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Enhancement of ferromagnetism and stability in Cu-doped ZnO by N_2O annealing

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Abstract

Copper-doped ZnO (ZnO:Cu) films were prepared by the filtered cathodic vacuum arc technique at room temperature on Si substrates. The as-grown ZnO:Cu exhibited a saturated magnetic moment (M_s) of 0.36 μ_B/Cu at room temperature. After an annealing treatment at 500 °C for 1 h under N_2O ambient, the M_s of the ZnO:Cu increased by 100% to 0.73 μ_B/Cu. The ferromagnetism of the annealed samples was relatively stable as compared to the as-grown sample in terms of temperature and storage time. *In situ* x-ray photoelectron spectroscopy of the N_2O annealed sample revealed that N was incorporated into the sample. The presence of N promotes the substitution of high-spin Cu^{2+} ions into Zn^{2+} sites, which leads to the enhanced ferromagnetism in ZnO:Cu. The cyclic annealing experiments of the ZnO:Cu films in air, N_2O and Zn vapor suggested that Zn interstitial defects were crucial to the N incorporation.

1. Introduction

The manipulation of electron charge and spin in diluted magnetic semiconductors (DMSs) has spawned an emerging field of electronics known as 'spintronics' [1]. Copper-doped ZnO (ZnO:Cu) is an unambiguous DMS in which ferromagnetic precipitates can be avoided as it does not contain any magnetic ions; neither in any compound with (Cu, Zn, O) is ferromagnetic [2, 3]. Buchholz *et al* [3] reported that ferromagnetic ZnO:Cu films prepared by pulsed laser deposition (PLD) could only be obtained when N_2O gas was used during deposition. However, it is not clear whether the ferromagnetic samples exhibited p-type

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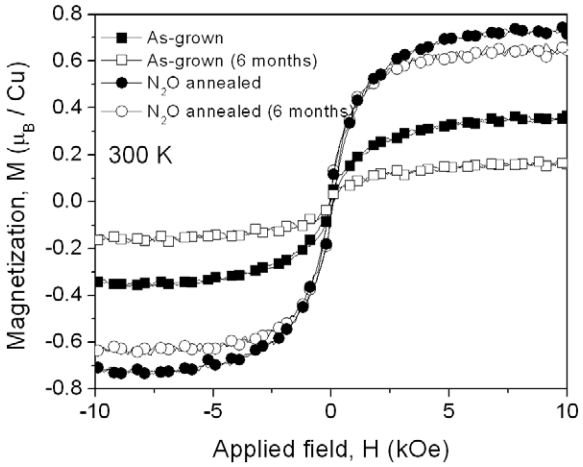

Figure 1. The magnetization curves of the as-grown and N_2O annealed ZnO:Cu films measured immediately and after a storage period of 6 months.

behavior as N_2O is believed to be a p-type dopant source for ZnO [4]. Herng *et al* [5, 6] reported that ferromagnetic ZnO:Cu could be prepared by the filtered cathodic vacuum arc (FCVA) technique using a Zn:Cu alloy target and O_2 gas only. The role of N_2O toward the observed ferromagnetism (FM) in ZnO:Cu is therefore not well understood. In this paper, we present the annealing results of FCVA-deposited ZnO:Cu under N_2O ambient. It is found that the magnetic moment of the N_2O annealed ZnO:Cu films has not only enhanced by more than 100%, but the process has also improved the stability of the FM in the samples significantly.

2. Experiment

ZnO:Cu films were deposited on silicon substrates by the FCVA technique at room temperature (RT). A Zn:Cu alloy target containing 1 at.% of Cu was used. The apparatus for the FCVA technique has been described elsewhere [7]. During the deposition, O_2 was kept at 60 sccm with a dc arc current of 60 A. The Cu content in the as-prepared film was 1.3 at.% as determined by x-ray photoelectron spectroscopy (XPS). The XPS measurements were performed at room temperature with a base pressure of 1×10^{-10} mbar using Al Kα as the x-ray source, which has an energy of 1486.6 eV. The annealing experiment was conducted in a tube furnace with flowing N_2O gas at a pressure of $\sim$0.4 bar with various temperatures for 1 h. The magnetic properties of the ZnO:Cu films were investigated with an alternating gradient magnetometer (AGM) with a maximum field of 10 kOe. To eliminate spurious magnetic data, the ZnO:Cu samples and polymer tweezers used were cleaned with acetone prior to magnetic measurement. The applied magnetic field was parallel to the surface of the sample. The structural properties of the ZnO:Cu films were studied by x-ray diffraction (XRD), and with a scanning electron microscope (SEM), high-resolution transmission electron microscope (HRTEM) and selective area electron diffraction (SAED).

3. Results and discussion

Figure 1 shows the magnetization curves of the as-grown ZnO:Cu films. The ZnO:Cu film demonstrated FM at room temperature with a saturated magnetic moment (M_s) of 0.36 μ_B/Cu

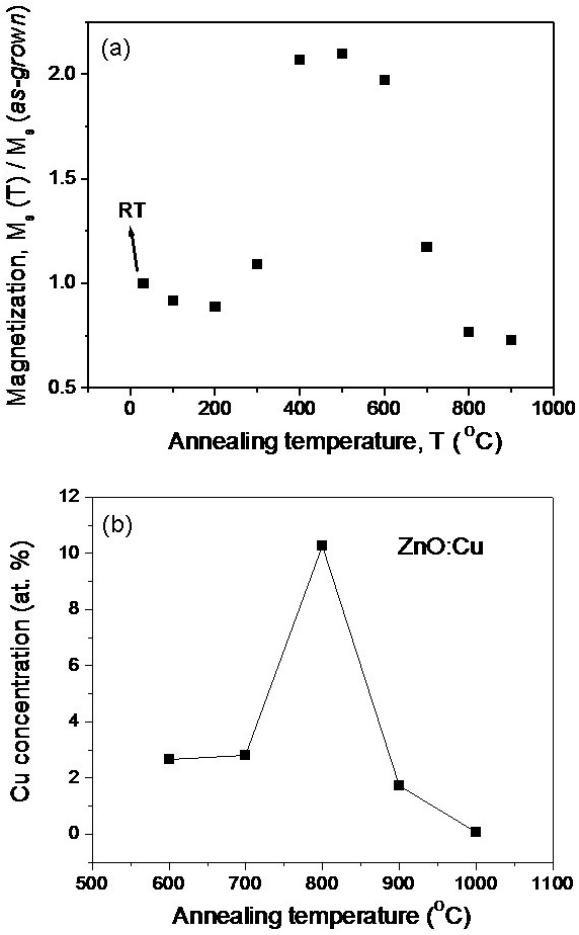

Figure 2. (a) The normalized saturated magnetic moment ($M_n = [M_s(T)/M_s$ (as-grown)]) of ZnO:Cu films annealed at temperatures ranging from RT to 900 °C. (b) The Cu concentration (at.%) as a function of annealed temperature from 600 to 900 °C.

and coercivity (H_c) of 81 Oe. The value of M_s of the as-grown ZnO:Cu film is comparable to that of PLD-deposited ZnO:Cu with N_2O gas [3]. Our work clearly shows that N is not necessary for the observation of FM in ZnO:Cu. In order to study the effect of N_2O on the FM in ZnO:Cu, a series of ZnO:Cu films was annealed in N_2O ambient at temperatures ranging from 100 to 900 °C. Surprisingly, the M_s of the annealed ZnO:Cu were enhanced by more than 100% in the temperature range 400–600 °C, as shown in figure 2(a). The M_s of the annealed samples at various temperatures are normalized by the corresponding as-grown samples, where $M_n = M_s(T)/M_s$ (as-grown). When the annealing temperature increases gradually to 200 °C, M_n is less than 1. The M_n increases rapidly to above 2 when the annealing temperature increases from 300 to 600 °C. Beyond 600 °C, the M_n decreases drastically and is even less than 1 at 900 °C. Since the decomposition temperature of N_2O is above 260 °C [4], the degradation of M_s at a temperature below 300 °C should not be related to N_2O. Indeed the degradation of FM can also be observed from samples annealed in air or N_2 ambient at temperature above 100 °C. The reduction of FM could be related to defect-mediated FM, which will be discussed later. The M_s of the ZnO:Cu increases substantially when annealed at

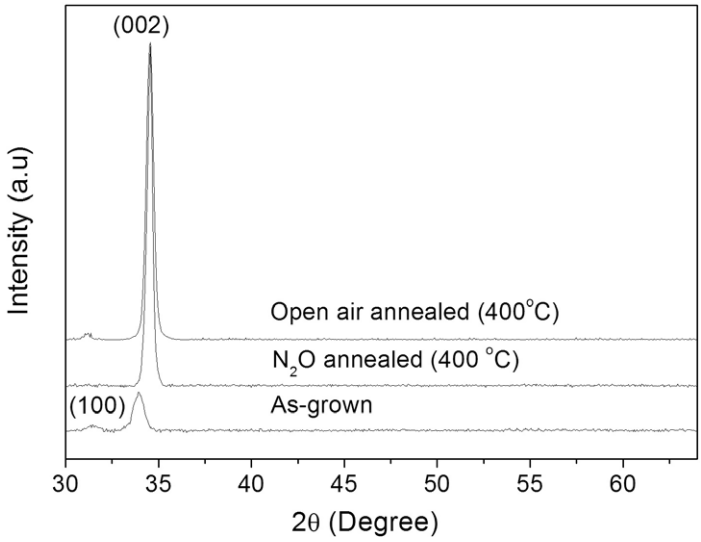

Figure 3. XRD spectra of the as-grown, open-air and N_2O annealed ZnO:Cu.

temperatures between 400 and 600 °C. The enhancement of FM in the ZnO:Cu films should be related to the N_2O annealing. When the annealing temperature reaches 700 °C, the M_s reduces drastically. This observation could be attributed to the out-diffusion of Cu to the surface at temperature above 700 °C. From the XPS analysis shown in figure 2(b), the Cu content in the ZnO:Cu is increased substantially from 1.3 to 10 at.% when the annealing temperatures increase from room temperature to 800 °C. This suggests that the Cu is out-diffusing into the subsurface layers, resulting in the reduction of Cu in the film. As a result of a decrease in Cu^{2+} concentration, this leads to weakening of magnetic ordering. The sample became paramagnetic after annealing at 1000 °C. This is because most Cu has escaped from the surface of the film, since no Cu can be detected by XPS. This is an indication that Cu is essential for the observed FM.

XRD spectra of the as-grown, open-air and N_2O annealed ZnO:Cu films at 400 °C are shown in figure 3. All the diffraction peaks correspond to the ZnO wurtzite structure with predominately *c*-axis (002) texture. The annealed ZnO:Cu films exhibited stronger XRD peak intensity and narrower peak width as compared to the as-prepared samples, indicating the annealing improved the crystallinity of the samples. There is no structural variation between open-air and N_2O annealed samples. Thus the enhancement of FM could not be due to the improved crystal structure of ZnO:Cu as the FM degraded once the sample was annealed in open air.

The surface morphology and microstructure of the as-grown and N_2O annealed ZnO:Cu films were investigated using an SEM and an HRTEM. Figures 4(a)–(c) show the SEM images of the as-grown, 400 °C and 900 °C N_2O annealed ZnO:Cu films, respectively. The as-grown sample exhibits smooth surface; however, the grain structure became apparent when the samples were annealed at 400 and 900 °C. The grain size is about 50 nm and 200 nm for the 400 °C and 900 °C annealed samples, respectively. This is consistent with the XRD results, as shown in figure 3, that the crystallinity of the samples improved with annealing temperature. Figure 4(d) reveals the HRTEM image of the ZnO:Cu annealed at 400 °C in N_2O ambient with its interplanar distance of 0.26 nm corresponding to the ZnO wurtzite structure. SAED patterns of the as-grown, 400 °C and 900 °C N_2O annealed samples are shown in figures 4(e)–(g),

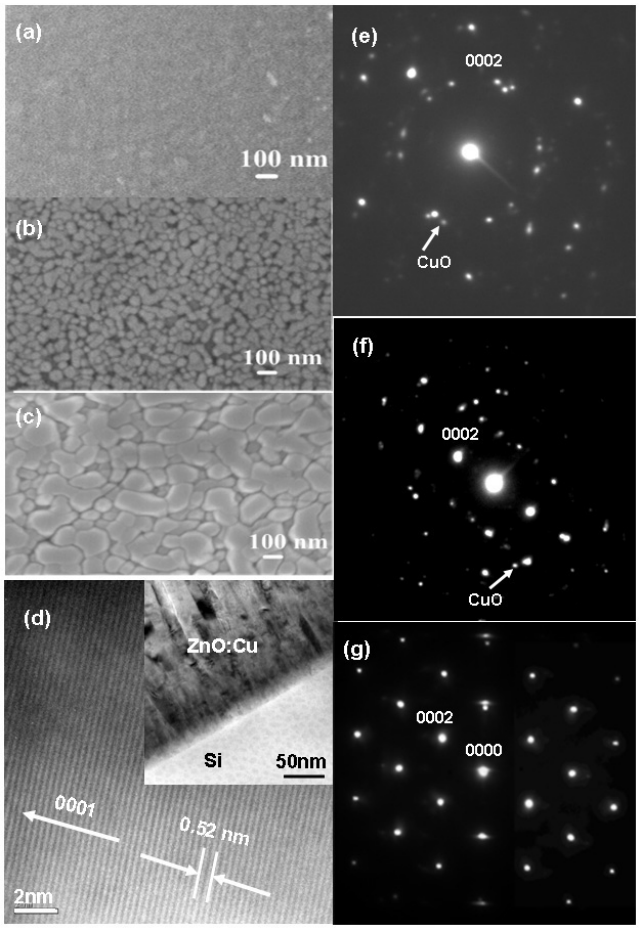

Figure 4. SEM images of (a) as-grown, (b) 400 °C and (c) 900 °C annealed ZnO:Cu films. (d) HRTEM image of ZnO:Cu film annealed at 400 °C in N_2O ambient; the inset shows the cross-sectional image of the sample at the interface. SAED patterns of (e) as-grown, (f) 400 °C and (g) 900 °C annealed ZnO:Cu films.

respectively. CuO-related diffraction spots could be found in the as-grown and 400 °C annealed samples only but no CuO spot was observed from the sample annealed at 900 °C, as shown in figure 4(g). The disappearance of CuO might be attributed to the out-diffusion of Cu under elevated temperature. As is evident from the XPS result (figure 2(b)), Cu could leave the surface of the ZnO:Cu at around 900 °C; thus no CuO can be found. It should be noted that there is no obvious difference between the surface morphology and microstructure of the samples annealed in air or N_2O ambient.

Concerning the homogeneity and interface distortion of the film, cross-sectional high-resolution transmission electron microscopy was performed in the ZnO:Cu sample annealed at 400 °C under N_2O ambient. The interface between the ZnO:Cu and Si substrate is sharp and smooth, as shown in the inset of figure 4(d). No Cu cluster can be observed in the HRTEM image. It appears that the ferromagnetism is not due to interface distortion or impurity at the interface [8]. In order to verify the ferromagnetism in the ZnO:Cu is a bulk effect rather than surface/interface effect, ZnO:Cu films were grown at identical conditions with various

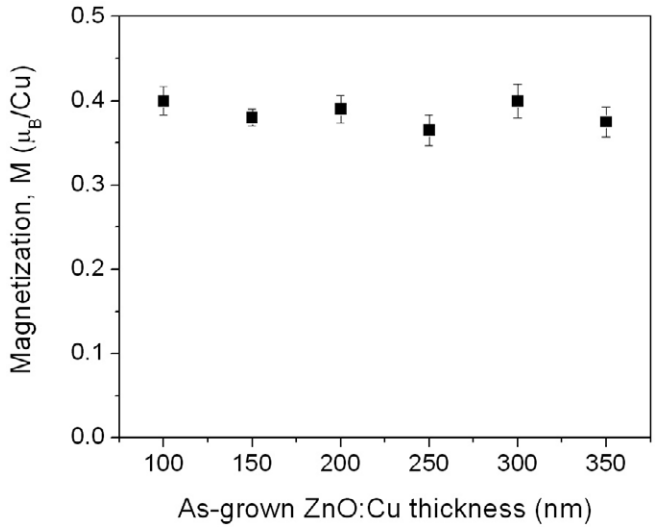

Figure 5. Saturated magnetic moment of the as-grown ZnO:Cu as a function of film thickness.

thickness ranging from 100 to 350 nm. As shown in figure 5, the M_s is almost constant at $\sim$0.38 $\pm$ 0.02 μ_B/Cu for various thicknesses, reflecting that the ferromagnetism is not due to interface distortion or surface/interface magnetization. This result also suggests that the ZnO:Cu samples are homogeneous, with Cu ions uniformly distributed in the film.

In order to investigate the role of N_2O or N in the enhancement of FM, *in-situ* XPS measurements were carried out on the ZnO:Cu. The as-prepared ZnO:Cu sample was first scanned by the x-ray photoelectron spectroscope. The sample was then annealed at 400 °C in the XPS analysis chamber for 1 h in N_2O ambient. The XPS scan was performed at room temperature after the N_2O annealing process. The XPS full scan revealed core level peaks that correspond to C, Cu, O, N and Zn, with no other impurity being detected. The annealed sample exhibited a similar M_s value to that of the sample annealed in the tube furnace. The incorporation of Cu and N in the N_2O annealed sample is clearly revealed by the core level spectra of Cu 2p and N 1s as shown in figures 6(a) and (b), respectively. The Cu $2p_{3/2}$ peak appears at 933.65 eV, which can be observed from both as-grown and N_2O annealed samples, indicating a divalent state of Cu [9, 10]. Chakraborti *et al* reported that the Cu $2p_{3/2}$ peak could also be an indication of Cu^{2+} ions substituted into ZnO lattice sites [2]. A weak N 1s peak can only be observed from the N_2O annealed sample. The N 1s band consists of two components, as depicted in figure 6(b). The peaks at 399.3 and 401.45 eV can be attributed to the Zn–N and N–O bond respectively [11–13]. These indicate that N is incorporated in the ZnO:Cu after N_2O annealing. The incorporation of N in the ZnO:Cu may also relate to the enhancement of FM.

It has been reported that the Zn interstitial (Zn_i) defect plays a significant role in the FM in ZnO:Co [14, 15]. The FM of ZnO:Co can be enhanced after exposing it in a Zn vapor at elevated temperature. Our ZnO:Cu samples also exhibited similar behavior after being exposed to Zn vapor. In order to study the interplay between Zn_i and N in the ZnO:Cu, the as-grown ZnO:Cu samples, denoted sample A and B, were subjected to a series of annealings in various ambient (i.e. open air, N_2O or Zn vapor) at 420 °C for an hour. An annealing temperature of 420 °C was chosen because it is the minimum temperature required to generate a Zn vapor, and the magnetic response of the sample is considerably large. The M_s of sample A increases substantially to $\sim$0.73 μ_B/Cu after the first N_2O annealing as shown in figure 7. The subsequent annealing

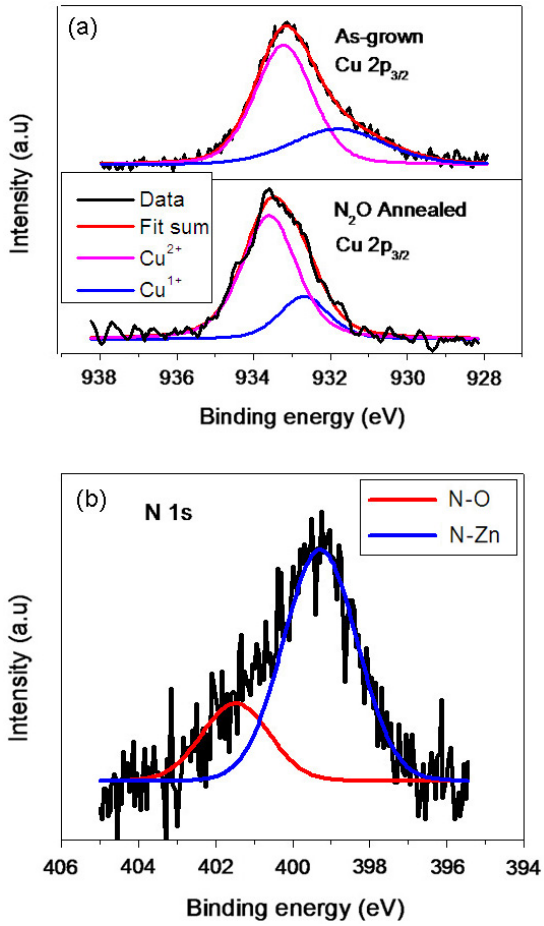

Figure 6. (a) XPS spectra of Cu 2p for as-grown and N_2O annealed ZnO:Cu film. (b) XPS spectrum of N 1s core level for the N_2O annealed ZnO:Cu film.

(This figure is in colour only in the electronic version)

cycles in air and N_2O do not have significant effect on the M_s (reduced by ∼6%). Besides the enhancement of FM, the stability of M_s with temperature seems to improve after the N_2O annealing. For sample B, the M_s reduces by ∼15% to 0.30 μ_B/Cu after open-air annealing (number 1), which is attributed to the reduction of Zn_i at elevated temperature. Surprisingly, there is no magnetic ordering improvement as compared to sample A after the subsequent N_2O annealing (number 2). However, the M_s increases to 0.35 μ_B/Cu, which is close to that of the as-grown sample after exposure to the Zn vapor (number 3). The result corroborates with the recent experimental [14] study that Zn_i is associated with FM ordering. The M_s increases further to 0.47 μ_B/Cu with the subsequent N_2O annealing (number 4). These intriguing results seem to suggest that there must be a relationship between Zn_i and N. According to first-principles total-energy calculations by Yan *et al* [16], N from the N_2O source could be incorporated spontaneously and controllably into ZnO if the sample is in the Zn-rich condition. In contrast, N is unlikely to be incorporated into ZnO under O-rich condition. This may explain why FM can only be enhanced in ZnO:Cu with the presence of Zn_i and N. Zn_i will lead to

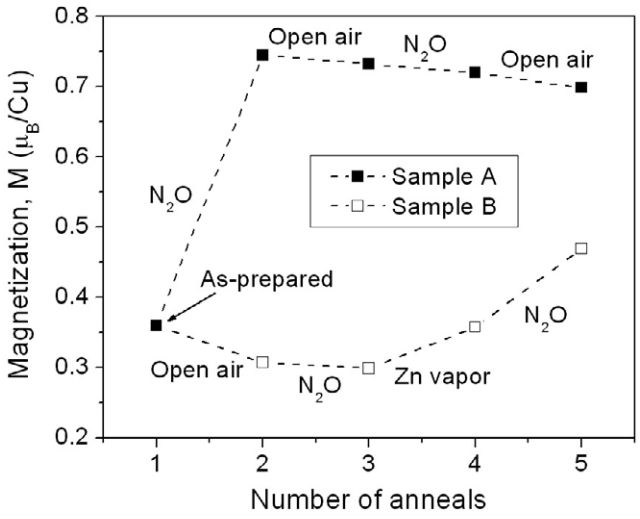

Figure 7. Variation of M_s for ZnO:Cu films in different annealing sequences. Sample A: N_2O → open air → N_2O → open air. Sample B: open air → N_2O → Zn vapor → N_2O.

instability of FM in ZnO:Cu, but it is also crucial and essential to the FM enhancement with incorporation of N. To further examine the magnetic stability of the N_2O annealed sample, the M_s of the N_2O treated and untreated samples were measured again after a storage period of 6 months. As shown in figure 1, the M_s of the N_2O treated and untreated samples after 6 months have reduced by ∼11% (0.65 μ_B/Cu) and ∼55% (0.16 μ_B/Cu) respectively as compared to their initial values. Our results show that N plays a vital role in enhancing the FM and improving the stability of ZnO:Cu.

Having obtained a clear picture that the presence of Zn_i favors N incorporation into the ZnO:Cu, we now turn to investigate the correlation between N and Cu. As shown in figure 6(a), the ratio of Cu^{2+}/Cu^{1+} (area under the curve) for the as-grown and N_2O annealed samples are 2.32 and 3.18, respectively. This indicates that the high-spin state of the Cu^{2+} component has indeed increased upon N_2O annealing. The introduction of the N element increases the substitutional Cu^{2+} concentration, resulting in the enhancement of crystal-field splitting of the 3d states into t_{2g} and e_g states. However, the moment per Cu atom is less than the theoretical value of 1 μ_B/Cu [17, 18]. This may be due to the existence of a magnetic 'silent' state of $Cu^{1+}(3d^{10}4s^0)$ in the films as its 3d orbitals are fully filled, thus not contributing to the magnetic moment. The evidence of N–Zn bonds in the N_2O annealed ZnO:Cu as shown in figure 6(b) suggested that N stabilizes Zn_i states through N–Zn bonding, which improved the magnetic stability in term of storage time and temperature. The high resistivity of ZnO:Cu led us to envisage that its magnetism is related to the bound magnetic polarons mechanism [19, 20]. However, further research is needed to understand the exact role of N and its underlying mechanism for the enhancement of FM.

4. Conclusion

In summary, we have demonstrated the magnetic and stability enhancement in ZnO:Cu through N_2O annealing. The presence of Zn_i is essential for the FM enhancement and it is a prerequisite for the incorporation of N. The incorporation of N increases the substitution of the high-spin Cu^{2+} ions into Zn^{2+} sites and stabilizes the highly diffusive Zn_i through N–Zn bonding.

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