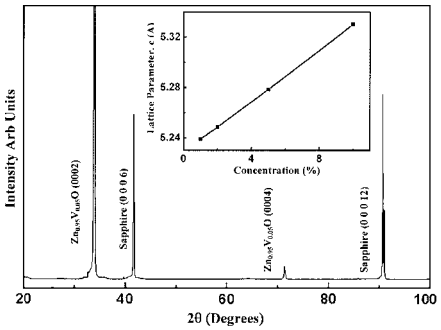

FIG. 1. X-ray diffraction of $Zn_{1-x}V_xO$ (x=0.05). Inset shows an increase in the lattice parameter with vanadium concentration.

Figure 1 shows x-ray diffraction measurements (Intensity vs 2θ) on the doped ZnO films. The inset shows an increase in the c-axis parameter with increasing V concentration in the ZnO. Samples used for this study were grown at 400 °C but for a particular composition, the temperature of growth does not seem to affect the lattice parameter significantly. The films are highly textured up to a concentration of 5%. At a concentration of 10% the films grown at the lower temperature of 400 °C do not show any second phase, whereas films grown at 500 °C show signatures of a segregating second phase (possibly a spinel of β-$Zn_3(VO_4)_2$ or ZnV_2O_6 as deduced from x-ray diffraction). This may be due to enhanced diffusion and chemical reactions that become activated at higher temperatures. The systematic increase in the c-axis parameter with V concentration implies that a uniform substitution of V is occurring in the lattice of ZnO at least up to 10% vanadium.

Low-magnification diffraction contrast bright field/dark field images did not show any evidence of clustering in the form of nano-sized particles. The precipitates or clusters in the nanosize range would show up as black-white contrasted images with the black-white vector always perpendicular to the diffraction (g) vector in the case of specified three-dimensional precipitates, or making a certain angle in the case of two-dimensional precipitates.[12] To confirm these observations, a detailed high-resolution TEM analysis was done to analyze the microstructure. Low magnification images indicated the thickness of the films to be around 400 nm for the $Zn_{0.95}V_{0.05}O$ sample. Figure 2 shows a HRTEM micrograph of the interface between the $Zn_{0.95}V_{0.05}O$ film and the sapphire substrate, showing the highly epitaxial nature of the film. The inset shows nearly perfect epitaxy of the film with the substrate, with the following orientation relationships: $(0001)_s \| (0001)_f$, $(01\bar{1}0)_s \| (\bar{2}110)_f$, $[2\bar{1}\bar{1}0]_s \| [01\bar{1}0]_f$ (this represents an in-plane rotation of 30° or 90°, of the film relative to the substrate about the c-axes). Also, the interface is compositionally sharp with no evidence of any interfacial reaction. In addition, below concentrations of 5% V in ZnO there are no signs of any additional phases separating from the parent material.

The bonding characteristics and the oxidation states of vanadium in the films were investigated with EELS at various points in the cross sectioned samples. Figure 3 shows the background reduced characteristic EELS spectrum of vanadium showing the L_2 and L_3 peaks in addition to the O-K peak. A detailed high-resolution scan of the peaks indicates the nature of the bonding of oxygen atoms to the vanadium atoms in the film. The results clearly show characteristic vanadium peaks of L_2/L_3 corresponding to an oxidation state of

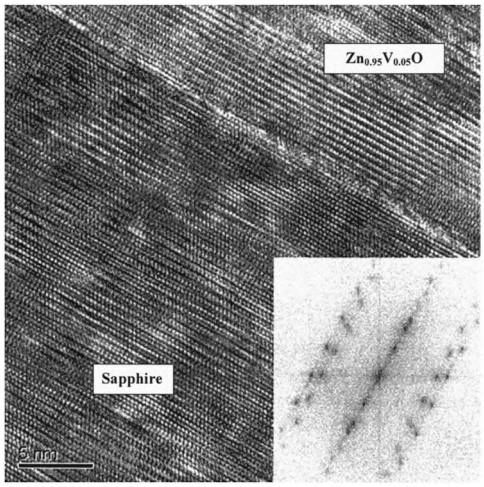

FIG. 2. High resolution TEM image of $Zn_{0.95}V_{0.05}O$ (grown at 500 °C) showing highly epitaxial film on sapphire, with a clean interface. Inset shows the fast fourier transform of the interface depicting a high degree of epitaxy.

+2 or +3.[13] The inset shows a high-resolution scan at the O-K peaks. The slope change at the onset of the oxygen peak, matches very closely to a mixture of +2 or +3 oxidation states for the dopant V ions. This is possible if vanadium is stable in various oxidation states, and would be facilitated by the presence of point defects in the system. Thus, both the high resolution TEM and EELS measurements suggest that most of the V atoms have substituted into the ZnO lattice points.

Optical absorption measurements were done on the V doped ZnO samples. Observations on samples doped with 1%, 5%, and 10% are shown in Fig. 4, where the transmitted intensity is plotted as a function of wavelength. All the samples for the optical measurements were grown at 450 °C. The spectra clearly illustrate the bandgap absorption edge for all these films in the range of 330 to 375 nm (corresponding ZnO bandgap wavelength at ~380 nm) with the bandgap increasing for increasing V concentration. This systematic change of bandgap with composition suggests a uniform substitution of the V for Zn ions in the lattice.

Magnetic measurements on $Zn_{1-x}V_xO$ films were performed in the temperature range 10–300K using a SQUID magnetometer. To preclude the existence of even a minute coercive field, measurements were taken in 25 gauss steps up to a magnetic field of 1.5 T. All the measurements were

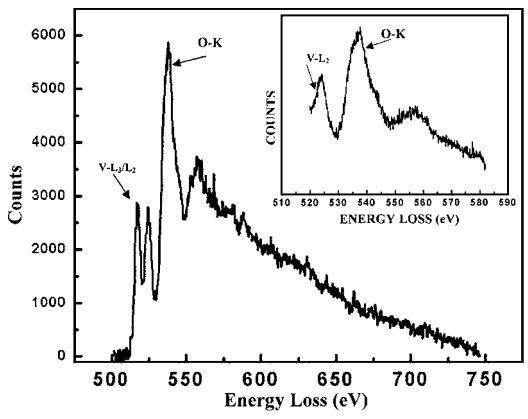

FIG. 3. Electron energy loss spectrum from the $Zn_{0.95}V_{0.05}O$ film grown at 500 °C showing L_3/L_2 peaks of vanadium along with O-K peak. Inset shows resolved O-K edge.

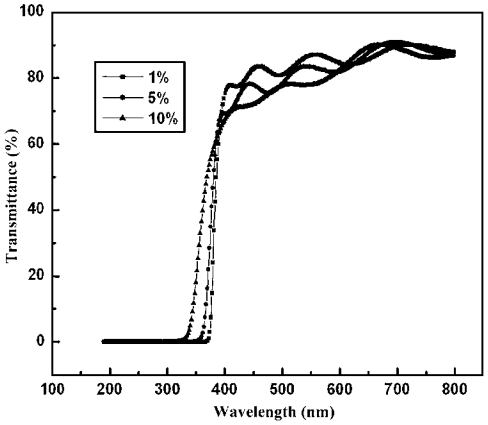

FIG. 4. Optical transmission spectrum of $Zn_xV_{1-x}O$ (x=0.99, 0.95, 0.1) films grown at 450 °C, showing the change in the absorption edge.

corrected for substrate effects. In Fig. 5 we have shown magnetization as a function of applied magnetic field (M versus H) data for $Zn_{0.95}V_{0.05}O$ film recorded at 10 K; the M versus H curve at 300 K shows similar behavior. The plot clearly indicates that the film does not exhibit any ferromagnetic character either at room temperature (300 K) or at 10 K, even up to fields of 5 T. Similar measurements were done on samples with 1% to 20% vanadium, and again no evidence of ferromagnetic behavior was observed. All the samples investigated in this study had electrical conductivities around $2(\Omega\ \mathrm{cm})^{-1}$, which according to Ref. 10 should have resulted in ferromagnetism. Finally, magnetization vs temperature measurements were performed on $Zn_{1-x}V_xO$ films under zero field (ZFC) as well as field cooled (FC) conditions at a field of 500 G. In both cases very similar behavior was observed, indicating that the films are not superparamagnetic and again ruling out the possibility of any kind of nanoclustering/precipitation in the system. In Fig. 6 we have shown a typical M versus T graph for $Zn_{0.95}V_{0.05}O$ taken at a field of 500 Gauss. The inset of this figure shows a plot of inverse dc magnetic susceptibility ($1/\chi$=H/M) as a function of temperature. As is clear from this figure, $1/\chi$ versus T follows a linear Currie–Weiss type behavior with a positive, nonzero intercept of the y-axis. This behavior is suggestive of paramagnetic behavior that is dominated by antiferromagnetic exchange coupling between the transition metal spins.

In summary, we have grown V-doped ZnO thin films by pulsed-laser deposition on c-plane sapphire single crystal substrates. As-grown films were single crystals, as shown by

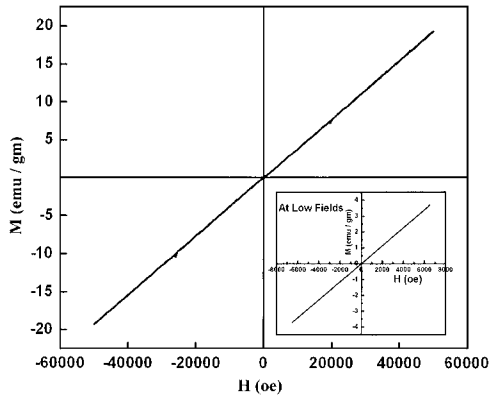

FIG. 5. Magnetization as a function of applied magnetic field for $Zn_{0.95}V_{0.05}O$ up to fields of 5 Tesla, at 10 K. Inset shows a close scan at low field intervals of 25 Gauss up to a field of 1.5 Tesla.

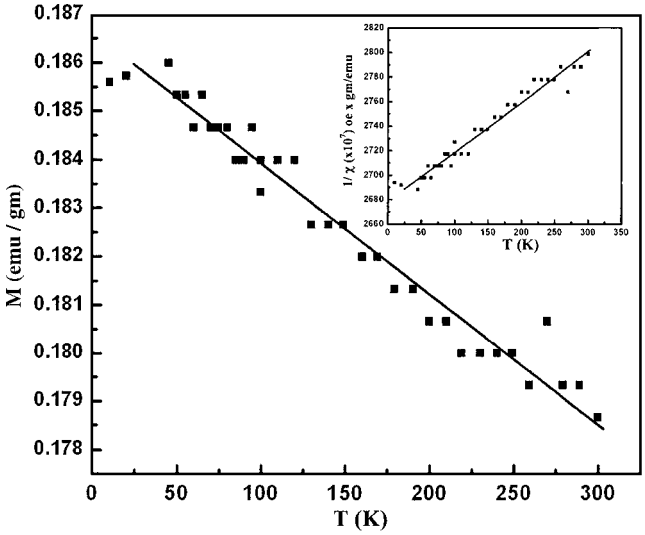

FIG. 6. Magnetization as a function of temperature of $Zn_{0.95}V_{0.05}O$ at a field of 500 Gauss showing a linear drop in magnetization with temperature. Inset shows $1/\chi$ as a function of temperature.

x-ray diffraction and TEM, with an epitaxial relationship on sapphire having a 30° or 90° rotation relative to the sapphire substrate. Atomic scale structural characterization, including HRTEM and EELS, suggests that these films are devoid of any nano-sized clusters or second phases. Optical measurements also indicate a systematic rise in bandgap with increase in concentration of the dopant. These results clearly suggest that vanadium was substituting for the Zn^{2+} in the ZnO lattice in both +2 and +3 oxidation states. Magnetic measurements showed the dc susceptibility of these films to follow a Curie–Weiss type of behavior. However, the possibility of any kind of magnetic ordering at lower temperatures (<10 K) cannot be ruled out at this point.

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