

# White Light Emission of ZnO-Cu Nano-Films

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**Abstract** The ZnO films were prepared by reactive rf-magnetron sputtering on silicon and sapphire substrates. For Cu-doping of the ZnO films, the close space sublimation method (CSS) was used at atmospheric pressure in air. After CSS processing, the ZnO and ZnO-Cu films were annealed in a wet media. The reference ZnO-Cu films, obtained from ZnO-Cu target by electron-beam evaporation (EBE) were treated at the same conditions. The microstructure and optical properties of the samples were compared and studied by atomic force microscopy (AFM), X-ray diffraction (XRD), photoluminescence (PL) and cathodoluminescence (CL) spectra. XRD results indicated that all the ZnO films have a polycrystalline hexagonal structure. The surface and crystal quality of ZnO thin film was improved when doped with Cu. The shape of the spectrum depends on the method of doping. Spectrum of the reference ZnO-Cu films has green band only. Spectrum of ZnO-Cu films consists of three emission bands at doping by CSS. The first band is in a blue region with a maximum at 465 nm. The second and third bands are in the green and orange regions with maximum at 520 and 580-600 nm, respectively. The green band is the most intensive. As a consequence, the emission looks like white light. Origin of observed emission bands is discussed.

**Keywords** Thin Films, ZnO, Cu, Close Space Sublimation, XRD, AFM, Photoluminescence, Cathodoluminescence

## 1. Introduction

Zinc oxide is a promising material for a variety of practical applications as a transparent conductive electrode, heterojunction laser diode, ultraviolet (UV) laser, luminescent material, etc. [1]. ZnO is a wide and direct band gap semiconductor (3.37 eV) whose room temperature photoluminescence (PL) is of the greatest importance. The ZnO has various luminescent transitions as different preparation techniques lead to varying structures and surface

properties in ZnO. Generally, ZnO exhibits two kinds of emissions: one is excitonic ultraviolet (UV) at 370-380 nm and the other is visible (VS) emission with a peak at 510-530 nm [2]. Many studies have attempted to improve the properties of ZnO by doping with transition metals such as aluminium [3], manganese [4], indium [5], and copper (Cu) [6-8]. Among them, Cu is mostly a preferable dopant due to follow: the Cu<sup>2+</sup> has similar with Zn<sup>2+</sup> (0.074 nm) ionic radii 0.073 nm [9] and relatively easy replace zinc in the lattice forming complex with neighbor oxygen ions. The Cu can interact with intrinsic defects of ZnO resulting in formation of different defect complex which effect optical transitions in ZnO. It was found that this allows changing of the emission color from green to white [10]. Cu-doped ZnO has shown an essential improvement on electrical, optical, magnetic and luminescence performance [11]. Different techniques are used to grow ZnO-Cu films such as pulsed laser deposition [12], magnetron sputtering [13], metal-organic chemical vapor deposition under atmospheric pressure [14]. The Cu can be added to ZnO films during the growth process [7, 8, 10, 14] or copper impurity can be introduced into already deposited ZnO film [15, 16] by different techniques. In this paper the isothermal close space sublimation (CSS) process [17] has been used for doping ZnO films by Cu under atmospheric pressure. Deposited ZnO-Cu films were heated in humid air. Beneficial effect of water vapor on growth of ZnO crystals and on structural properties of ZnO films is well known for a long time [18, 19, 20]. This method represents favorable condition at appropriate temperature for the impurity to be effectively introduced into ZnO film. The present work was aimed to investigate the effect of Cu doping by CSS technique on structure and luminescent properties of ZnO thin films.

## 2. Materials and Methods

ZnO films (approximately 0.5 μm) were deposited by radio frequency magnetron sputtering of Zn target in vacuum

chamber on silicon and sapphire substrates. The ZnO films were deposited at substrate temperature  $T_s = 150^\circ\text{C}$ . The 10 nm of  $\text{SiN}_x$  buffer layer was introduced to accommodate lattice mismatch between ZnO and Si. The mismatch of lattice constants (15%) and thermal expansion coefficients (56%) between ZnO and Si are quite large.  $\text{SiN}_x$  has a relatively small lattice mismatch (5%) and thermal expansion coefficient. The deposition of films was carried out by layer-by-layer method that was detailed in [13].

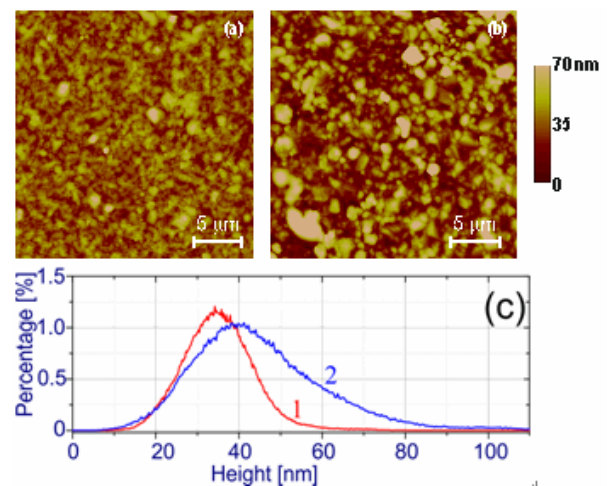
The Cu doping of ZnO films was performed by CSS processes at atmospheric pressure during 1 hour. Copper block was used as Cu source and  $\text{ZnO/SiN}_x/\text{Si}$  and  $\text{ZnO/a-Al}_2\text{O}_3$  films were used as a substrate. The Cu source and the substrate were separated by a ceramic spacer with thickness of 1 mm. The Cu was introduced in the ZnO by condensation of their vapor on the film surface in the furnace at the temperature  $500\text{-}600^\circ\text{C}$ . The doping method is based on the process of the impurity diffusion through the surface of the film under heating. This method allows correlating the concentration of the doping elements by changing the temperature in the furnace. We have found that noticeable changes of luminescence spectra start at the temperature higher  $500^\circ\text{C}$ . The doping temperature varied within  $500\text{-}700^\circ\text{C}$ . The Cu vapor pressure was within  $10^{-9}\text{-}10^{-4}$  Pa [21]. We used three doping levels. The low level of doping corresponds to  $1.33 \times 10^{-9}$  Pa. The mediate level of doping corresponds to  $1.33 \times 10^{-7}$  Pa. The high level of doping corresponds to  $7 \times 10^{-5}$  Pa. After the CSS processing ZnO-Cu films were annealed at the temperature  $600^\circ\text{C}$  in wet media during 1 hour (a density of water vapors was about  $0.08\text{ g/m}^3$ ). Beside the ZnO-Cu films the ZnO reference films were treated at the same conditions in order to separate the effects of the temperature annealing on the properties of films.

The ZnO-Cu films were deposited by EBE from ZnO-Cu target onto sapphire substrates. The Cu concentration in the target was from 0.06 to 0.25wt%. The substrate was heated to  $150^\circ\text{C}$  and the film thickness was  $0.6\ \mu\text{m}$ . ZnO:Cu films were annealed at the temperature  $600^\circ\text{C}$  in wet media during 1 hour (a density of water vapors was about  $0.08\text{ g/m}^3$ ).

X-ray diffraction measurements (XRD) were performed by DRON-3M X-ray diffractometer operated with  $\text{CuK}_\alpha$  irradiation ( $\lambda = 0.1541\text{ nm}$ ). The morphological properties of films studied by NanoScope IIIa Dimension 3000 atomic force microscope. To provide high lateral resolution and sensitivity the tapping mode of measurements was applied. Measurements performed using commercial NSG-11 Si probes with the nominal tip apex radius of 10 nm (NT-MDT, Russia). Photoluminescence (PL) emission was excited by a He-Cd laser ( $\lambda_{\text{exc}} = 325\text{ nm}$ , power 25 mW). The PL spectra were recorded with the use of a Horiba JobinYvon T64000 spectrometer. The cathodoluminescence (CL) signal was detected using an Oxford Instruments MonoCL2 system in Philips XL30 SEM at the electron energy in the beam of 15 keV. The spectra were measured at room temperature.

### 3. Results and Discussions

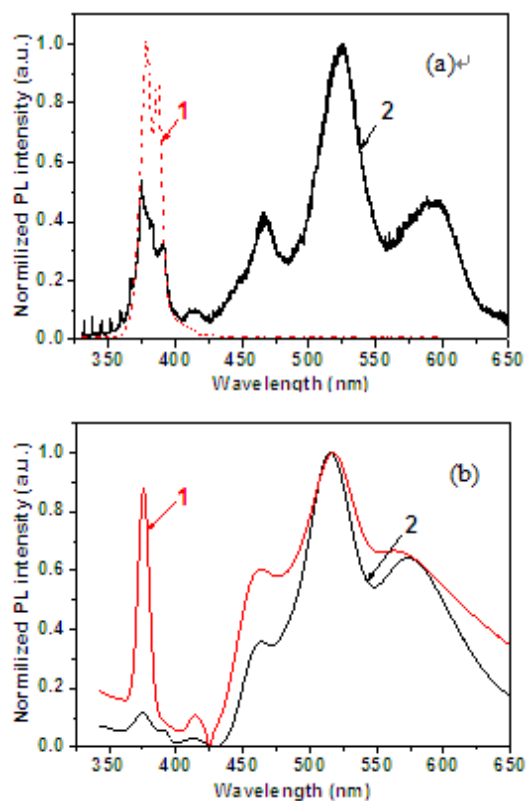
XRD measurements showed that all ZnO films have a polycrystalline hexagonal structure. The films consist of grains with a strong preferred (002) orientation. Doping by a small amount of copper does not change the texture of the ZnO film. The surface morphology modification caused by doping process was investigated by AFM since an introduction of the Cu impurity by CSS methods is based on the diffusion of Cu ions into the films through the grains or grain boundaries. Figure 1 illustrates the effect of doping on morphology of film surface at the mediate level of doping. The surface of reference ZnO film (Fig.1,a) shows complex nano-granular structure. The smallest grains (diameters of 15-20nm) aggregated into elongated clusters (typically  $360 \times 60\text{ nm}$ ). Clusters are randomly oriented and separated with depressions of the 10-15 nm in depth. Surface morphology transforms drastically at the Cu doping (Fig. 1b). Many elongated clusters transforms into faceted pyramidal grains. The size of their long axis ranged within 300 - 450 nm. The size of a small fraction of grains increased up to the 60 -120nm. Depth of the depressions between grains enlarged to the 25 -50 nm. From statistical point of view, the surface transformation at doping could be illustrated with height histograms. Height distributions for ZnO (curve 1) and ZnO-Cu (curve 2) films are shown in Fig. 1c. Significant widening of the surface height takes place for doped films. Corresponding RMS values are equal to the 9 and 17nm for initial and Cu-doped films.



**Figure1.** AFM images of ZnO reference (a) and Cu-doped (b) ZnO films deposited on Si substrate. Surface height histograms (c) for the corresponding films (curves 1, 2).

The PL properties of ZnO films depend on the substrate temperature at film deposition and Cu doping level. For the ZnO films deposited at the low temperature of substrate ( $T_s = 150^\circ\text{C}$ ), the luminescence was not observed, which is related to the low crystal perfection of the films and a high concentration of nonradiative recombination centers in them [22]. Such films were selected specially in order the annealing-doping effect marked greatly. Emission becomes

observable after doping and annealing of the films. The normalized PL spectra of the ZnO-Cu films on Si substrate at low, mediate and high levels of doping are shown in Figures 2a and 2b as well as the reference one (Figure 2a, curve 1). The PL spectrum of each film was normalized to the maximal value of the intensity in it. The spectra were normalized in order to present them in one figure because the PL intensities for the films are significantly different.

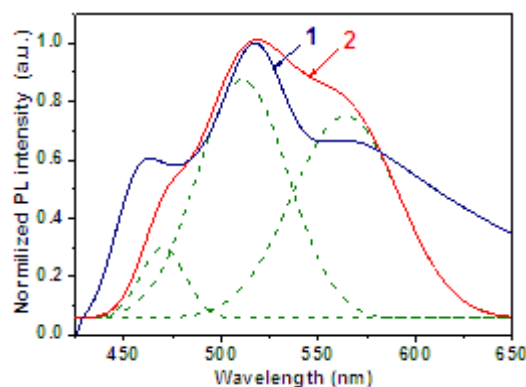


**Figure 2.** PL spectra of ZnO films with different concentrations of Cu: a) 1- the reference ZnO film, 2- the mediate concentration of Cu, b) 1- the minimum and- 2 the maximum of Cu concentrations

After hydrothermal annealing at 600°C, an intense UV emission of ZnO films is appeared. The luminescence spectrum of ZnO film has a narrow peak of UV luminescence at 375 nm with an approximate half-width of 15 nm and the absence of VS emission (Figure 2a, curve 1). The significant difference is observed between doped (Figure 2a, curve 2) and the reference films spectra (Figure 2a, curve 1). After doping with Cu, the suppression of UV component is observed and an intense visible spectra (VS) emission is appeared. It is correlated with other author's results [15, 23]. The degree of suppression of the UV band is determined by the Cu concentration. The UV band is suppressed for 10 times at high Cu concentration (Figure 2b, curve 2). The fine structure of the UV emission band is observed at mediate Cu concentration (Figure 2a, curve 2). The energy separation between adjacent peaks is about of 72 meV. This value matches well with the longitudinal optical (LO) phonon energy in ZnO. As a rule, phonon replicas have low intensity compared with the intensity of the UV bands. Thus, in the PL spectra, as a rule, only one to three

longitudinal optical phonon features can be distinguished. We observed 6 phonon replicas. In fact, as a rule, such a structure is observed in the emission of single crystals at low temperature  $\sim 77$  K [24]. The presence of the phonon structure at ambient temperature suggests that the crystal structure of the films is of high quality. Phonon properties of our ZnO-Cu films with mediate copper concentrations were investigated using the method of Raman scattering [25]. In the Raman spectra of the films authors observed from 6 to 8 phonon repetitions, similar to the bulk ZnO crystal. The presented results also clearly show that ZnO films obtained by the technique applied here possess rather perfect crystal structure which is really close to that of bulk ZnO single crystals [25].

The VS emission of ZnO films consists of the bands with the center at 415 nm, 465 nm, 520 nm, 580- 600 nm, respectively. The intensity of the small band at 415 nm does not depend on the Cu concentration and its intensity is very low (approximately of 5%). The origin of the peak at 415 nm is attributed to the intrinsic defects [26, 27] and therefore, it is excluded out from the consideration in this paper. The VS emission intensity increases with increasing Cu concentration. The VS emission intensities differ 5 times for low and high Cu concentration (Figure 2b, curves 1 and 2). Three peaks structure of the VS emission is expressed most clearly for the mediate concentration of copper (Figure 2a, curve 2).



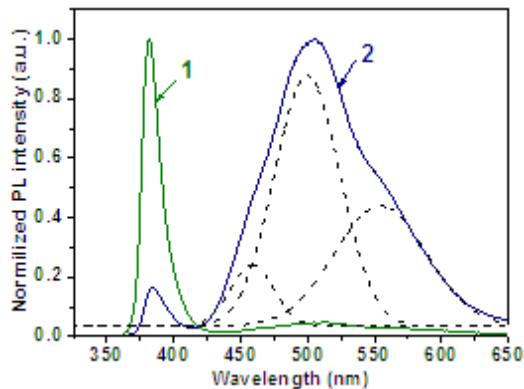
**Figure 3.** PL spectra of ZnO-Cu films on silicon (1) and sapphire (2) substrates at low level doping. The dashed lines show the results of the Gaussian multi-peaks fitting

Figure 3 shows the VS emission spectra of the samples with low level doping but grown on different substrates  $\text{SiN}_x/\text{Si}$  (1) and  $\text{a-Al}_2\text{O}_3$  (2), respectively. At first sight the spectra are different greatly. The emission spectrum of ZnO-Cu on  $\text{Al}_2\text{O}_3$  substrate has a complex shape and we have resolved them into Gaussian component. We obtained the same three component - blue, green and orange - but with other intensities relationship. The difference between these spectra is due to the difference in the intensity ratios of the constituent bands. The first band is in a blue region with a maximum at 465 nm (2.67 eV). The second and third bands are in the green and orange regions with the maximum at 520 and 580-600 nm, respectively. The green band is the most

intensive. As a consequence, the emission looks like white light with (0.31, 0.43) color coordinate for the mediate concentration of copper. Only green band at 520 nm was observed in the spectrum of ZnO-Cu film grown by EBE. The emission band has gauss shape in temperature range from 4.2 K to 300 K.

In order to determine whether Cu ions penetrate into the depth of the film or they remain mainly on the surface, we investigated the cathodoluminescence (CL) spectra of the ZnO-Cu films. It is known that a short wavelength light is absorbed at the surface of film while the electron beam excited of film's volume. The CL spectra of the ZnO (reference) and ZnO-Cu films on sapphire substrate with the high concentration of Cu are shown on Figure 4 (curve 1 and 2, respectively). The CL spectrum of the ZnO film consists of the UV band and a very small VS emission. The UV band is suppressed greatly, VS emission is increased in the ZnO-Cu film spectrum similar to their PL spectra. This is evidence of Cu-doping of the film's volume.

The VS emission of CL demonstrate the three peak structure similar to the VS emission of PL, but the positions of the band peaks are different. The maxima of the emission bands observed upon excitation by an electron beam are shifted to the higher energies by 0.1 eV, comparing with the band maxima observed under optical excitation. This is due to the different conditions of emission centers formation within the film volume and at the film surface.



**Figure 4.** CL spectra of the ZnO reference (1) and ZnO-Cu with mediate concentration of Cu (2) films, respectively. The dashed lines show the results of the Gaussian multipieaks fitting.

S.U.Yuldashev, et al. [28] observed a similar three band structure of ZnO film white emission in n-Zn<sub>0.9</sub>Mg<sub>0.1</sub>O/ZnO/p-Zn<sub>0.9</sub>Mg<sub>0.1</sub>O heterojunction structures. It was found that the electroluminescence spectrum of this heterostructure consists of at least three emission bands. The first band is in a blue region with a maximum at 420 nm. The second and third bands are in the green and orange regions with maximums at 505 and 610 nm, respectively. The blue emission band is attributed to the radiative recombination of the donor-acceptor pairs (DAP), in which the acceptors are the nitrogen atoms, and this emission band might be originated from radiative recombination in the p-Zn<sub>0.9</sub>Mg<sub>0.1</sub>O. The green emission band is due to the

recombination of DAP, where the deep donors are the vacancies of oxygen and the orange emission band is attributed to the oxygen interstitials. These last two emission bands originate from the ZnO active layer. However, following facts demonstrate the other structure of the centers of a luminescence ZnO-Cu films. Similarity of ZnO-Cu film's emission spectra on various substrates (see. Figure 3) shows that the luminescence centers might be attributed precisely to the ZnO film and not to its interface or to the substrate as in [29].

The dependence of the emission spectra on the doping level of copper (Figure 2) indicates that the luminescence centers are the copper ions or complexes, which include copper. It has been shown, that the copper doping gives three types of Cu<sub>Zn</sub>(3d<sup>9</sup>), Cu<sub>Zn</sub>(3d<sup>10</sup>) and Cu<sub>i</sub> point defects in ZnO [15]. The first two are the acceptors in two charge states - 3d<sup>9</sup> and 3d<sup>10</sup> and the third is the donor. The 3d<sup>9</sup> state is in close proximity to the valence band. Another electronic state, 3d<sup>10</sup>, lies deeper in the forbidden band of ZnO. At high copper impurities concentrations it begins to compensate itself, forming the donor's and acceptor's point defects.

We can assume that the presence of three bands in the VS emission is caused by these defects. The reason for this is the following. The optical depths of the copper acceptor levels relative to the valence band are 0.1 eV and 0.38 eV for the two charge states 3d<sup>9</sup> and 3d<sup>10</sup>, respectively [15]. The difference in the emission energy of Cu<sup>+</sup> and Cu<sup>++</sup> luminescence centers should reach 0.28 eV. This value is in good agreement with the difference of the blue (2.67eV) and green (2.38eV) radiation energy of 0.29 eV. Orange band can be attributed to the impurity defects associated with interstitial copper in combination with its own lattice defect acceptors. The introduction of copper in ZnO in the form of three types of defects is a feature of copper doping by thermal diffusion techniques through the film surface. Doping from the target during film growth (EBE) provides luminescence centers of only one type. It follows from the results of hydrothermal annealing films with different copper concentrations obtained by EBE deposition. The emission spectra had only one green band at 520 nm in a wide temperature range from 4.2 K to 300K.

The UV radiation intensity attenuation with the copper introduction may be the result of the deterioration of the film's crystal structure or the appearance of competitive additional radiative recombination channels. However, the morphological and optical results indicate that the deterioration in crystal structure was not observed. AFM investigation of doped film's surface indicates a strongly developed surface with larger grains and nanocrystals in comparison with films without doping. The presence of the phonon replicas in the emission spectra indicates the high crystal quality of ZnO-Cu films.

## 4. Conclusions

The close-space sublimation method was first applied for

Cu doping of ZnO thin films. Doping was carried out throughout the whole thickness of the films. The crystal quality of Cu doped ZnO thin films has been improved, which follows from the AFM and optical studies. After doping with Cu, an intense VS emission was appeared and the suppression of UV component was observed. The VS emission consists of the bands with the center at 465 nm, 520 nm and 580-600 nm. An intensity ratio of the constituent bands is determined by the Cu concentration and substrate type. The green band is the most intensive in the emission spectra. As a consequence, the emission looks like white light with (0.31, 0.43) color coordinate for the mediate concentration of copper. On the basis of the experimental data analysis it was found that the three types of point defects  $Cu_{Zn}(3d^9)$ ,  $Cu_{Zn}(3d^{10})$  and  $Cu_i$  in ZnO are responsible for the VS emission. The introduction of copper into ZnO in the form of three type's defects is a feature of copper doping by thermal diffusion techniques through the film surface.

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