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Ferromagnetism in Cu-doped ZnO nanoparticles at room temperature

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Abstract Cu-doped ZnO nanoparticles were successfully synthesized and structurally characterized by using X-ray diffraction (XRD) and transmission electron microscope (TEM). XRD shows that $Zn_{1-x}Cu_xO$ ($x \leq 0.04$) samples are single phase with the ZnO-like wurtzite structure, while the secondary phase Cu is observed in $Zn_{0.95}Cu_{0.05}O$ sample. Magnetic measurements indicated that $Zn_{1-x}Cu_xO$ ($x = 0.02, 0.03, 0.04$) are ferromagnetic at room temperature and the magnetic moment per Cu atom decreased with increasing Cu concentration. XRD, TEM and X-ray photoelectron spectroscopy (XPS) analysis revealed that no ferromagnetic-related secondary phase was detected. The origin of the ferromagnetism in $Zn_{1-x}Cu_xO$ ($x \leq 0.04$) was mainly due to Cu ions substituted into the ZnO lattice.

1 Introduction

Diluted magnetic semiconductors (DMSs) have provoked intense interest because semiconductor properties can be integrated with magnetic properties to realize the objective of fabrication of spin-based devices. For realizing practical spintronic devices, wide band gap diluted magnetic semiconductor system with large magnetic moments M and with a high Curie temperature T_C have attracted a great deal of attention [1–4]. ZnO with wide band gap has been identified as a promising semiconductor material, exhibiting room temperature ferromagnetism (RTFM) when doped with most of the transition metal elements [5–11].

However, the origins of FM in these results remain controversial and some reports claim that the magnetic signature arises from clustering or impurities while others claim that the magnetic property is intrinsic. Hence, non-magnetic element of Cu is a preferred choice to avoid controversies regarding the ferromagnetic ordering for the secondary phases such as CuO and Cu_2O or clustering are antiferromagnetic which may make the interpretation of ferromagnetism in ZnO:Cu easier [3, 12]. Very recently, some theoretical results indicated that in Cu-doped ZnO (whether n type or p type) the energy of the ferromagnetic state is lower than that of the antiferromagnetic state [13]. And experimental studies have reported RTFM in Cu-doped ZnO [14–16]. However, to date, most of the research on ferromagnetic Cu-doped ZnO focused on thin films and bulk materials. DMSs nanostructures are expected to have a longer coherence time, which may provide a pathway for increasing the spin lifetime for practical spintronics applications [17]. In this paper, Cu-doped ZnO nanoparticles were synthesized by decomposing citrate technique. We studied the structure and magnetic properties of $Zn_{1-x}Cu_xO$ and the origin of room temperature ferromagnetism in $Zn_{1-x}Cu_xO$ ($x \leq 0.04$) was analysed.

2 Experimental

Appropriate proportions of $Zn(NO_3)_2 \cdot 6H_2O$ (99.9%) and $Cu(NO_3)_2 \cdot 3H_2O$ (99.9%) high-purity powders were

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thoroughly mixed according to the desired stoichiometry; the powders were dissolved water to get homogeneous solution. The mixture were mixed into citric acid [$C_6H_8O_7$] (99.5%) while stirring. The solution was dried at 80 °C to obtain xerogel. After the swelled xerogel was completed at 130 °C, a reticular substance was obtained, then grinded to powders in agate mortar. Sintering the powders at 600 °C was carried out under Ar atmosphere for 10 h. The reaction mechanism of decomposing citrate technique was described previously (Ref. [18]). The nitrates were dissolved in the solution of citric acid formed the citric acid complexes of compound ions AB (AB = Zn, Cu), citric acid as a chelator in the reaction. While drying xerogel at 130 °C, chained dehydration reaction occurred between carboxy and hydroxy of citric acid, and the polymer resin was obtained. As heating the polymer resin at 600 °C, target mating material (ABO) was formed.

This method allows mixing of the chemicals at atomic level thus reducing the possibility of undetectable impurity phase. Additional advantages are the good reproducibility and the simple experimental procedure. The structural properties of $Zn_{1-x}Cu_xO$ were studied by XRD on D/max-2,500 copper rotating-anode X-ray diffractometer by using Cu Kα radiation (40 kV, 200 mA), The size distribution and interplanar distance were investigated by TEM (200 keV, JEM–2100HR, Japan). The $Zn_{0.96}Cu_{0.04}O$ was determined by XPS (VG ESCALAB Mark II). Magnetic hysteresis loops of $Zn_{1-x}Cu_xO$ ($x \leq 0.04$) were measured by a Lake Shore 7407 vibrating sample magnetometer with a maximum field of 10 kOe.

3 Results and discussion

The Fig. 1 shows the XRD patterns for $Zn_{1-x}Cu_xO$ (x = 0.02, 0.03, 0.04, 0.05). All peaks correspond to wurtzite structure ZnO with Cu doped concentration up to 4 at%. No trace of copper metal, oxides, or any binary zinc copper phases is observed within the sensitivity of XRD. For $Zn_{1-x}Cu_xO$ ($x \leq 0.04$), with the increase of x, these peaks shift by 0.02°–0.06° towards lower angles. The shift illustrates the incorporation of Cu ion into the ZnO lattice. Calculation shows larger cell parameters of a and c for $Zn_{1-x}Cu_xO$ than the undoped sample. The radius of Cu^{2+} ion (radius = 0.057 nm) is smaller than the Zn^{2+} ion (radius = 0.074 nm). The reason of increment may be due to the nonuniform substitution of Cu ion into the Zn site. A similar observation was also observed in ZnO:Cu films [13]. The $Zn_{0.95}Cu_{0.05}O$ shows segregation of a second phase (Cu as deduced from the X-ray diffraction). This means the doped limit is around 5% in our experiment settings.

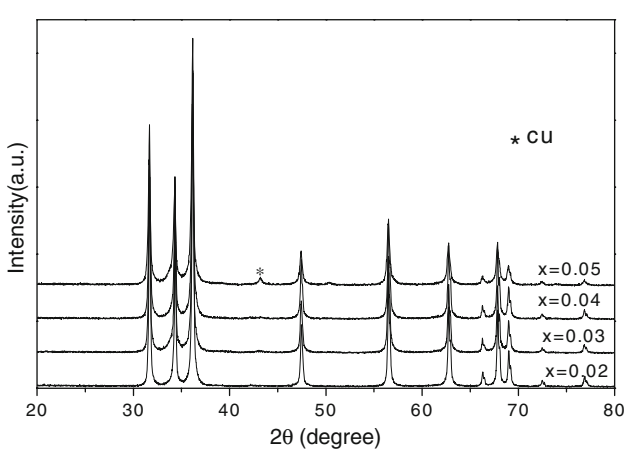

Fig. 1 XRD patterns of the $Zn_{1-x}Cu_xO$ (x=0.02, 0.03, 0.04, 0.05)

The Fig. 2 shows the results of TEM characterization. These nanoparticles have an average diameter of ~50 nm, consistent with the results deduced from XRD. High-resolution TEM micrograph shows that the interplanar distance of fringes is 0.26 nm which is corresponding to the (002) planes of wurtzite ZnO. Both XRD and the high-resolution TEM measurements suggest that most of the Cu atoms have substituted into the ZnO lattice sites.

Magnetic measurements on $Zn_{1-x}Cu_xO$ (x = 0.02, 0.03, 0.04) were performed at room temperature using vibrating sample magnetometer. All the samples show ferromagnetic ordering at room temperature. As the Cu concentration increasing, the magnetic moment per Cu atom decreases markedly (Fig. 3). The 2% Cu sample possesses a net moment of 0.66 μ_B/Cu atom, the 3% Cu sample has a moment of 0.40 μ_B/Cu atom, and the 4% Cu sample has a moment of 0.19 μ_B/Cu atom. The coercive fields (Hc) of the 2%, 3%, and 4% Cu doped are 103, 80, and 73 Oe, respectively. The largest moment observed was 0.66 μ_B/Cu. This value is larger than the experimental value reported by Herng et al. [16] and less than the theoretical value (1.00 μ_B/Cu).The moment per Cu atom can be less due to nanostructured nature of the material, and weaker interparticle exchange is also responsible for the low magnetic moment. The consistent drop in moment per Cu atom of dopant at higher Cu concentration could be an increasing occurrence of anti-ferromagnetic coupling between Cu pairs occurring at shorter separation distances, which has been predicted in earlier theoretical studies [16] Theoretical modeling of the $Zn_{1-x}Cu_xO$ system indicates that the location of the Cu atoms relative to each other can strongly affect the magnetic properties of the system [19–21].

The secondary phase and metal clusters sometimes contributed to the ferromagnetism for ZnO-based diluted magnetic semiconductors [22]. XPS measurement shows Cu $2p3/2$ peak at 932.90 eV and Cu $2p1/2$ peak at 952.76 eV, which corresponds to a mixed oxidation state of +1 or +2 (Fig. 4) In other words, Cu in the system exhibits

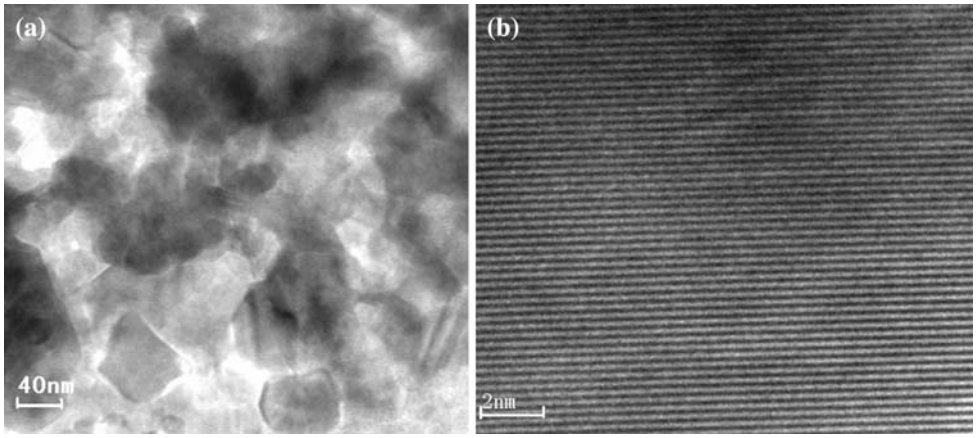

Fig. 2 (**a**) Low-resolution TEM micrograph of $Zn_{0.96}Cu_{0.04}O$ nanoparticles. (**b**) High-resolution TEM micrograph of $Zn_{0.96}Cu_{0.04}O$ nanoparticles

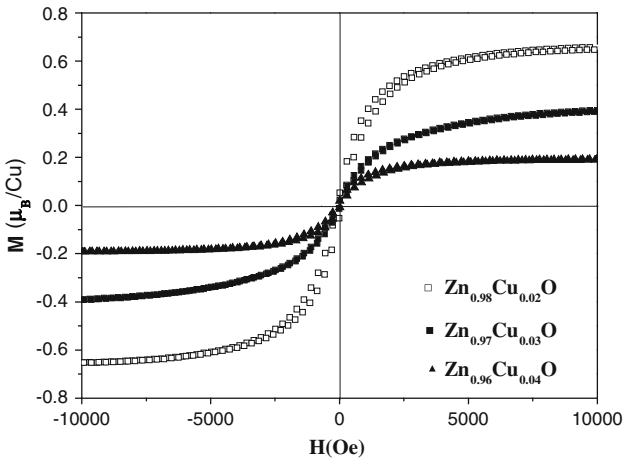

Fig. 3 Magnetization hysteresis curve of $Zn_{1-x}Cu_xO$ (x = 0.02, 0.03, 0.04) at room temperature

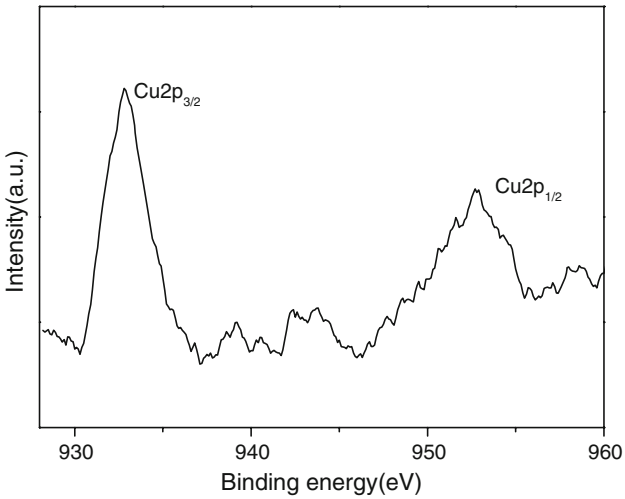

Fig. 4 XPS spectrum of $Zn_{0.96}Cu_{0.04}O$. Peak positions are referenced to the adventitious C1s peak taken to be at 285.1 eV

a mixed valence state of Cu^{1+} and Cu^{2+} rather than zero-valent state of metal clusters or particles. This ease is similar to that observed in the $Zn_{0.9814}Cu_{0.0186}O$ manocrystals which synthesized by solvothermal route [23]. The 3*d* orbitals in Cu^{1+} ($3d^{10}4s^0$) are fully filled and hence do not contribute to ferromagnetism. The existence of CuO phase in the sample is antiferromagnetic [12], and effects ferromagnetism of the sample. The low moment per Cu atom for the 4% Cu sample can also be attributed to the presence of Cu^{2+}. From above analysis, we can conclude that the ferromagnetism in $Zn_{1-x}Cu_xO$ ($x \leq 0.04$) is not from clustering or impurities but expected to be intrinsic. The substitution of Cu ion into Zn sites nonuniformly leads to the ferromagnetism in ZnO.

In conclusion, we have prepared Cu-doped ZnO nanoparticles from zinc nitrate and copper nitrate reduced by citrate with the Cu content up to 5 at%. The results of XRD show that the samples ($x \leq 0.04$) are of single phase with the ZnO-like wurtzite structure, while a secondary phase Cu is observed in $Zn_{0.95}Cu_{0.05}O$ sample. The magnetization data show ferromagnetic ordering at room temperature doped with up to 4% Cu. The analysis shows the origin of room temperature ferromagnetic in $Zn_{1-x}Cu_xO$ ($x \leq 0.04$) is the existence of the Cu element in the ZnO lattice and the Cu ion substitute into Zn sites.

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