Magnetic properties of V-doped ZnO thin films

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(Presented on 11 November 2004; published online 6 May 2005)

Ferromagnetic V-doped ZnO films were fabricated by the conventional pulsed-laser deposition technique on *R*-cut sapphire substrates from a ceramic target that was made by sol-gel method. All films are highly crystallized to be wurtzite. V-doped ZnO thin films grown at 600–650 °C show room-temperature ferromagnetism along with a spin-glass-like behavior at low temperatures. It is found that V atoms were distributed very uniformly in the ZnO matrix. However, different growth conditions could result in different values of the saturation magnetic moment, and an increase of the substrate temperature above 650 °C seems to favor a secondary phase, which is antiferromagnetic. © *2005 American Institute of Physics*. [DOI: 10.1063/1.1848451]

Recently, many research groups have been pursuing the search for ferromagnetic semiconductors with a Curie temperature (T_C) well beyond room temperature. One of the most recent interests is the quest for high T_C ferromagnetism (FM) in oxides such as ZnO doped with Co[1] and TiO_2 doped with Co,[2,3] Fe,[4,5] Ni,[5] or V,[6] and SnO_2 doped with Co (Ref. 7) or Fe.[8]

Besides the search for materials having a high T_C and a large magnetic moment, it is also important to find doped compounds that have great homogeneities, or in other words, the dopants could be well dissolved and dopant atoms are distributed uniformly among the host matrices.

Theories predicted that V doping might introduce FM into semiconducting oxides;[9] however, so far, not much work has been done in this direction. V-doped TiO_2 thin films are room-temperature ferromagnets with a very large magnetic moment,[6] while V:ZnO films might be ferromagnetic but only when the films were conductive.[10] (Note that, in fact, in Ref. 10, V:ZnO films were deposited on top of a 5-nm-thick layer of ZnO; therefore, the properties of those are not of V:ZnO monolayers alone.[10]) In this study, we investigated the magnetic properties of V-doped ZnO thin films.

A $Zn_{0.95}V_{0.05}O$ ceramic target was made by a sol-gel method. V:ZnO films were grown by the pulsed-laser deposition technique using KrF laser ($\lambda = 248$ nm) on *R*-cut sapphire (1 −1 0 2) substrates. The typical thickness of the films is 200 nm. The repetition rate was 3 Hz and the energy density was 2 J/cm^2. The temperature of the substrate was kept as 600, 650, or 700 °C. During deposition, the oxygen partial pressure (P_{O_2}) was 10^{-1} Torr, and after deposition, films were cooled down slowly to room temperature under a P_{O_2} of 300 mTorr. The structural study was done by x-ray diffraction (XRD). The resistance of the samples were measured by the two-probe method using a resistance meter. Magnetization measurements were performed by a Quantum Design superconducting quantum interference device system from 0 up to 0.5 T under a range of temperatures from 400 K down to 5 K. The chemical compositions were determined by the Rutherford backscattering spectroscopy (RBS) method.

As seen from Fig. 1(a), the XRD pattern showed that V:ZnO films are well crystallized to be single-phased hexagonal wurtzite and no impurity peak is found (note the high intensity of the peaks). Based on the RBS data, the V content in V:ZnO films is determined to be 12.87%, 11.11%, and

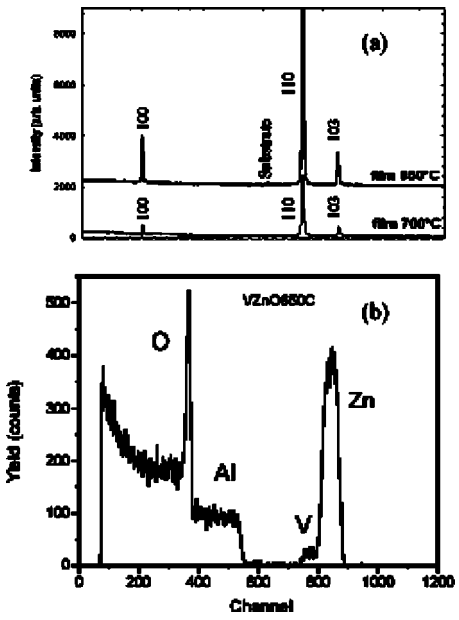

FIG. 1. Structural analysis: (a) XRD patterns of (a) V-doped ZnO films fabricated at 650 and 700 °C and (b) RBS spectra of the V-doped ZnO films fabricated at 650 °C.

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8.36% for films fabricated at 600, 650, and 700 °C, respectively.

All of our V:ZnO films are semiconductors with a resistivity at room temperature of about 1.5 Ω cm, it rises up quickly when the temperature decrease. This is worth noting, because if the FM in the samples is not associated with the semiconductivity, it might be due to the remaining of V metal clusters or, as in the case of V:ZnO films[10] or $Co:TiO_2$ films,[11] the FM observed originated from dopant clusters; therefore the films are metallic at room temperature.

RBS spectra showed that both Zn atoms and V atoms are distributed very uniformly in the films. As seen from Fig. 1(b), the peaks of Zn and V are clearly separated, indicating that the determinations of Zn and Co content in the films could be rather precise (if there is an overlapping, it is not possible to determine precisely the number of atoms of each element). The V peak has a rectangular shape similar to that of the Zn peak, showing that the V distribution in the V-doped ZnO films is greatly uniform over the whole thickness of the film (the same result is found from detailed simulations for the ratio of V and Zn in each layer). This is completely different from what was found in Co/Fe/Ni-doped TiO_2 film[12,13] and Co-doped ZnO film,[14] where the dopant atoms were localized mostly in the layer of 40 nm taken from the surface. While Jin *et al.* reported that among all the elements of the transition-metal group, Cr, Mn, Fe, and Co are the most soluble,[15] on the contrary, our case shows that compared to Co and Fe, V seems to be easier to dissolve into ZnO. Therefore, we must say that not only does the nature of dopant decide whether its distribution is uniform or not, but it must also depend to some extent on the growth conditions.

V:ZnO films fabricated at either 600 or 650 °C are ferromagnetic at room temperature (see Figs. 2 and 3). However, the saturation magnetization (M_s) of the films fabricated at 650 °C is one order larger than that of films grown at 600 °C. The maximum value of M_s that we could obtain in V:ZnO films is 0.6 μ_B/V, and it is rather modest (it is much smaller than the value as of 4.23 μ_B/V obtained in $V:TiO_2$ films).[6] From the $M(T)$ curve, one can see that there is a shoulder at about 220 K and it shows that in the film, there are some minor parts that tend to be antiferromagnetic, but the majority certainly remains ferromagnetic, and such a ferromagnetic phase is still dominant over the whole range of temperatures. As evidenced from the value of θ at 335 K seen from the inset of Fig. 2(a), and from well-defined hysteresis loops in $M(H)$ curves taken at various temperatures in the range from 10 to 300 K [see Fig. 2(b) and Fig. 3], even though the M_s is small, the films are clearly room-temperature ferromagnetic. At low temperatures, there is a clear discrepancy between the zero-field-cooled (ZFC) and field-cooled (FC) temperature dependence of magnetization, which indicates a spin-glass-like behavior. It is similar to what was observed in Co-doped ZnO thin films[16,17] and Mn-doped ZnO bulk,[18] and it seems to be typical for a transition-metal-doped ZnO system. Since the isolated V atom has a magnetic moment of $3\mu_B$ and bulk V is paramagnetic, the value of M_s as small as $0.6\mu_B$ cannot come from those. Some theoretical work reported that when the size of the V cluster is two atoms, it can give such a value.[19] However, from the uniform distribution of V seen from the RBS data, it is not possible to assume that the whole specimen consists of many clusters with the same size (two atoms), distributed homogeneously in the samples (note that the number of V atoms on the films of 5×5 mm^2 is about 2.5×10^{16} atoms). Thus, it is more convincing if the magnetism we found in V:ZnO films originates from the V-doped ZnO matrix. However, when the substrate temperature was increased to 700 °C, the antiferromagnetic phase, which appeared slightly in the samples grown at 600 and 650 °C, seemed to be more prevailing below 200 K (see Fig. 4). Even though the $M(H)$ curve taken at 10 K with a hysteresis proves that the sample is still weakly ferromagnetic at low temperatures,[19] the $M(T)$ curve confirms the existence of the antiferromagnetic phase with $T_{\text{Néel}} \approx 200$ K. This may be explained that at higher temperatures, there are more dopant-dopant associations, which may decrease the magnetic moment, and some precipitations thus

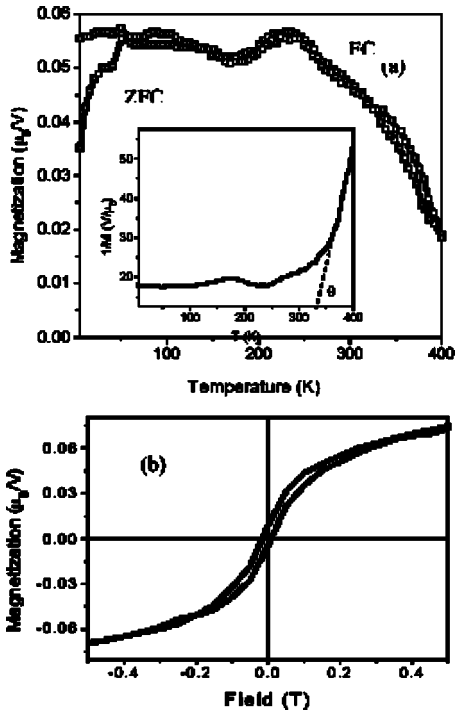

FIG. 2. Magnetization of a V-doped film fabricated at 600 °C (a) versus temperature measured at ZFC and FC of 0.2 T and (b) versus magnetic field at 10 K. The inset shows $1(M$ (at FC) versus T. The interception of the dashed line and T axis indicates θ at 335 K.

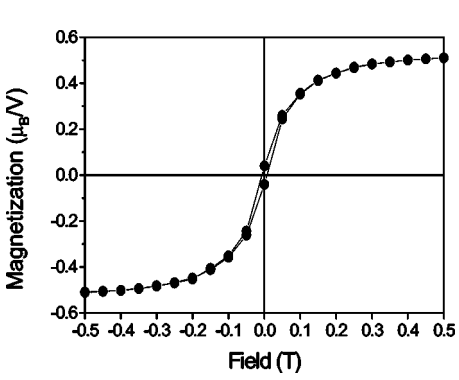

FIG. 3. Magnetization versus magnetic field taken at 300 K for a V-doped ZnO film fabricated at 650 °C.

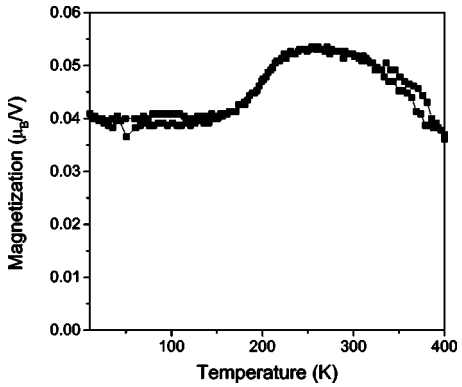

FIG. 4. Magnetization versus temperature under 0.2 T for a V-doped film fabricated at 700 °C (FC and ZFC).

may exist (the magnetic moment of a V cluster of a size bigger than 15 atoms can give a value of about $0.03\mu_B$).[20,21]

In conclusion, V-doped ZnO thin films grown at 600–650 °C by laser ablation on sapphire substrates show room-temperature ferromagnetism along with a spin-glass-like behavior at low temperatures. It is found that V atoms were distributed very uniformly in the ZnO matrix. Films fabricated with different conditions could have different values of the saturation magnetic moment, and an increase of the substrate temperature above 650 °C likely favors a secondary phase, which is antiferromagnetic.

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[21]RBS data for the sample fabricated at 700 °C showed more fluctuations in the ratio of V compared to those fabricated at 600 and 650 °C, and it may be related to some precipitations.