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Hole-mediated ferromagnetic enhancement and stability in Cu-doped ZnOS alloy thin films

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Abstract
We report room temperature ferromagnetism enhancement of Cu-doped ZnOS ($Zn_{1-x}Cu_xO_{1-y}S_y$) alloy thin films with high hole concentration. The $Zn_{0.91}Cu_{0.09}O_{0.92}S_{0.08}$ alloy thin films with a hole concentration of 4.3×10^{19} cm^{-3} show the strongest magnetization of 1.5μ_B/Cu. First-principles calculation shows that high hole concentration stabilizes the ferromagnetic ordering in the $Zn_{1-x}Cu_xO_{1-y}S_y$ system, indicating a strong correlation between ferromagnetic stability and hole concentration. These results suggest that the $Zn_{1-x}Cu_xO_{1-y}S_y$ alloy with high hole concentration is promising to find applications in spintronic devices.

(Some figures may appear in colour only in the online journal)

Semiconductor devices now, such as Si, GaAs or GaN, widely make use of not only the charge and mass of electrons (or holes), but also the electron (or hole) spin. It is because most of the semiconductors used for devices are very weakly paramagnetic or antiferromagnetic, which makes further enhancement of the performance of devices using both charge and spin of electrons very difficult. Recently, the possibility of incorporating magnetic degree of freedom into semiconductor devices has attracted great interest for spintronics and its applications. Diluted magnetic semiconductors (DMSs) are predicted to provide a promising approach to achieving high spin-injection efficiency [1–3]. Since Dietl [4] predicted that Mn-doped p-type GaN and ZnO can realize room temperature ferromagnetism (RTF), a great deal of research has been carried out on ferromagnetism of transition metals (TMs) having d shell electron structure, such as Mn-, Cr-, Ni-, Co-, Fe- or Cu-doped GaN and ZnO and the RTF was actually discovered in ZnO-based DMS [5–10]. However, the origin of ferromagnetism is still controversial [11, 12]. Even Yi *et al* found that Li-doped ZnO also shows RTF [13]. The origin of RTF in DMS becomes more ambiguous and imperative to understand. The precipitates or clusters of the doping magnetic elements make the mechanism of ferromagnetism in DMS confused. In these metals, Cu and related compounds are nonmagnetic. Therefore, Cu doping can avoid such problems. Recently, both theoretical and experimental studies of many research groups revealed that Cu-doped ZnO shows RTF properties [11, 12, 14–16]. The prepared Cu-doped ZnO has always shown poor electronic conductivity so far, and hence cannot meet requirements to combine with the optical and electrical properties of ZnO for device applications. Although p-type ZnMnO is expected to have a high Curie temperature (T_C), it is still difficult to prepare p-type ZnO reproducibly due to low acceptor solubility and high acceptor ionization energy [17, 18]. In our previous work, p-type $Zn_{1-x}Cu_xO_{1-y}S_y$ alloy films with high hole concentration were obtained [19]. The

Table 1. Cu and S content and electric properties of Cu-doped ZnOS alloy thin films.

Sample	S content	Cu content	Working gases O_2/Ar	Resistivity (Ω cm)	Carrier conc. (cm^{-3})	Type
S1	0	0.03	0	286	1.7×10^{16}	Unstable p
S2	0.13	0.05	1/80	1224	4.0×10^{15}	n
S3	0.08	0.09	1/80	0.3	4.3×10^{19}	p

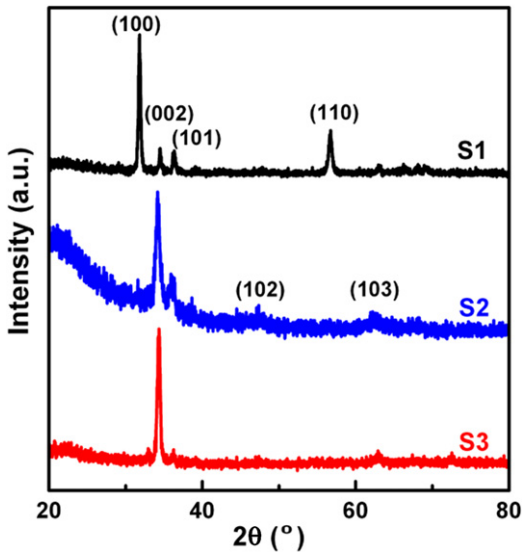

Figure 1. XRD patterns of Cu and S codoped $Zn_{1-x}Cu_xO_{1-y}S_y$ alloy thin films.

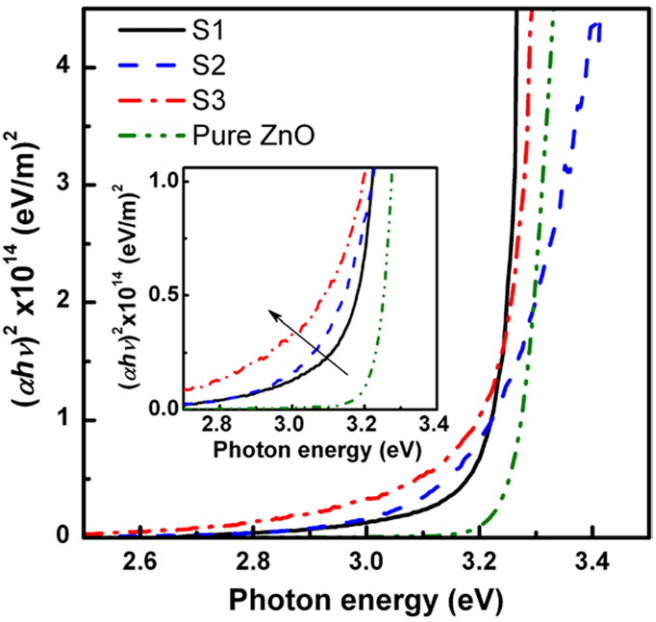

Figure 2. RT optical absorption spectra of pure ZnO and Cu-doped ZnOS thin films. The inset shows an enlarged absorption edge in the band tail region.

conductivity type and carrier concentration of the CuZnOS alloy films can be modulated by changing the content of the Cu and S, which helps us to further investigate the mechanism of RTF in Cu-doped ZnO-based DMSs.

In this work, we have investigated enhancement and stability of RTF in Cu-doped ZnOS alloys with high hole concentration by experiment and first-principles method. A strong correlation was found between enhancement and stability of ferromagnetism and hole concentration.

Cu-doped ZnOS alloy thin films ($Zn_{1-x}Cu_xO_{1-y}S_y$) were grown on quartz substrates by the radio-frequency (rf) magnetron sputtering technique, using Ar and O_2 as working gases. The chamber pressure was fixed at 0.5 Pa, and the growth temperature was 573–773 K. All the as-grown films were highly insulating. To improve the quality of the films, they were annealed for 15 min at temperatures between 873 and 973 K in vacuum. The Cu and S contents in these films are determined by energy-dispersive x-ray spectroscopy (EDX), as shown in table 1. The samples are denoted as S1, S2 and S3 for $Zn_{0.97}Cu_{0.03}O$, $Zn_{0.95}Cu_{0.05}O_{0.87}S_{0.13}$ and $Zn_{0.91}Cu_{0.09}O_{0.92}S_{0.08}$, respectively. X-ray diffraction (XRD), absorption spectrum, Hall effects and superconducting quantum interference device (SQUID) were used to characterize the structural, optical, electric and magnetic properties of the thin films. In the SQUID measurement, the diamagnetic background of the substrates was carefully calibrated and subtracted from the raw data.

XRD measurement shows that all samples in this work have single hexagonal structure, as shown in figure 1, and no other phases are found, such as Cu, Cu_2O or CuO. The electrical properties of the thin films are listed in table 1. The Cu-doped ZnO thin film (S1) shows unstable p-type conductivity, with a low hole concentration of 1.7×10^{16} cm^{-3} and high resistivity of 286 Ω cm. Such poor conductivity is due to Cu doping with a deep acceptor level, and the acceptors may be from univalent Cu on the sublattice of zinc site [20]. Samples S2 and S3 show n- and p-type conductivity with low electron concentration of 4.0×10^{15} cm^{-3} and high hole concentration of 4.3×10^{19} cm^{-3}, respectively. The origin of the high hole concentration in the $Zn_{1-x}Cu_xO_{1-y}S_y$ alloy film is discussed in detail in our previous work [19]. Figure 2 shows the absorption spectrum of all samples. For comparison, the absorption spectrum of an undoped ZnO film is also shown in figure 2. According to the relationship between absorption coefficient α and photon energy $h\omega$, we calculated the band gap of S1 (3.26 eV), slightly smaller than undoped ZnO (3.28 eV) due to Cu doping. As S concentration increases to 0.08, the band gap decreases to 3.20 eV. The reduction in the band gap is attributed to the increase in the level of the valence-band maximum (VBM) as S is alloyed into ZnO [21]. Thus, high hole concentration of S3 can be explained well by the fact that the acceptor ionization energy decreases as the VBM level increases. In addition, the intensity of the band tail increases as the S concentration increases, as shown in the inset of figure 2, indicating that the band tail state is related to the alloying of S and Cu with ZnO.

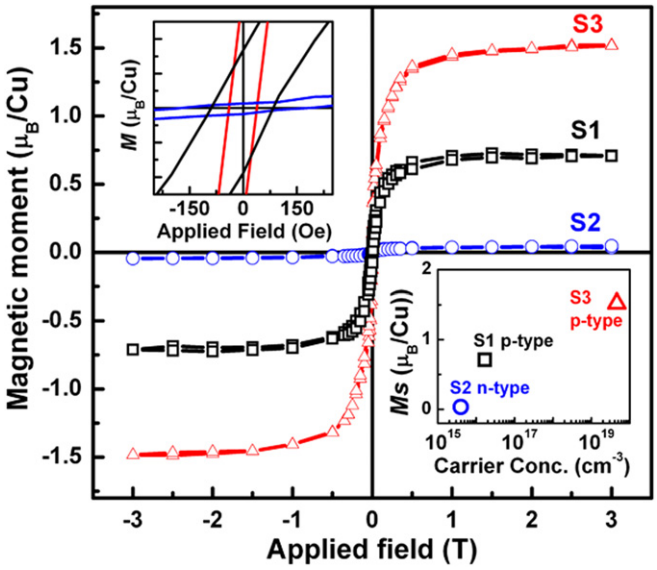

Figure 3. M–H curves of Cu-doped ZnO and ZnOS alloy thin films. The upper left and lower right insets show the enlarged area in the near-zero field and saturation magnetic moment as a function of carrier concentration, respectively.

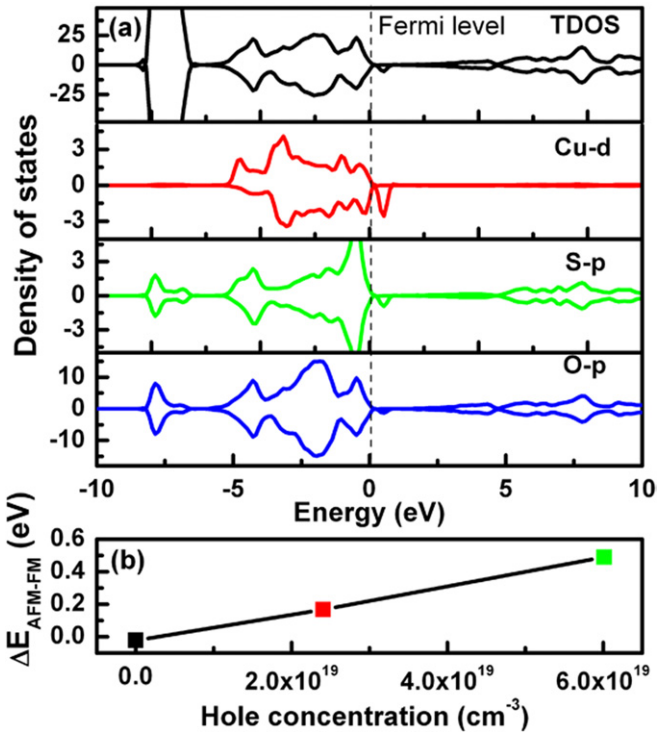

Figure 4. (*a*) Calculated total and partial DOS of the $Zn_{30}Cu_2O_{24}S_8$ system with a hole concentration of 6×10^{19} cm^{-3} and (*b*) energy differences of AFM and FM states for $Zn_{30}Cu_2O_{24}S_8$ systems as a function of hole concentration by first-principles calculation.

SQUID measurements were carried out at 300 K to study the magnetic properties of all the samples. Figure 3 shows the magnetization versus magnetic field parallel to the film surface (M–H) curve. The RTF with a magnetic moment of $0.7\mu_B$/Cu is found in S1, which agrees with the previous reports of RTF in Cu-doped ZnO [14]. For the n-type Cu-doped ZnOS alloy film (S2), a very weak magnetization is observed at 300 K. However, for the p-type Cu-doped ZnOS alloy film (S3), the magnetic moment increases significantly to $1.5\mu_B$/Cu. The lower right inset in figure 3 shows the saturated magnetic moment as a function of carrier concentration, indicating the magnetic moment increases with the increase in hole concentration. The upper left inset in figure 3 shows the enlarged area of M–H curve in the near-zero field. The coercivity is 89 Oe, 167 Oe and 50 Oe for S1, S2 and S3, respectively. The small coercivity indicates the intrinsically soft nature of the samples [14, 16, 22]. The above results help us to have a clear picture of RTF in the Cu-doped ZnOS alloy that the RTF should be hole-mediated and enhanced, which is different from the origin of RTF in the insulating Cu-doped ZnO bulk in our previous work [16]. Tiwari *et al* also observed FM in n-type Cu-doped ZnO films, and revealed that the FM in n-type Cu-doped ZnO will vanish completely when additional electron carriers are increased [15]. Therefore, these results indicate that the T_C of p-type Cu-doped ZnOS is at least above 300 K, and also support the prediction that high-concentration p-type carrier favours RTF in ZnO : Mn-based DMS by Dietl [4, 23].

There is still an important question as to what causes the local magnetic moment in $Zn_{1-x}Cu_xO_{1-y}S_y$ alloy films. To further understand this problem, we carried out first-principles calculation using the frozen-core projector-augmented-wave method within density functional theory (DFT), as implemented in the VASP code [24, 25]. The exchange and correlation effects are treated with GGA + U (U = 7 eV for Zn and 3 eV for Cu) [16, 26]. Two Cu and eight S atoms substitute Zn and O sublattices, respectively, in a 2 × 2 × 2 ZnO supercell containing 64 atoms. All the atoms are allowed to relax until the Hellmann–Feynman forces acting on them became less than 0.01 eV Å^{-1}. To shed light further on the role of hole concentration, additional holes were introduced into the Cu-doped ZnOS system. Figure 4(*a*) shows the calculated spin-resolved total and partial density of states (DOS) of the $Zn_{30}Cu_2O_{24}S_8$ system with a hole concentration of 6×10^{19} cm^{-3}. There is a significant splitting above the VBM with a total magnetic moment of $1.8\mu_B$, which are mainly contributed by the Cu-d (51%), O-p (34%) and S-p (10%) orbitals. Furthermore, the calculated Cu is in the d^9 state, indicating the chemical valence state is Cu^{2+}. Recently, Herng *et al* [27] found from the theoretical and experimental studies that the local magnetic moment originates from Cu^{2+} in ferromagnetic Cu-doped ZnO, consistent with our present calculated result. Therefore, we conclude that the local magnetic moment in the Cu-doped ZnO or ZnOS comes mainly from Cu^{2+} ion.

To further understand the origin of hole-mediated FM, we also calculated the energy difference between AFM and FM states (ΔE_{AFM-FM}) as a function of hole concentration, as shown in figure 4(*b*). As S is induced into ZnCuO systems without additional holes, the system shows an AFM ground state (ΔE_{AFM-FM} = −22 meV). Interestingly, the energy difference significantly increases with the increase in hole concentration and the value increases to 490 meV at a hole concentration of 6×10^{19} cm^{-3}, indicating that high hole concentration benefits more stable FM, supporting our

experimental results. Based on the discussion above, it is suggested that the magnetization in $Zn_{1-x}Cu_xO_{1-y}S_y$ is hole-mediated and enhanced by an increase in hole concentration.

In summary, we have prepared Cu-doped ZnO and ZnOS alloy films on quartz substrates by the radio-frequency magnetron sputtering technique. A significant RTF enhancement is observed for the sample with a high hole concentration of $\sim 10^{19}\,cm^{-3}$, indicating that the magnetization of the Cu-doped ZnOS alloy films originates from hole-mediated ferromagnetic order of the local magnetic moments contributed by Cu^{2+} ions and high hole concentration plays a key role in realizing strong room temperature ferromagnetism.

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