Low-temperature Cathodoluminescence of Cu-doped ZnO Films

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Abstract

ZnO films were doped with Cu by tharmal diffusion and studied by cathodoluminescence (CL) spectroscopy method. Substantial increase of green band (GB) intensity of CL spectra compared to the non-doped films has been observed, the maximum positions, FWHM and the shapes of the GB being the same in both cases. These data say that the green emission in ZnO emerges from the Cu-centers. At 4.2 K GB of CL spectra of ZnO:Cu films have clearly visible phonon structure of ZnO:Cu films that is explained by annigilation of acceptor excitons.

Key words: ZnO; cathodoluminescence; green emission; acceptor exciton

1. Introduction

ZnO, a perspective wide-band-gap semiconductor for optoelectronics applications, is under intense investigations today. Despite many years of investigations many basic features of ZnO remain non-understood yet. For example, there is no common point of view on the nature of the intrinsic shallow donors in ZnO still [1]. Another puzzle, which is a subject of this paper, is the origin of the green emission, ever present in its luminescence spectra, no matter what method is used for growth. This emission is attributed by some researchers to the oxygen vacancies V_O of the lattice [2,3], and to the not-controllable copper (Cu)atoms by the others [4,5]. Thus, this question remains open. In this work, trying to bring in some clearness in this question, Cu- doped ZnO films were studied by cathodoluminescense (CL) spectroscopy. By comparison their spectra with the spectra of non-doped and with high-resistive policrystalline ZnO films it is made a conclusion that unitentional substitutional Cu- centers serve as the origin of the green emission in ZnO.

2. Experimental

Used in this work doped and non-doped monocrystalline epitaxial ZnO films of the thickness $\sim 3\mu$m were grown by chemical vapor deposition (CVD) method on sapphire substrates. Doping with Cu - by thermal diffusion from deposited onto ZnO by magnetron sputtering Cu-layer of the thickness $100\mathring{A}$. The diffusion was performed by annealing at 750 C for 20 h. It is important for thermal diffusion for ZnO films to be thermostable because at annealing the properties of the films may change strongly. For this purpose, such high thermostable ZnO films were grown using GaN buffer layers [6]. At the same conditions as a ZnO:Cu sample, a reference sample ZnO films without Cu-layer was also annealed. After thermal diffusion, the Cu concentration (N_{Cu}) and resistitivity (ρ) of the films were measured by secondary ion mass spectroscopy (SIMS) and Van der Pauw methods respectively. SIMS analysis gave a value of Cu concentratrion as $\sim 5 \times 10^{17}$. The resistivity of doped films increased dramatically, by the order of 4, with respect to non-doped films. Such resistivity incrising with Cu doping is typical to ZnO crystals. For comparison, high-resistive polycrystalline

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ZnO films were obtained by oxidation of metallic Zn layers with the resistivity comparable with the that of Cu- doped films. The CL spectra were measured at temperatures 300, 78 and 4.2 K, electron-beam current of 0.2μA and accelerating voltage of 20 keV were used for excitation.

3. Results and discussion

The CL spectra of the studied films consisted of narrow near-band edge ultra-violet (UV) emission with the maximum at 385 nm at 300 K, and broad green band (GB) with maximum positions at 510 nm for CVD films and 500 nm for polycrystalline films which did not change with CL temperature. This difference in GB maximum positions of the films is explained by various growing methods resulting in different electron-phonon interaction constants in crystals. It has been found out that the intensity of GB of Cu-doped films grew substantially, almost four times compared to that of non-doped reference sample, maximum positions, FWHM and the shapes (at 300 and 78 K) being the same in both samples. These results were well reproducible. These data allowed us to make a conclusion that green emission luminescent transitions occur at identical centers in both samples, namely at divalent Cu^{2+} centers substituting Zn atoms in lattice. This conclusion supports the data of 4.2 K CL measurements, which are given in Fig.1. As seen from this figure, GB of Cu-doped ZnO sample has clearly visible phonon structure with a period of LO- phonon energy 71 meV whereas this one of non-doped films is very week. 4.2 K the GB of high-resistive polycrystalline ZnO film (not given in the figure) was almost the same as that of non-doped reference. Such difference between GB of Cu- doped and non-doped ZnO films suggests that for phonon structure of the samples responsible are Cu- centers and can be explained if to accept that green emission is a result of multiphonon annigilation of acceptor excitons (AE)[7] formed at copper atoms. The term "acceptor exiton" as well as "donor exciton" was introduced first in [8] and applied to AE on acceptor type $3d-$ element Cu means the following. As is known, Cu ($3d^{10}4s^1$) behaves in ZnO as an isoelectronic impurity and on zinc site has a ground state Cu^{2+} ($3d^9$) which presents a neutral deep acceptor. When excited Cu^{2+} state captures an electron from the valence band and a formed hole in the vicinity localizes in a hydrogen-like orbit around the excited ion Cu^{+} ($3d^{10}$). This excited hydrogen-like state Cu^{2+} is AE. Annigilation of these AE emitting LO phonons leads to formation of green band in ZnO CL spectra. Although in neither of the spectra of the samples were present zero-phonon line with energy 2.85 eV (433 nm), much more clearness of the phonon replica of ZnO:Cu samples GB compared to that of the non-doped samples can be explained with higher concentration of Cu- centers forming AE. There were another interpretation of the GB phonon structure of ZnO in [9]. The authors explained such structure of GB in their films seen at 2 K as the result of shallow-donor/deep-acceptor (D-A) transitions. Our results, however, strongly contradict with this assumption since according to this model we should expect a reverse picture of GB since the concentration of shallow donors in ZnO:Cu much more less than that in non-doped sample. Besides, according to it the similar GB shapes of both ZnO:Cu and non-doped high resistive polycrystalline films must also be expected due to their comparable resistivities.

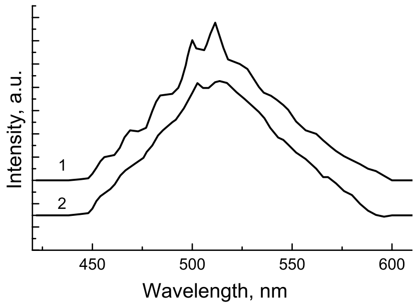

Fig. 1. The green bands of 4.2 K CL spectra of Cu- doped (curve 1) and non-doped (curve 2, enlarged) ZnO films

4. Conclusion

Thus, experiments carried out show considerable increase of GB intensity of Cu- doped ZnO films in comparision with that of non-doped reference ZnO films, muximum position, FWHM and the shape of GB being te same in both cases. At 4.2 K the GB of Cu- doped film has distinct phonon replica in contrast to reference sample that can be explained as a result of multiphonon annigilation of acceptor exitons localized on Cu centers. These data suggest that the tipical green luminescence of ZnO emerges from not-contrallable Cu-impurities.

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