

Origin of room temperature ferromagnetism in ZnO:Cu films

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Copper-doped ZnO (ZnO:Cu) films were prepared on silicon substrates by filtered cathodic vacuum arc technique at room temperature using a Zn target containing 5 at. % of Cu. Room temperature ferromagnetism was observed in the ZnO:Cu films with saturation magnetization of $0.037\mu_B/\text{Cu}$ atom. The origin of the ferromagnetism in ZnO:Cu was mainly due to Cu ions substituted into the ZnO lattice. X-ray diffraction, x-ray photoelectron spectroscopy, and transmission electron microscopy revealed that no ferromagnetic-related secondary phase could be detected in ZnO:Cu.

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There is considerable interest in the development of transition-metal-doped zinc oxide based (ZnO:TM) diluted magnetic semiconductors (DMSs) because of their high Curie temperature (T_c) (Ref. 1) which is essential for spintronic devices. Ferromagnetism was observed in ZnO:Co and ZnO:Mn.^{2,3} However, Jin *et al.*⁴ and other groups⁵ have found no ferromagnetism in ZnO:Co and ZnO:Mn based semiconductors. The controversial results seem to come from either the low quality or the poor reproducibility of thin films. Another suspicion is that ferromagnetism might be caused by secondary phase rather than the substitution of TM ion into the Zn site.⁶ These issues motivated researchers to probe experiments on Cu-doped ZnO (Refs. 6 and 7) as Cu is a potential magnetic ion with a total spin of $\frac{1}{2}$ by Hund's rule. The Cu-related secondary phases are antiferromagnetic which may make the interpretation of ferromagnetism in ZnO:Cu easier.⁸ In addition, Cu is also well known as a potential *p*-type dopant with high reproducibility that aroused an interest to realize ferromagnetic ZnO:Cu films.^{7,9} The use of hole doping has been predicted by Dietl *et al.*¹ that ZnO based DMSs could exhibit ferromagnetism above room temperature with the incorporation of hole doping. Indeed, Buchholz *et al.*¹⁰ reported the ferromagnetism of ZnO:Cu on sapphire under conditions that prepared *p*-type ZnO using N₂O as doping gas.

Recent experimental^{3,7,10} and theoretical works¹¹ showed that room-temperature ferromagnetism of ZnO:Cu films would not be possible without additional hole doping or co-doped with Fe, Mn, or N. Feng¹¹ reported that Cu clustering is unstable at ground level and it is likely to form during the high temperature preparation process¹¹ such as pulsed laser deposition (PLD) (Ref. 12) and solid state reaction.⁶ The existence of unstable Cu clusters in intrinsic *n*-type ZnO semiconductor would result in an electron occupying a Cu 3d state which leads to antiferromagnetism.¹³ To tackle this

problem, we prepared ZnO:Cu films at room temperature by the filtered cathodic vacuum arc (FCVA) technique. The homogeneous and high-crystal-quality ZnO films have been deposited on Si at room temperature by FCVA.¹⁴ It is due to the energetic nature of the plasma and the 100% ionized target material that high-crystal-quality films can be deposited at room temperature. In this paper we report the room temperature ferromagnetism of ZnO:Cu films prepared by FCVA. Si substrate is chosen rather than sapphires as sapphire may induce ferromagnetism.¹⁵ The origin of ferromagnetism in ZnO:Cu films was investigated.

Thin films of ZnO:Cu with a typical thickness of 800 nm were deposited by FCVA on Si at room temperature using a Zn:Cu alloy target of 99.99% purity containing 5 at. % of Cu. The details of the FCVA apparatus have been described elsewhere.¹⁴ The arc was operated in dc mode with a current of 60 A. The chamber base pressure was kept below 1.3×10^{-5} torr and the oxygen flow rate was kept at 60 (cubic centimeter per minute at STP) SCCM. The Cu content in the ZnO:Cu film was determined to be 2.4 at. % by x-ray photoelectron spectroscopy (XPS). Magnetic hysteresis loops of ZnO:Cu films were measured by an alternating gradient magnetometer (AGM) with a maximum field of 6 kOe. The structural properties of ZnO:Cu films were studied by x-ray diffraction (XRD) (Siemen D5005), scanning electron microscope (SEM), and high resolution transmission electron microscope (HRTEM).

Figure 1 shows the magnetization versus magnetic field (M - H) loops for the ZnO:Cu film. The sample shows clear ferromagnetic behavior with a saturation magnetization (M_s) of $0.037\mu_B/\text{Cu}$ atom, by assuming that all the Cu atoms contribute to the magnetization. Although this value is rather modest as compared with $0.1\mu_B/\text{Mn}$ atom of Zn_{0.85}Mn_{0.1}Cu_{0.05}O,¹² it is significant to show that ZnO:Cu on Si does exhibit room temperature ferromagnetism without co-doped with other transition metal elements (such as Fe or Mn) or N₂. Indeed the magnetic moment of our ZnO:Cu film

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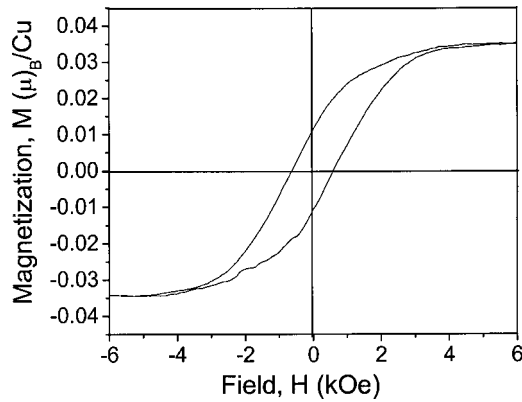


FIG. 1. Magnetization hysteresis curve of the ZnO:Cu at room temperature.

is compatible to the ZnO:Fe ($0.025\mu_B/\text{Fe}$).⁶ The T_c of the ZnO:Cu film is expected to be well above room temperature as the hysteresis loop is reasonably large at room temperature. It is confirmed that no ferromagnetism can be detected from the undoped ZnO sample and Si substrate.

The typical XRD pattern of the polycrystalline undoped ZnO and ZnO:Cu films is shown in Fig. 2. All peaks are perfectly indexed and it is corresponding to a ZnO hexagonal wurtzite structure. No secondary phase and metal-related peak can be detected within the sensitivity of XRD. However, the peak position of ZnO:Cu is shifted by 0.1° – 0.2° toward the left as compared with the undoped ZnO. The peak shift illustrates the incorporation of Cu ion into the ZnO lattice. By calculating the lattice constant of ZnO:Cu films, it is found that the ZnO:Cu film cell parameters of a and c have values of 0.3259 and 0.5242 nm, respectively, which are larger than the undoped ZnO ($a=0.3250$ nm and $c=0.5207$ nm).¹⁶ The cell parameters a and c of the ZnO:Cu film are increased by 0.28% and 0.68%, respectively, as compared with the undoped ZnO. The slight increase in lattice parameter revealed that the ionic size of tetrahedrally coordinated Cu^{2+} is larger than Zn^{2+} . The reason of increment may be due to the nonuniform substitution of Cu ion into the Zn site as the radius of Cu^{2+} ion (radius = 0.057 nm) is smaller than the Zn^{2+} ion (radius = 0.06 nm). A similar observation on the increment of lattice parameter has been found in ZnO:Co where the radius of the Co (0.058 nm) ion is smaller than the Zn ion.¹⁷ The dominant

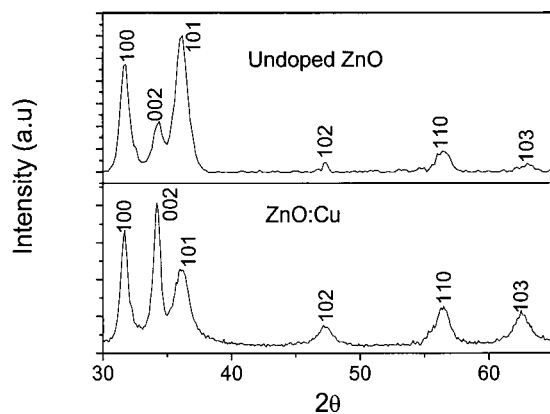


FIG. 2. XRD patterns of the undoped ZnO and ZnO:Cu films.

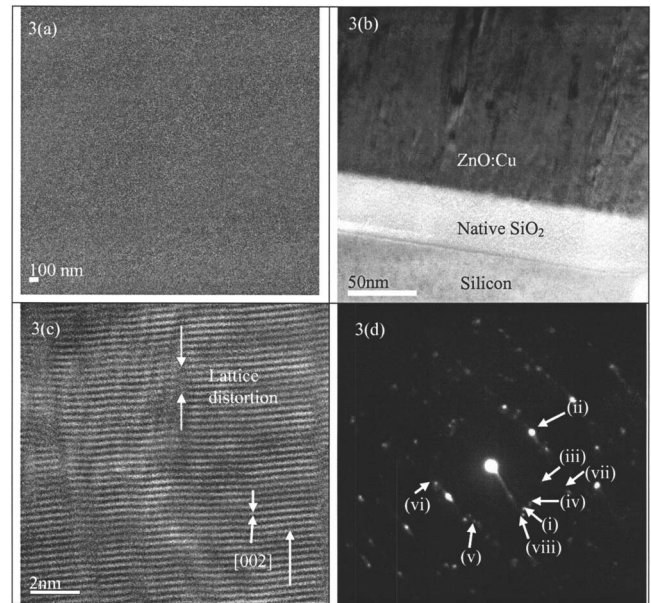


FIG. 3. (a) SEM image of the ZnO:Cu. (b) TEM image at the interface of ZnO:Cu and Si. (c) HRTEM image of the ZnO:Cu showing (002) planes. (d) SAED pattern of the ZnO:Cu. Lattice points (i), (ii), and (iii) represent wurtzite ZnO (0002), (01 $\bar{1}$ 0), and (01 $\bar{1}$ 1), respectively. Lattice points (iv), (v), and (vi) represent cubic Cu_2O (01 $\bar{1}$), (110), and (101), respectively. Lattice points (vii) and (viii) represent monoclinic CuO ($\bar{1}$ 10) and (020), respectively.

peak of (002) in the ZnO:Cu film further illustrates Cu^{2+} and prefers to substitute into Zn sites along the c axis which results in ferromagnetism. According to the theoretical study, Feng¹¹ suggested that ferromagnetism of ZnO:Cu films is only possible to occur if two Cu^{2+} substitute two Zn^{2+} sites in the c plane with a separation distance of 5.2424 Å (lattice constant c) which gives well separation distance at the lowest total energy at room temperature. However, if two Cu^{2+} ions are in the ab plane with a distance of 3.2587 Å (lattice constant a), this will lead to an antiferromagnetic state.

The detailed morphology and microstructure of the ZnO:Cu films were investigated using SEM and HRTEM as shown in Fig. 3. The surface of ZnO:Cu is very smooth and no Cu clustering is found as shown in Fig. 3(a). A polycrystalline ZnO:Cu structure is clearly seen in Fig. 3(b). Besides, there is a thin layer of native oxide (~ 35 nm) underneath the ZnO:Cu. The interface between the native oxide and ZnO:Cu is sharp and smooth. It appears that ferromagnetism is not due to interface distortion or impurity at the interface, but intrinsically from Cu^{2+} substitution to Zn^{2+} sites.¹⁸ However, the selected area electron diffraction (SAED) pattern of the ZnO:Cu reveals secondary phases other than ZnO as indicated in Fig. 3(d). The SAED not only can be indexed as ZnO wurtzite structure but also indicates the presence of secondary phases such as monoclinic CuO and cubic Cu_2O .¹⁹ However, Cu_2O (Ref. 8) and CuO (Ref. 13) are antiferromagnetic even down to 10 K which indicates that the observed room temperature ferromagnetism in ZnO:Cu cannot be due to the secondary phases of Cu_2O and CuO. It is very likely that the observed ferromagnetism in ZnO:Cu is due to the intrinsic magnetic moment of Cu^{2+} in ZnO:Cu. The interplanar distance of fringes is 0.26 nm which is correspond-

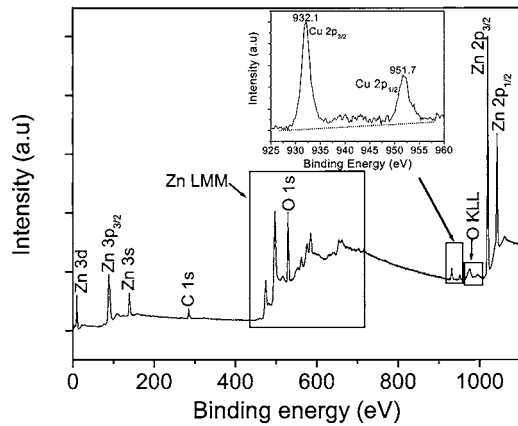


FIG. 4. XPS spectrum of the ZnO:Cu film. Inset: Cu $2p$ core level spectrum.

ing to the (002) planes of wurtzite ZnO as shown in Fig. 3(c). This is in good agreement with the XRD result as (002) plane is dominant in the ZnO:Cu films. Lattice distortion can also be observed in Fig. 3(c). This is primarily due to the lattice constant mismatch between the host material (ZnO) and secondary phases as they have different crystal structures. This phenomenon further illustrates the existence of the Cu element in the ZnO lattice which results to the ferromagnetism in ZnO. It is due to the presence of Cu-related secondary phases that the actual saturation magnetization should be much higher than the estimated $0.037\mu_B/\text{Cu}$ atom as determined earlier.

Concerning the presence of ZnO:Cu ferromagnetism that might be caused by foreign impurity contamination, XPS spectra of ZnO:Cu films were studied. All the indexed peaks are corresponding to C, Cu, O, and Zn as shown in Fig. 4; no other transition metal ions other than Cu can be detected implying that the ferromagnetism of ZnO:Cu is not induced by other foreign impurities. The peaks at 931.2 and 951.7 eV (Fig. 4 inset) were corrected with the C_{1s} reference (284.8 eV), which is corresponding to the binding energy of $\text{Cu}_{2p}^{3/2}$ and $\text{Cu}_{2p}^{1/2}$, respectively. The presence of Cu^{2+} satellite structure around 9.8 eV above the main peak of ZnO:Cu reveals the existence of CuO phase.²⁰ The presence of anti-ferromagnetic CuO may be attributed to limited Cu solubility in ZnO. The results are in good agreement with HRTEM data as shown in Fig. 3.

The presence of Cu ions is expected to influence the electrical properties of ZnO. The electron concentration of the ZnO:Cu film was greatly reduced by four orders of magnitude; the electron concentration reduced from 10^{19} cm^{-3} (undoped ZnO) to 10^{15} cm^{-3} . The resistivities of ZnO and ZnO:Cu were 5.35×10^{-3} and $2.36 \times 10^3\Omega\text{ cm}$, respectively.

It is due to the low carrier concentration of our ZnO:Cu carrier-mediated exchange¹ is unlikely responsible for the observed ferromagnetism. Kaspar *et al.*²¹ reported that structural defects could be associated with ferromagnetism in Cr-doped TiO_2 . We speculate that the observed ferromagnetism in our ZnO:Cu may also be related to structural defects as the samples grown at room temperature are defective as compared with the films grown at elevated temperature. Experimental work is in progress to clarify the type of structural defects in ZnO:Cu which may be responsible for the ferromagnetism.

In conclusion, we have demonstrated room temperature ferromagnetism in ZnO:Cu films prepared by FCVA at room temperature. The ferromagnetism is primary associated with the substitution of Cu^{2+} into Zn^{2+} sites. The presence of Cu in ZnO induces the p - d hybridization between $3d$ of Cu and ZnO valence bands (O - p bands), which leads to a magnetic moment. Furthermore, the well separation of Cu-Cu ions in the c axis of ZnO structure could also contribute to the observed ferromagnetism.

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