Ferromagnetism in ZnO

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Abstract

We report the growth of high quality Cu,Ag, Ga and In doped ZnO thin films by magnetron sputtering. High level of Cu, Ga doping has been achieved at higher growth temperature. Room temperature ferromagnetism, with magnetic moment decreasing with increasing Cu and Ag content, has been observed in the thin film, whereas no RTFM has been observed in Ga and In doped ZnO.

Introduction

The possibility of achieving ferromagnetic properties in semiconductor has resulted great enthusiasm for an emerging field of electronics known as spintronics,[1] which aim at using both spin and charge of the electron for promising spin based devices. Dietl [2] predicted that transition metal doped ZnO might display Curie temperatures above room temperature. Recently, it is being attempted to dope ZnO with nonmagnetic ions for achieving ZnO based DMS. In view of conflicting results regarding room temperature ferromagnetism (RTFM) in ZnO and stability of observed magnetism, it is highly desirable to study RTFM in ZnO. In this paper, we report on magnetism in ZnO doped with non magnetic impurities.

Experimental details

ZnO thin films were deposited on quartz and silicon substrates using RF magnetron sputtering at substrate temperatures varying from 100°C to 600°C. The target was synthesized by conventional solid state reaction route using commercially available (Aldrich, USA) ZnO, Ag_2O, CuO, Ga_2O_3, and In_2O_3 powders all (99.999%) pure, which were mixed in stoichiometric ratio, grounded for sixteen hours and sintered at 700 °C for twelve hours. Argon and oxygen were used as sputtering gases. X-ray diffraction (XRD) studies were performed using PANalytical Xpert Pro system. Data was collected for 2θ values from 20 to 80 degrees using Cu (Kα = 1.54 Å) operating at 45 KV and 40mA current. Magnetic measurements were performed using a Quantum Design USA, Ever Cool MPMS XL-7 SQUID magnetometer with the thin film samples parallel to applied field at 300K and 10K.

Results and discussions

XRD of the Cu doped ZnO (ZnO:Cu) thin films showed pronounced c-axis orientation resulting in strong (002) peak at 34.4° and (004) peak at 72° respectively corresponding to wurtzite ZnO structure (SG: $P6_3mc$)[3], as shown in Figure 1. The absence of any peak corresponding to CuO planes indicate homogenous mixing of dopant atom with the host insulating matrix and negates the presence of any secondary phases of either metallic Cu or oxides of Cu. FWHM of (002) peak of all the films are comparable to thin films grown by pulse laser deposition (PLD) [4]. The ionic radii of Cu^{+2} (73 pm) and Zn^{+2} (74 pm) [5] are almost same, so one would expect XRD peak shift little at higher doping. Figure 1 shows that in addition to the (002) and (004) peaks, there are smaller peaks corresponding to (100), (101), (102), (110) and (103) orientations, which are due to deviation from c-axis orientation in undoped ZnO, but these peaks disappear upon doping of Cu. It has been shown that this enhancement of c axis orientation is due to the moderate quantity of Cu^{+1} atoms which exist as interstitials that share the oxygen with Zn atoms improving the c-axis orientation. Hence doping of Cu enhances the crystallinity and c-axis orientation of the host thin films.XRD of the Ag doped ZnO (ZnO:Ag) thin films showed c-axis orientation for doping below 1% resulting in strong (002) peak at 34.4° and (004) peak at 72°, respectively which indicate wurtzite ZnO structure, as shown in Figure 1. The presence of Ag_2O (011) peak at around 38 degree in samples with doping concentration of 1% or more indicate secondary phase formation and inhomogeneous mixing of dopant atom with the host insulating matrix. The large ionic radius of Ag^{+1} (128 pm) as compare to Zn^{+2} (74 pm) [5]is probably responsible for secondary phase formation. Ag_2O phase drives the c-axis oriented thin films to misoriented thin films. Recently it has been shown that c-axis orientation of host ZnO deteriorates and impurity peaks start to appear in ZnO thin films with 2% Ag.

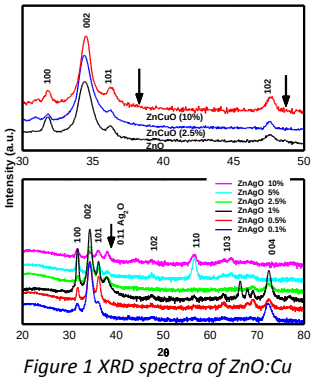

Figure 1 XRD spectra of ZnO:Cu and ZnO:Ag

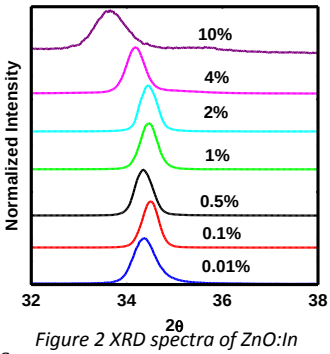

Figure 2 XRD spectra of ZnO:In

The normalized XRD profile of Ga doped ZnO (GZO) films with different Ga content from

0.01% to 10% grown at 600 ^{o}C is (not shown here). All the films show pronounced c-axis orientation resulting in strong 2θ (002) peak corresponding to hexagonal wurtzite structure. The absence of Ga_2O_3 phases in XRD patterns of GZO films marked by arrows in Figure 2 indicate homogeneous mixing of Ga_2O_3 with ZnO. The normalized XRD profile of In doped ZnO (IZO) thin films grown at 600 ^{0}C substrate temperature is shown in Figure 2. The absence of In_2O_3 phase in the x-ray diffraction pattern of IZO films indicates homogenous mixing of In_2O_3 with ZnO. XRD results shows that, in IZO thin films as In content increases the diffraction peak 2θ (002) shifts slightly towards lower diffraction angle. This behavior indicates that the incorporation of In into ZnO increase the c-axis lattice constant and there is a residual stress developed within the IZO films. This may be due to larger ionic radius of In^{3+} (0.094nm) than that of Zn^{2+} (0.074 nm).

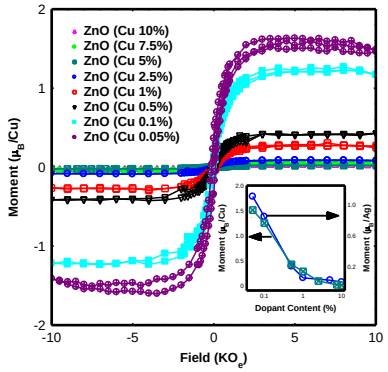

Figure 1 Room temperature magnetisation of ZnO:Cu samples. Inset show variation of magnetic moment with dopant concentration

Magnetic measurements on undoped, ZnO:Cu, ZnO:Ag, ZnO:Ga and ZnO:In films were performed in the temperature range of 10–300 K using a SQUID magnetometer. All the measurements were corrected for substrate effects. The magnetization as a function of applied field at 300K for undoped ZnO shows diamagnetic behavior. The magnetization as a function of applied field at 300 K for ZnO:Cu is shown in Figure 3. All the RF sputtered ZnO:Cu and ZnO:Ag samples grown at 600°C show FMO at room temperature. The moment per Cu atom at 300 K decreased with increasing dopant concentration as shown in inset of Figure 3. In order to understand the observed high magnetic moment of the films, it is essential to have an insight into the possible electronic configurations of Cu ions inside ZnO host. Cu atoms in its unionized state have an outer shell electronic configuration of [Ar] $3d^{10}4s^{1}$ and, hence Cu^{+} and Cu^{2+} ions are expected to possess $3d^{10}$ and $3d^{9}$ configurations, respectively. In $3d^{10}$ configuration, all the *d* electrons are paired and, hence Cu^{+} ion inside ZnO host does not possess any magnetic moment. On the other hand, in the case of Cu^{2+} ions (Cu on Zn site) with d^{9} configuration, one unpaired electron is available. This will give rise to a spin angular momentum of 1/2 which can result in a net magnetic moment of $M \approx 1.73\ \mu_B$ according to relation $M = g\ \mu_B \sqrt{S(S+1)}$ for g = 2, S = 1/2 [6].Observed magnetic moment value of $1.51\mu_B$/Cu atom in our films is quite close to above estimated magnetic moment value for Cu^{2+} ions, implying that for low doping, Cu ions in our thin films are predominantly in magnetically active Cu^{2+} state confirmed by XPS studies. Tiwari et al. [6], have observed a saturation magnetic moment of 1.45 μ_B/Cu atom for 5% ZnO:Cu thin films. The consistent drop in moment per Cu atom of dopant at higher Cu concentration could be due to either (i) antiferromagnetic ordering between Cu ions occurring at shorter separation or (ii) breaking of FMO due to doping induced disorder or alloy disorder in case of samples with higher Cu content. The Bohr magnetron value of $1.51\mu_B$/Cu atom is more than that in PLD grown epitaxial layers [4] .

The moment per Ag atom at 300 K decreased with increasing Ag concentration as shown in inset of Figure 3. Observed maximum magnetic moment value of $1.17\mu_B$/Ag atom in our films is less than above estimated magnetic moment value for Ag^{2+} ions, implying compared to ZnO:Cu less no of Ag ions are in magnetically active state. This is not surprising because size of Ag^{2+} is higher than that of Zn^{2+}, whereas size of Cu^{2+} is very close to that of Zn^{2+}. Magnetisation measurement of ZnO:Ga and ZnO:In samples revealed diamagnetic character as shown in Figure 4.

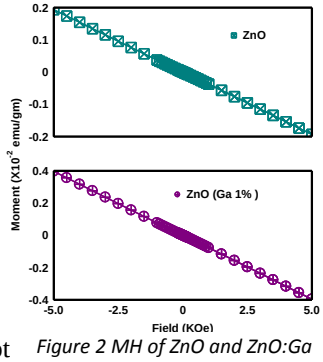

Figure 2 MH of ZnO and ZnO:Ga

Conclusions

In conclusion, we have shown that stable room temperature ferromagnetism can be observed in ZnO:Cu and ZnO:Ag thin films grown at higher growth temperature without post growth annealing. It is important to optimize growth conditions and concentration of dopant to have maximum magnetization in ZnO:Cu and ZnO:Ag thin films. It is further observed that the moment per dopant atom decreases with increasing dopant concentration. The vacant d orbital plays an important role in observation of RTFM in Ag and Cu doped ZnO.

References

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