Cathodoluminescence Spectrum of ZnS:Cu – Binder Layer.

Olusogo O. Odusote, M.Sc.[1*] and Johnson A. Adepitan, M.Sc.[2]

[1]Department of Physics, Olabisi Onabanjo University, Ago-Iwoye, Ogun State, Nigeria.
[2]Department of Physics and Mathematics, TASUED, Ijagun, Ogun State, Nigeria.

E-mail: sog-odusote@yahoo.com*

ABSTRACT

The cathodoluminescence of ZnS:Cu – binder layer was investigated. Emission was observed in the wavelength range 400nm to 600nm, corresponding to the blue - green region of the visible electromagnetic spectrum. A full width at half maximum (FWHM) of 60nm and peak emission around 525nm was observed. The asymmetric emission curve suggests that different groups of shallow traps are in operation. The trap depths are at 1.22eV and the Fermi energy for the electrons in the material was calculated to be 0.1eV.

(Keywords: zinc sulphide, luminescence, binder layer, electrons, mini CRT)

INTRODUCTION

Luminescence, the emission of light (not ascribable to incandescence) has been of interest because of the various possible applications. It is utilized by biological organisms for various purposes which include defense, mating, and territorial discrimination. It finds technological applications in imaging and low power illumination devices.

Various methods exist for the production of luminescence, chemical action and friction being commonly employed by living organisms. For technological applications, excitations by light (photoluminescence), electric field (electro-luminescence), and by electrons (cathodoluminescence) are frequently employed.

Zinc sulphide (ZnS) is a II–VI semiconductor which has been employed in luminescent panels and in ZnS–CdS superlattices. When activated with copper to form ZnS:Cu it finds application in various ways. Thin films of ZnS:Cu have been deposited from chemical bath and their structural, optical and photoluminescence properties determined as a function of dopant concentration and quantum confinement effect [3].

The microstructure and luminescence properties of ZnS:Cu powders have also been investigated for possible use in electroluminescent lamps [1]. The electroluminescent properties of ZnS:Cu prepared by metal-organic chemical vapor deposition (MOCVD) and thermospinning have been investigated [5] and a new technique for electro- and cathodoluminescent screen fabrication with the application of a new method of doping ZnS:Cu and ZnO:Cu thin film phosphors via electron beam evaporation has been proposed [6]. The Cu have been found to be doped in the ZnS crystal in a study of ZnS:Cu/Poly(vinyl alcohol) (PVA) composite nanofibers prepared by electrospinning technique [10]. In materials science and semiconductor engineering, cathodoluminescence has been employed in the scanning electron microscope and the scanning transmission electron microscope [12, 7]. Also, as an efficient luminophor, ZnS:Cu binder layers could be employed in X-ray intensifying screens [7].

However, the costs of the above schemes are high and the use of ZnS:Cu binder layers for the surface in display panels will lead to reduced cost. This work looks at the emission characteristics of ZnS:Cu binder surfaces produced from low cost active material/epoxy binder matrix.

METHOD

A mini CRT was fabricated from a transparent perspex bottle with wall 5mm thick, radius 3cm, and length 5cm, open at one end. On the inside perimeter of the transparent closed end was a loop

of bare 12 s.w.g. copper wire. This wire which came out of a tight fitting hole drilled to the side of the tube was connected to the positive pole of the H.T. supply.

The active surface was compounded from a mixture of commercially available ZnS:Cu and slow setting conductive epoxide. The mixture was poured onto the sealed end of the bottle to cover the copper strip and the bottle was stuck on the rubber cup of a valve grinding tool. The spindle was hand spun at a slow rate for 3 minutes, after which the epoxide was left to set. The set surface of the epoxide was then polished with soft sandpaper to expose the phosphor. At the open end of the tube was inserted a tight fitting rubber bung which carried a thermo-emissive cathode (to which was connected the negative pole of the H.T. supply) and a heating filament. The bung also carried a central metal tube for the evacuation of air.

Every hole or junction was sealed with epoxide. Vacuum pump down to about 10^{-6} torr was done with an Edwards vacuum pump, heating current was supplied to the filament through a 12V d.c. supply and an accelerating H.T. voltage of 15kV was applied through a Leybold – Heraeus high voltage supply. The emission characteristics were recorded with an Intercontinental Light IL700 spectroradiometer.

RESULTS AND DISCUSSION

The cathodoluminescence spectrum is presented in Figure 1. Since the luminescence is due to electronic interband transitions, the emission spectrum is of the form:

$$I(\nu) \propto \nu^2 \langle M \rangle^2 F_c(E) F_v(E) \rho(\nu) \quad \textbf{(1)}$$

where $\langle M \rangle$ is the transition matrix element, $I(\nu)$ is the measured intensity, $F_c(E)$ and $F_v(E)$ are the respective electron and hole Fermi – Dirac distribution functions, and $\rho(\nu)$ is the density of states per unit range of transition frequency ν.

If the electron transition from the conduction band to the hole in the valence band is considered as an oscillating dipole, then the emission profile is a Lorentzian:

$$I(\nu) = I_0 \left(\frac{\Gamma}{2\pi} \right) \left[(\nu - \nu_0)^2 + \frac{\Gamma^2}{4} \right]^{-1} \quad \textbf{(2)}$$

where Γ is the natural linewidth i.e. the full width at half maximum (FWHM) and I_0 is the maximum intensity at $\nu = \nu_0$.

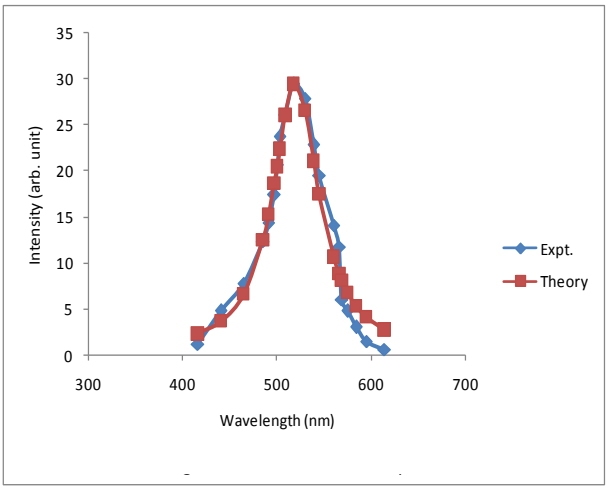

Figure 1: Cathodoluminescence Spectrum.

From Figure 1, $\Gamma = 60\text{nm}$. and on substitution in Equation 2, the theoretical curve is obtained. This theoretical curve is symmetrical and identical with the experimental curve at intermediate frequencies, but the experimental curve shows asymmetry at the low frequency region. This contrasts an observed peak shift towards the short wave region observed in laser processed ZnS:Cu thin film [4] where the asymmetry was explained by taking into account two alternative possibilities: an inhomogeneous distribution of the emission centers along the direction of the growth of the film and the laser processing of ZnS–Cu film. We attribute the asymmetry in this current work to the presence of shallow traps within the conduction band. This view is supported by theoretical calculations which show that in ZnS: Cu phosphors, additional electronic states corresponding to the hybridized states of copper atoms (Cu sp^3) can be formed in the band gap [8]. For extrinsic transitions as obtained from ZnS:Cu, the emission is with the photon energy smaller than the band gap energy of the intrinsic ZnS. The emission spectrum for electron transitions from the conduction band to acceptor levels near the valence band is given by [9]:

$$I(\nu) \propto \nu^2 (h\nu - E_g - E_a)^{\frac{1}{2}} \left(\exp\left(\frac{h\nu - E_g + E_a - E_{F_n}}{kT} \right) + 1 \right)^{-1} \quad \textbf{(3)}$$

where h and k are Planck's and Boltzmann's constants, respectively, T is the temperature of the specimen, E_g is the band gap energy, E_a is the impurity ionisation energy and E_{F_n} is the electronic Fermi energy. In this case, the emission peak occurs near $E_g - E_a$. If the intensity values I_1 and I_2 at the respective frequencies ν_1 and ν_2 are substituted in Equation 3, we obtain:

$$E_{F_n} = h\nu_1 - E_g + E_a - kT \ln \left(\frac{I_2}{I_1} \left(\frac{\nu_1}{\nu_2} \right)^2 \left(\frac{h\nu_1 - E_g + E_a}{h\nu_2 - E_g + E_a} \right)^{\frac{1}{2}} \left(\exp\left(\frac{h\nu_2 - E_g + E_a - E_{F_n}}{kT} \right) + 1 \right) - 1 \right) \quad \textbf{(4)}$$

Equation 4 is transcendental and has to be solved by an iterative process.

We have that $E_g = 3.60\text{eV}$ for ZnS, and peak emission occurred at 525nm, therefore, $E_a = 0.9\text{eV}$. This value is comparable with the thermal depths of acceptor levels in a ZnS:Cu phosphor crystal determined to be in the range 0.9 – 1eV for the 525nm emission band [2, 11]. If the above values and the quartet (I_1, I_2, ν_1, ν_2) obtained from any two points on figure 1 are substituted into equation 4, the value of $E_{F_n} = 0.1\text{eV}$ is obtained after seven iterations.

CONCLUSION

The cathodoluminescence of ZnS:Cu binder layer has been studied with a fabricated mini CRT. The use of conducting epoxy as the binder enabled the formation of a compact and void-free polymer matrix that limited water diffusion which prevented the corrosion of particles and luminescence quenching.

The cathodoluminescence intensity was also enhanced as a result of the improved electrical conductivity afforded by the conductive binder, resulting in the decrease of charging effect on the phosphor. The application of the theoretical equations to the system enabled the determination of the impurity depth, electron Fermi level and the natural line width. The emission profile was fitted closely as a Lorentzian . The value of 60nm for the FWHM is too broad, which renders the ZnS:Cu – binder layer useless for coherent illumination applications.

REFERENCES

1. Armelao, L., D. Camozzo, S. Gross, and E. Tondello. 2004. *Journal of Non-Crystalline Solids*. 345-346: 402-406.

2. Baur, G., R. Wengert, and V. Wittwer. 2006. *Physica Status Solidi (a)*. 18: 337 –345.

3. Jayanthi, K., S. Chawla, H. Chander, and D. Haranath. 2007. *Cryst. Res. Technol.* 42: 976.

4. Khomchenko, V., L. Fedorenko, N. Yusupov, V. Rodionov, Yu. Bacherikov, G. Svechnikov, L. Zavyalova, N. Roshchina, P. Lytvyn, and M. Mukhlio. 2005. *Applied Surface Science*. 247:434-439.

5. Khomchenko, V., V. Rodionov, L. Zavyalova, G. Svechnikov, N. Roshchina, V. Khachatryan, A. Savin, Y. Bacherikov, O. Marchilo, Y. Tzyrkunov and J. Stiles. 2003. *Semicond. Sci. Technol.* 18: 512-516.

6. Kryshtab T.G., V. S. Khomchenko, V.P. Papusha, M.O. Mazin, and Y.A. Tzyrkunov. 2002. *Thin Solid Films*. 403-404: 76-80

7. Parish, C.M. and P.E. Russell. 2007. "Scanning Cathodoluminescence Microscopy". In: *Advances in Imaging and Electron Physics.* P.W. Hawkes (ed.).147:1.

8. Savchenko, N.D., T.N. Shchurova, K.O. Popovych, I.D. Rubish, and G. Leising. 2004. *Semiconductor Physics, Quantum Electronics & Optoelectronics*. 7(2):133-137.

9. Sze, S.M., 1969. *Physics of Semiconductor Devices*. Wiley- Interscience: New York, NY.

10. Wang H., X. Lu, Y. Zhao, and C. Wang. 2006. *Materials Letters*. 60(20).

11. Wang, L.W., Z. Xu , F. Teng , F.J. Zhang , L.J. Meng, and X.R. Xu. 2005. *Guang Pu Xue Yu Guang Pu Fen Xi.* 1537-1541.

12. Yacobi, B.G. and D.B. Holt. 1990. *Cathodoluminescence Microscopy of Inorganic Solids.* Plenum: New York, NY.

ABOUT THE AUTHORS

Olusogo Odusote, is a Lecturer at the Olabisi Onabanjo University, Nigeria. He is a physicist and is a member of the Nigerian Association of Mathematical Physics. He holds a Master of Science (M.Sc.) in Physics from the University of Jos. His research interest is in condensed matter physics.

Johnson Adepitan, is a Lecturer at the Tai Solarin University of Education, University, Nigeria. He is a physicist and educator. He holds a Master of Science (M.Sc.) in Physics from the University of Ibadan and a Postgraduate Diploma in Education (PGDE) from the Olabisi Onabanjo University. His research interest is in lower atmospherics physics.

SUGGESTED CITATION

Odusote, O.O. and J.A. Adepitan. 2012. "Cathodoluminescence Spectrum of ZnS:Cu – Binder Layer". *Pacific Journal of Science and Technology*. 13(1):202-205.