

# Magnetic Properties of Cu Nanoclusters Embedded in ZnO Thin Films

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**Cu nonmagnetic metallic nanoclusters were embedded in the ZnO thin film by using nanocluster beam deposition. No presence of secondary phase was detected in X-ray diffraction (XRD) analysis, but secondary phases CuO and Cu<sub>2</sub>O nanoclusters were detected in films by transmission electron microscopy (TEM). Cu nanoclusters embedded in ZnO films have the average particle size around 8–10 nm. Cu atoms were surrounded by ZnO matrix, and the interface effect caused overlapping of p-orbital from O contributed by ZnO and d-orbital contributed by Cu as suggested by XPS and UV-Vis absorbance results. Alternating gradient field magnetometer (AGM) results show that the embedment of nonmagnetic Cu nanoclusters in ferromagnetic ZnO thin films can enhance the room temperature ferromagnetism of ZnO thin film up to maximum  $M_s = 2.64$  emu/cc with small coercivities lower than 70 Oe. The saturation magnetization ( $M_s$ ) value increases with Cu volume fraction in ZnO and decreases with Cu volume fraction after certain volume fractions of Cu were achieved. Based on the clues given by XPS results, +1 valence state of Cu is in the ferromagnetism favorable state, indicating possible spin polarization occurred and ferromagnetism induced in the system.**

*Index Terms*—Copper nanoclusters, magnetic films, magnetic semiconductors, zinc oxide.

## I. INTRODUCTION

**R**ECENTLY, diluted magnetic semiconductors oxide (DMSO) has drawn intensive attention due to the prospects of integrating intrinsic magnetic and electronic functionalities into a single material for the application of spintronics. Among the semiconductor matrices, ZnO is of particular interest because it holds the possibility of a DMSO with a Curie temperature above the room temperature [1]. ZnO doped with various transition metals such as Mn, Co, Cr, Ni, V, or Fe were reported to show ferromagnetism at room temperature [2], [3]. There still exists a debate on whether the magnetic behavior is an intrinsic property of thin film or due to the presence of nanoclusters of magnetic phase or both due to the difficulty of the microstructure characterization in large scale. In order to exclude the contribution of ferromagnetic nanoclusters, Cu-doped ZnO thin films were investigated since neither metallic Cu nor Cu<sub>2</sub>O or CuO in the bulk is ferromagnetic. Room-temperature ferromagnetism of ZnO:Cu films was found by many researchers [4]–[7]. Various mechanisms of the origin of ferromagnetism in ZnO:Cu films such as free-carrier and defects mediated mechanism, bound magnetic polarons model, indirect double-exchange model, etc. [6]–[9], were proposed to interpret their wide range of experimental observations. However, nanometer-sized CuO nanoparticles have been reported to show ferromagnetic behavior as size was below 10 nm [10]. Especially, planar nanoscale CuO inclusions in Cu-doped ZnO films were found by HRTEM, which was considered as the origin of ferromagnetism [11]. Due to the difficulty in the observation of the small amount of CuO nanometer-scale inclusions/precipitate, the debate on the origin of ferromagnetism of ZnO:Cu films either from the Cu ions substituted in Zn cation sites or some Cu/CuO nanoclusters

or both still exists. In this paper, we deliberately fabricate Cu nanoclusters-embedded ZnO and SiO<sub>2</sub> films by combination of nanocluster beam deposition technique and radio frequency (RF)—magnetron sputtering. The ferromagnetism and microstructure of Cu nanoclusters-embedded ZnO films were investigated. Since the nanoclusters were softly landed on the ZnO films and it was unlikely to cause the large-scale diffusion of Cu atoms into the ZnO lattice during deposition, the effects of Cu substitution with Zn can be neglected, and only nanocluster effects on ferromagnetism can be investigated.

## II. EXPERIMENT

Cu-embedded ZnO was prepared by combining nanocluster beam deposition and RF sputtering. ZnO thin films were deposited on the glass substrate by RF sputtering prior to the embedment of Cu nanoclusters, while Cu nanoclusters were formed by gas-aggregation technique. The details of this nanocluster deposition technique were described in our previous report [12]. After the Cu nanoclusters were softly landed on the surface of 50-nm ZnO thin film, another 50-nm cover-layer ZnO was deposited on top of the nanoclusters to completely surround Cu nanoclusters within ZnO thin films. The nanocluster deposition time was tuned between 2–200 s to produce volume fraction of Cu in ZnO from 0.1 vol.% to 10 vol.%. Another three sets of samples that are comprised of Cu-embedded ZnO and Cu and Cu-oxides-embedded SiO<sub>2</sub> multilayer with Cu nanoclusters volume fraction ranging from 0.4 vol.% to 10 vol.% were fabricated for comparison of hybridization effect between nanoclusters and matrixes. Notice that the volume fraction was calculated based on the deposition rate of nanocluster assembly film. Since the nanocluster assembly films were very porous, the actual volume fraction should be less than those stated in the present work. The structures and the chemical state of Cu-embedded ZnO thin film were studied using X-ray diffraction (XRD), transmission electron microscopy (TEM), and X-ray photoelectron spectroscopy (XPS), respectively. Room temperature magnetic properties were examined by an alternating gradient field magnetometer (AGM). Optical

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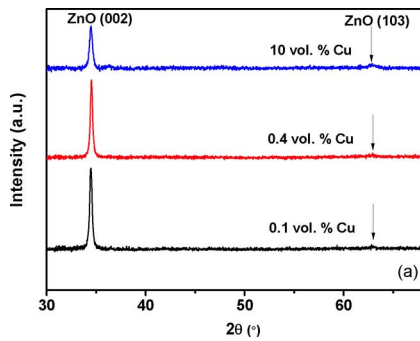


Fig. 1. (a) XRD patterns of the pure Cu nanoclusters, pure ZnO, and Cu-embedded ZnO films.

properties of the films were probed by UV-Vis spectroscopy and photoluminescence (PL).

### III. RESULTS AND DISCUSSION

Fig. 1(a) shows the XRD patterns of Cu nanoclusters-embedded ZnO films with different volume fractions of Cu nanoclusters. It was found that the ZnO (002) peak intensity decreased with the increase of Cu nanoclusters volume fractions in ZnO, and ZnO (103) diffraction peak became more observable. This may be explained that the increase of porous Cu nanoclusters in the ZnO caused the interruption of ZnO (002) grain growth in film normal direction and promoted the growth of grains with other orientation. In addition, it is worth noting that the lattice constant  $c$  of pure ZnO film was larger than  $c$  value of bulk ZnO (5.205 Å). Upon insertion of Cu nanoclusters in ZnO film, the lattice constant  $c$  was sharply decreased to 5.200 Å and then decreased slightly with further increase of the Cu contents. Since the Cu nanoclusters were softly landed on ZnO, the change in lattice constant due to Cu substitution of Zn can be ruled out. The larger lattice constant in the sputtered ZnO films than the value of bulk were attributed to the tensile stress in the film [13], [14]. The addition of Cu nanoclusters in ZnO thin film resulted in the relief of the stress and thus caused the decrease of the lattice constant  $c$ .

The plan-view TEM image of Cu nanoclusters softly landed on carbon covered with Cu grid is showed in Fig. 2(a). The Cu nanoclusters were randomly distributed on the Cu grid surface with particle size ranging from 6 to 12 nm. High-resolution TEM (HRTEM) image [Fig. 2(b)] revealed Cu nanoclusters were crystallized with hexagonal or icosahedra shape. When the Cu nanoclusters were embedded in ZnO films, it was found that the Cu nanoclusters existed in pure Cu and oxidized Cu form such as  $\text{Cu}_2\text{O}$  and  $\text{CuO}$  phase, which were proved by the selected area diffraction and HRTEM as shown in Fig. 2(c).

In UV-Vis absorption spectrum, as-grown ZnO had absorption edge at 370 nm and the corresponding band gap 3.35 eV determined from wavelength  $\lambda_{1/2}$  based on Meulenkamp's method [15]. As the nanoclusters volume fraction increases, the absorption edge showed a redshift. The band-gap reduced to 3.31 eV at 0.1 vol.% Cu and further reduced to minimum band-gap 3.30 eV at 0.4 vol.% Cu. The band-gap remained constant with further increase of the Cu content. The changes in band-gap with Cu nanoclusters were consistent with the change

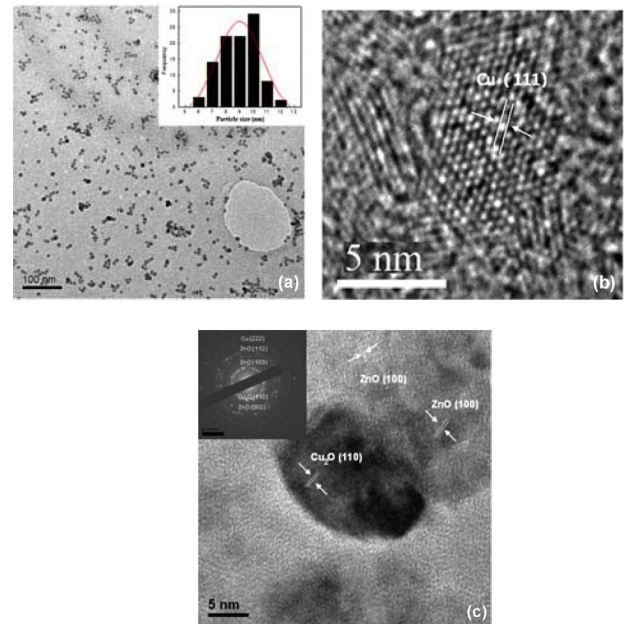


Fig. 2. (a) Plan-view TEM image of Cu nanoclusters deposited on carbon grid with sputtering time 30 s. (b) HRTEM image shows lattice fringes of Cu nanoclusters that have facet in (111) plane. (c) HRTEM image of Cu nanoclusters in as-deposited Cu-embedded ZnO.

of lattice constant. It has been reported that the relaxation of compressed lattice led to the formation of narrower band-gap (redshift) due to decrease of repulsion between the oxygen 2p and the zinc 4s bands [16]. This further confirmed that the decrease of lattice constant of ZnO thin films with the addition of Cu nanoclusters was due to the release of the stress.

AGM measurement was carefully conducted on Cu-embedded ZnO thin film deposited on the glass substrate to investigate ferromagnetism of the Cu nanoclusters-embedded ZnO films. Field-dependent magnetization curves of ZnO film, Cu nanoclusters assembled film, and ZnO embedded with different contents of Cu nanoclusters are shown in Fig. 3(a). Both the magnetization curves of pure ZnO film and Cu nanoclusters assembled film showed anhysteresis behavior. However, both films revealed a small magnetization. For pure ZnO film, its saturated magnetization is about 0.49 emu/cc. Since the ZnO film was deposited by RF sputtering without feeding oxygen at room temperature, some defects such as oxygen vacancies, etc., existed in films. These defects might be the origin of the weak magnetization of ZnO film [17]. A weak magnetization of about 0.5 emu/cc was also observed in Cu nanoclusters assembled film. Since the Cu nanoclusters assembled film was porous, real magnetization should be larger than this value. The nanoclusters are very reactive due to large surface-to-volume ratio, and the oxidations of Cu nanoclusters were observed. The uncompensation of surface spin  $\text{Cu}^{2+}$  might be attributed to the weak magnetization of surface oxidized Cu nanoclusters assembled film [10]. Cu oxide nanoclusters assembled fabricated by feeding oxygen when nanoclusters were softly landed on the substrate showed increased magnetization as shown in Fig. 3(b). After the Cu nanoclusters were embedded in ZnO thin film, the total magnetization values were increased, and small coercivities were observed in the hysteresis loops, which

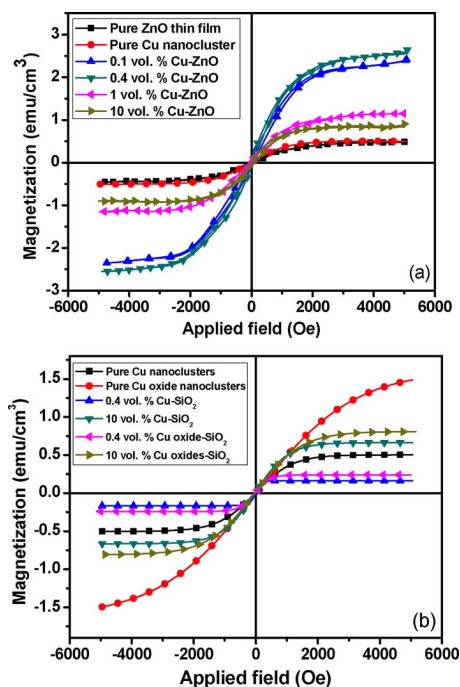


Fig. 3. (a) Field-dependent magnetization curve of pure ZnO, pure Cu nanoclusters assembled films, and Cu-embedded ZnO films deposited at various Cu volume fractions. (b) Field-dependent magnetization curve of pure Cu and pure Cu-oxide nanoclusters assembled films and Cu and Cu-oxide nanoclusters-embedded  $\text{SiO}_2$  films deposited at various Cu volume fractions.

indicated these films were ferromagnetic at room temperature. The film with 0.4 vol.% Cu showed maximum magnetization. With the increase of Cu nanoclusters content, the magnetization decreased toward that of Cu nanoclusters assembled films. These may be associated with the microstructure change of the films. With the increase of their volume fraction, the Cu nanoclusters become closer to each other and finally formed a continuous layer of Cu nanoclusters in the ZnO films. Based on the above results, it can be deduced that the room-temperature ferromagnetism and increase of magnetization were not due to the intrinsic properties of ZnO film and Cu nanoclusters, but may be originated from the reaction between Cu nanoclusters with ZnO matrix.

In order to clarify the effect of ZnO matrix, various volume fractions of Cu nanoclusters were embedded in  $\text{SiO}_2$  matrix where the films fabrication procedure were same as that of Cu nanoclusters-embedded ZnO films. The field dependent magnetization curves of Cu-embedded  $\text{SiO}_2$  and Cu-oxides-embedded  $\text{SiO}_2$  films with various volume fractions are shown in Fig. 3(b). It was indeed observed that Cu oxidation can slightly increase the magnetization. However, all samples showed anhysteretic behavior. Therefore, the local environment of Cu nanoclusters played an important role in the room temperature ferromagnetism of Cu nanoclusters-embedded ZnO films. It was reported that the p-d hybridization effect between O 2p orbital in ZnO and Cu 3d orbital was possible mechanism for the induced ferromagnetism in the Cu-ZnO system due to their close energy level [18]–[21].

In order to investigate the interaction between ZnO matrix-Cu nanoclusters, the chemical state of the Cu in ZnO thin

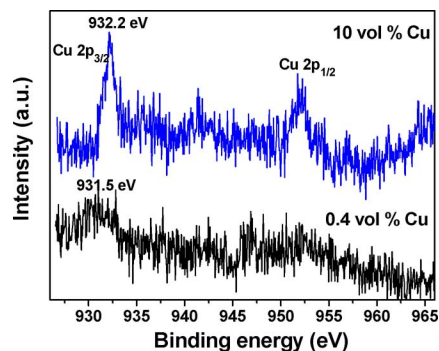


Fig. 4. Cu 2p XPS spectra of Cu-embedded ZnO thin film with various nanocluster concentrations.

films was examined by XPS spectra. Based on survey scan and Cu 2p spectra, there is no evidence that indicates the Zn-Cu bonding existed in the samples. Cu 2p spectra of 0.4 vol.% Cu and 10 vol.% Cu in ZnO matrix are shown in Fig. 4. In 0.4 vol.% Cu nanoclusters-embedded ZnO film, Cu 2p  $_{3/2}$  peak was detected at 931.5 eV corresponding to existence of  $\text{Cu}^+$  [22]. After the volume fraction of Cu nanoclusters was increased to 10 vol.%, the Cu 2p  $_{3/2}$  peak shifted to higher oxidation state at 932.2 eV to become  $\text{Cu}^{(1+x)+}$  where  $0 < x < 1$ . The Zn 2p $_{3/2}$  peak in pure ZnO thin film is located at 1020.84 eV. Its binding energy decreased to 1020.6 eV after Cu was embedded in ZnO with volume fraction 0.4 vol.%, and the binding energy remained at same position even though volume fraction increased to 10 vol.%. For O 1s peak, O 1s in as-grown ZnO had binding energy 529.7 eV and decreased to 529.5 eV after 0.4 vol.% Cu were embedded in ZnO. When the Cu nanoclusters content increased to 10 vol.%, O 1s peak was maintained at the same position. Zn 2p, Cu 2p, and O 1s XPS spectra suggest that there were charge transfers between Cu nanoclusters and the neighboring atoms once Cu nanoclusters were embedded in ZnO. The interface effect was induced between the surface atoms of nanoclusters and the ZnO where the Cu nanoclusters impurities energy levels were accommodated within ZnO surface bands [23].

The presence of defects in the samples can be detected in photoluminescence spectra of pure ZnO thin film and Cu-embedded ZnO films with nanoclusters volume fraction 0.4 vol.%, 1 vol.%, and 10 vol.%, as shown in Fig. 5. As-grown ZnO thin film has UV emission centered at 390 nm, which is attributed to near band-edge transition. The position of UV emission redshift as the Cu nanoclusters concentration is increased, indicating narrowing of the band-gap of matrix ZnO, which is matched with UV-Vis absorption results. The full width at half-maximum (FWHM) of UV emission peak increased with the increment of Cu nanoclusters volume fraction. This is due to the decrease of crystallinity [24] with increasing porous nanoclusters content inside ZnO, as evidenced by XRD patterns shown in Fig. 1. When the Cu was embedded in ZnO in very low concentration  $< 0.4$  vol.%, the valence state of Cu is between 0 and +1, and no green luminescence was detected at PL spectra. However, when 0.4 vol.% Cu volume fraction was achieved, Cu valence state becomes +1, and a weak green luminescence emission was detected at 588 nm, which is attributed to the presence

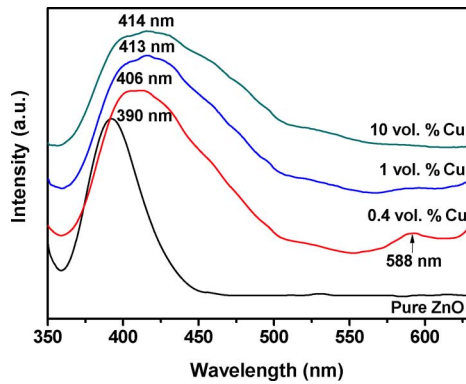


Fig. 5. PL spectra of pure ZnO and Cu-embedded ZnO films.

of oxygen vacancies [25]. Consequently, electron donated by Cu will compensate the defects such as oxygen vacancies whose presence was proved by photoluminescence spectra, and the resulting compensated charged oxygen vacancies will be in a more ferromagnetic energetically favorable state. The roles of electrons, oxygen vacancies, and Cu ions in enhancing the ferromagnetism of the Cu-ZnO system can be explained by the “indirect double-exchange” mechanism [9].

#### IV. CONCLUSION

Cu nanoclusters were softly landed and embedded in ZnO thin film by using nanocluster beam deposition and RF sputtering. The secondary phases  $\text{Cu}_2\text{O}$  and CuO were detected by using HRTEM and SADP analysis. However, AGM measurement showed anhysteresis loops of pure Cu nanoclusters, Cu-oxides nanoclusters, and pure ZnO thin film, ruling out the possibility of intrinsic ferromagnetism. The as-grown Cu-embedded ZnO thin films can exhibit room-temperature ferromagnetism due to the interface effect between nanoclusters and the matrix. The oxidation of Cu species and reduction of Zn and O species were detected in XPS spectra. These results suggest that nanoclusters-matrix charge transfer and the existence of defects as indicated in PL spectra could lead to possible interaction between defects and the Cu species and hence created favorable ferromagnetism environment for the Cu-embedded ZnO films.

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