Celal Bayar University Journal of Science
Volume 15, Issue 2, 2019, p 145-149
Doi: 10.18466/cbayarfbe.475150

Investigation on Cathodoluminescence Properties of Copper Implanted ZnO Samples

Yasemin Tuncer Arslanlar[1*], İlker Çetin Keskin[1], Mehmet İsmail Katı[2], Murat Türemiş[3], Ahmet Çetin[1], Rana Kibar[1]

[1]Department of Physics, Faculty of Art and Science, Manisa Celal Bayar University, Manisa, Turkey
[2]Experimental Science Applications and Research Center, Manisa Celal Bayar University, Manisa, Turkey
[3]Faculty of Engineering and Natural Sciences, Department of Physics, Bursa Technical University, Bursa, Turkey
[*]tunceryasemin@hotmail.com

Received: 26 October 2018
Accepted: 24 June 2019
DOI: 10.18466/cbayarfbe.475150

Abstract

ZnO single crystals has been implanted with 400 keV Cu ions at fluences of 2,5 x 10^{16} ions/cm^2 at room temperature. The cathodoluminescence (CL) measurements of pure and Cu implanted samples has been reported at UV-visible range at both room and different temperatures. After the implantation process, the samples were annealed for 1 hour at 1000ºC. The effects of ion implantation and annealing temperature and on the CL signals were researched with the data obtained. The CL spectrum of pure ZnO exhibited two emission bands at 385 nm and 550 nm. There are some changes in the emission bands in the CL spectrum that are thought to be due to the presence of Cu ions. Also it is possible to say that the annealing temperature can strongly influence CL intensity.

Keywords: ZnO, Ion Implantation, Nanoparticles, Cathodoluminescence.

1. Introduction

ZnO having wurtzite hexagonal crystal structure is a semi-conductor with high radiation resistance, 60 meV exciton binding energy, and obtains 3.4 eV energy bond range at room temperature [1, 2].

It has a wide range of application area including optoelectronic, piezoelectric devices, semiconductor detectors, LEDs, gas sensors and laser technology [3].

Cathodoluminescence is the light emitted by a specimen when bombarded with electrons. The electrons only penetrate a small distance (a few microns) into the sample and therefore, the method can only be used to study the surface region of the material. It offers a precise analysis of the surface region of insulating and semiconducting materials. As the wavelengths of radiation depend on the nature of the sample, it is possible to identify its chemical composition, defects, impurities and imperfections [4].

Characteristic and luminescence properties of many materials, that have a wide range of application area in the industry, may be changed by the ion implantation process. Ion implantation is made by inserting high velocity ions into the target and this process changes the surface properties of the material. Ion implanted samples are widely used for development of the photonic and optoelectronic devices. By this method, different type and structured crystals can be obtained [5, 6].

In this study, the ion dose was increased as much as possible and the sample was annealed. In addition, CL measurements were taken between 300-40 K temperatures. In such spectroscopic methods, the change in crystal behavior with lower temperatures leads to significant alterations in the emission band obtained. The formation of metal nanoparticles by implantation of Cu ions to the ZnO single crystal and the variation of the cathodoluminescence properties in relation to this process has been investigated. There are some differences in relative peak positions and intensities between pure and implanted samples. The CL spectra of Cu implanted ZnO were also taken following furnace annealing at 1000 ºC at 1 hour in air.

2. Materials and Methods

The polished wurtzite ZnO single crystals 10x5x0.4 mm^3 purchased from MATECK, Germany. The samples were implanted with Cu ions at room temperature in a vacuum of 10^{-6} mbar at energy of 400 keV at fluence of 2,5x 10^{16} ions/cm^2 on an EATON 3204 implanter in Juelich in Germany on a ZnO crystal surface layer. After implantation process, the samples were annealed at 1000 $^{\circ}$C using a Proterm tube furnace in air.

After these processes, the surface morphology of the crystal has been investigated by Shimadzu SPM-9500 AFM in İTÜ Physics Department. The surface photos

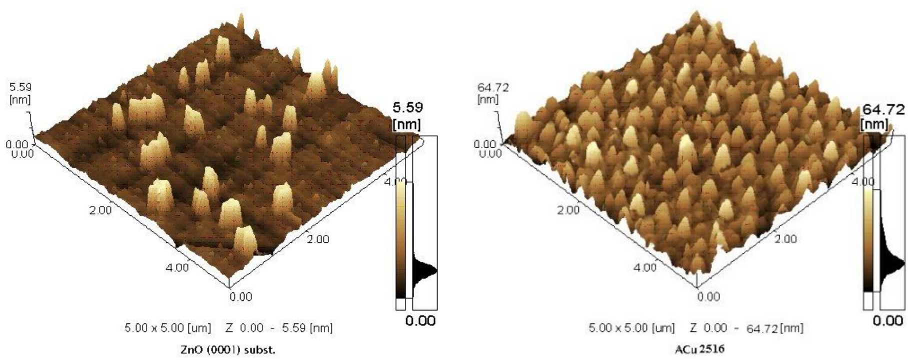
Celal Bayar University Journal of Science
Volume 15, Issue 2, 2019, p 145-149
Doi: 10.18466/cbayarfbe.475150

of the samples were taken at room temperature. The CL spectrums at different temperatures between room temperature and 40 ºK has been taken at also 250-825 nm wavelengths under DC electron beam excitation.

The data collected are for an accelerating potential of 10-24 keV and a current of 20 nA, which corresponds to an incident power density of 0.8 $mWcm^{-2}$. The light from the sample was focused via a quartz lens, onto the entrance slit of a grating monochromator with f/4 light collection and detected by a blue-sensitive photomultiplier tube (PMT, EMI 9813Q). The quantum efficiency of EMI 9813Q is between 15% and 25% in the range of 200 nm to 600 nm.

3. Results and Discussion

In Figure 1a, the present impurity atoms in pure ZnO could be seen. After the ion implantation, the atoms join the target. By this process, the surface roughnesses occur. In the photos taken after annealing process, it is clearly seen that the ion clusters expanded.



a) **b)**

Figure 1. a) The AFM photo of single ZnO (0001) crystal **b)** The AFM photo of ZnO: Cu $2.5x10^{16}$ $ions/cm^2$ sample after 1 hour annealing process.

It is known that, generally ZnO has a few luminescence band in the UV and visible region. The UV band is related to excitonic transitions, either free or bound, and their phonon replicas, and eventually some donor acceptor pair transitions. The visible luminescence due to recombination in deep levels is related to either impurities or native defects [7,8]. These defects play very important roles in the optical properties of materials.

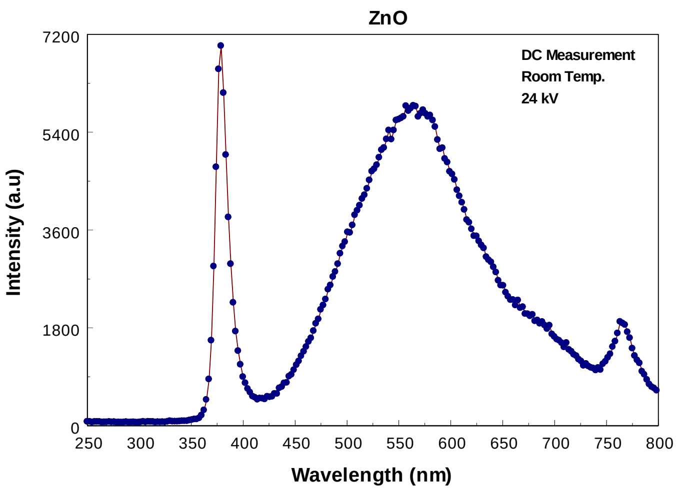


Figure 2. The CL spectrum of pure ZnO at room temperature.

It can be seen that variation of the emission spectrum when pure ZnO single crystal is bombarded with 24 kV electron beam (Fig.2). The luminescence spectrum of ZnO exhibit two luminescence bands a short-wavelength band (the edge luminescence), which is located near the absorption edge of the crystal, and a broad long-wavelength band, the maximum of which usually is in the green spectral range There is a sharp peak at 385 nm with a maximum. This peak corresponds to UV radiation. The edge luminescence at 385 nm associated with exciton and exciton-like states is observed in the near-UV spectral range. The wide emission band between 400-700 nm obtains maximum at 550 nm. This band shows that ZnO is a material that emits green light. The luminescence centers that are zinc vacancies (V_{Zn}), oxygen vacancies (V_O), interstitial zinc ions (Z_{ni}) and transitions Z_{ni} - V_{Zn} were assumed to be responsible for the green luminescence. These results are compatible with the literature [9, 10].

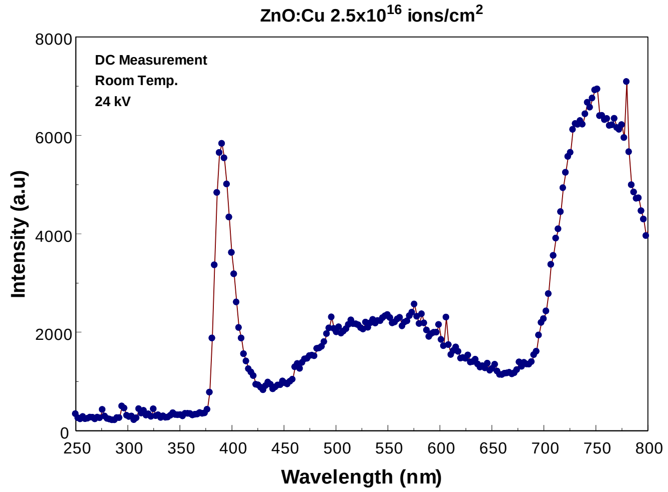


Figure 3. CL spectrum of Cu implanted ZnO with concentration 2.5x10^{16} ions/cm^2 when bombarded with 24 kV electron beam.

In Figure 3, the effect of the ion implantation to the CL intension can be seen. The intension of the peak at 385 nm is rationally decreases. The peak originated from ion implantation and electron vacancy couples. This situation is thought to be originated from the bonding of the ions with the bombarded electron vacancy couples. After Cu bombardment, the wide emission band at 550 nm loses its strength. It is thought that the Cu atoms bonded to the oxygen atoms and create metallic structure and because of this structure, Cu ions and oxygen vacancies loses contribution to radiation.

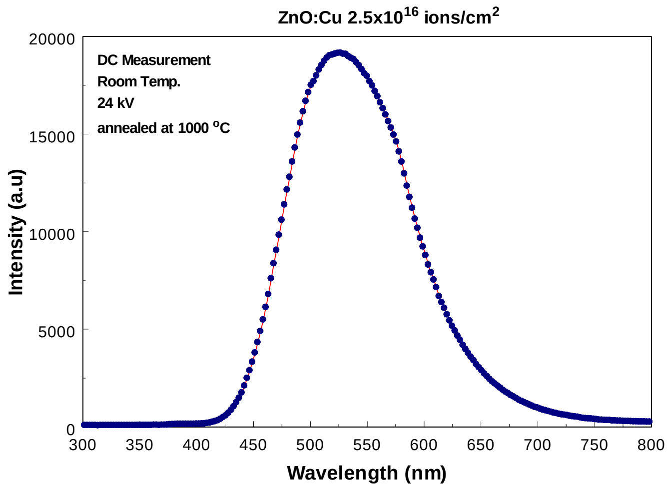


Figure 4. CL spectra of ZnO with 2.5x10^{16} ions/cm^2 Cu ions implanted and annealed in air.

In Figure 4, the recorded CL spectrum of the ZnO sample after implanted with Cu and one hour annealing at 1000ºC can be seen. The intensity of the visible emission increased approximately 3 times according to pure ZnO after annealing. This situation is related with the increment of the diameter of atom clusters that affected by the implantation and annealing processes. Furthermore, both the oxygen in metallic structure that is thought to be formed by implantation and the burning of free oxygen during annealing copper ions are revealed. Revealed Cu ions have a big importance in the increment of the intensity of the peak [11].

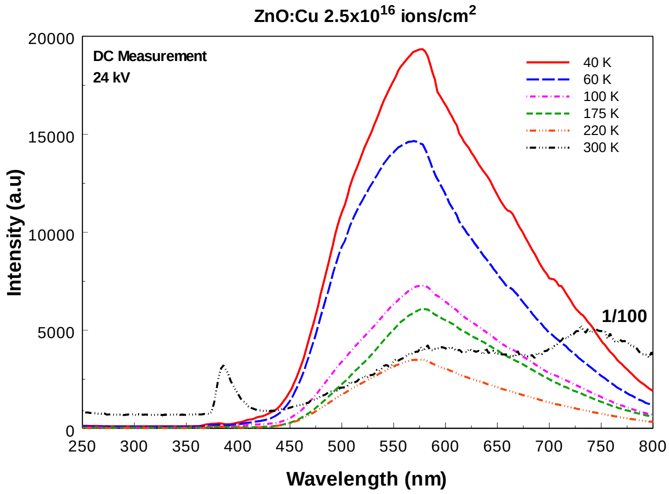


Figure 5. The DC CL spectra of the Cu implanted ZnO at 2.5 $x10^{16}$ ions/cm^2 dose crystal at different temperatures.

In Figure 5, DC CL spectrums at selected temperatures can be seen during heating from 40 K to room temperature. Luminescence signals were found to be strongly affected by temperature. As can be seen in the CL spectrum of the Cu implanted ZnO sample, the intensity of the sharp peak at about 390 nm resulting from excitons was influenced by the temperature-dependent behavior of electron-hole pairs. This effect can be clearly seen in Figure 5. The UV emission present at room temperature disappeared at 40 K. However, the visible emission intensity increases significantly as the temperature decreases. One of the reasons for this increase is the substantial elimination of non-radiative transitions.

4. Conclusion

Cu implanted samples differ from pure ZnO in terms of defect structure and the luminescence properties of the material has changed. There are some differences in relative peak positions and intensities between pure and implanted samples. The UV and visible emission of ZnO is widely used especially in LED technology. The visible emission intensity significantly increased by the implantation and annealing processes. However, different dosage usages for ZnO samples can also be investigated in order to find out the effects on luminescence efficiency.

Author's Contributions

Yasemin Tuncer Arslanlar: Drafted and wrote the manuscript, performed the experiment and result analysis.
İlker Çetin Keskin: Assisted in analytical analysis helped in manuscript preparation.
Mehmet İsmail Katı: Wrote the interpretation of AFM.
Murat Türemiş: Performed the experiment and result analysis and drawed
Ahmet Çetin: Supervised the experiment's progress, result interpretation and helped in manuscript preparation.
Rana Kibar: Supervised the experiment's progress, result interpretation and helped in manuscript preparation.

Ethics

There are no ethical issues after the publication of this manuscript.

References

1. Jadwisienczak,W. M, Lozykowski, H. J, Xu, A, Patel, B. 2002. Visible emission from ZnO doped with rare-earth ions. Journal of Electronic Materials; 31(7) 776–784.

2. Coskun, C, Look, D C, Farlow, G C, Sizelove, J R. 2004. Radiation hardness of ZnO at low temperatures. Semiconductor Science and Technology; 19(6) 752-754.

3. Jagadish, S, Pearton, S, 2006. Zinc Oxide Bulk, Thin Films and Nanostructures; Australian National Univ. Australia.

4. Karali, T, Can, N, Valberg, L, Stephanov, A.L, Townsend, P.D, Buchal, C.H, Ganeev,R.A Ryasnyanskya, A.L, Belik, H.G, Jessett, M.L, Ong, C, 2005. Physica B: Considered Matter; 363(1-4) 88-95.

5. Kibar, R, Farklı Metal İyonları ile bombalanan $SrTiO_3$ Kristalinin ve Bazı Minerallerin Nükleer ve diğer Yöntemlerle İncelenmesi Ege Üniv. Fen Bilimleri Enstitüsü, İzmir 2007; pp 4.

6. Bird, J.R, Williams, J.S, Ion Beams for Materials analaysis Acedemic Press: Australlia, 1989.

7. Sanjeev, S, Kekuda, D, Effect of Annealing Temperature on the Structural and Optical Properties of Zinc Oxide (ZnO) Thin Films Prepared by Spin Coating Process; ICMST 2012(2015); 73 01214.

8. TsungHsieh, P, ShanChin, H, KuanChang, P, MingWang, C, ChungChen, Y, PhonHoung, M. 2010. Effects of the annealing environment on green luminescence of ZnO thin films. ,Physica B: Condensed Matter; 405(11): 2526-2529.

9. Rodnyi, P.A and Khodyuk, I.V. 2011. Optical and Luminescence Properties of Zinc Oxides. Optics and Spectroscopy; 111(5): 776-786.

10. Rodnyi, P.A, Chernenko, K.A, Venevtsev I.D. 2018. Mechanisms of ZnO Luminescence in the visible Spectral Region. Spectroscopy of Considered States; 125(3): 357-363.

11. Çetin, A, Farklı Metalik İyonlarla Bombalanan ZnO Örneklerinin Fiziksel ve Yapısal Özelliklerinin Nükleer,Lüminesans ve Diğer Teknikler Kullanılarak İncelenmesi. Ege Üniversitesi Fen Bilimleri Enstitüsü, 2007.