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# PHOTOLUMINESCENCE STUDY ON CHEMICALLY DEPOSITED $CuBiS_2$ THIN FILMS

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Using chemical bath deposition (CBD) technique, $CuBiS_2$ thin films of different bath temperature and deposition time were prepared on glass substrates. There is a blue shift in the PL spectrum of $CuBiS_2$ thin films were observed. A strong emission peak is observed at 419 nm. The excitation wavelength was 209 nm. This effect may be related to the quantum effects. PL emission intensity increases with bath temperature and deposition time. The emission peak occurs at a higher wavelength than that of the absorption peaks. In fact, the peak emission wavelength is invariably shifted towards red end of spectrum compared to the peak of the absorption spectrum. This phenomenon is known as the Stokes shift.

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*Keywords*: Copper Bismuth sulphide; Chemical bath deposition; Photoluminescence studies; Thin films

## 1. Introduction

Semiconductror compounds have drawn much attention during the last few years because of their novel optical and transport properties which have great potential for many applications. To fit the need of different temperatures, scientists are looking for large intrinsic bandgap semiconductor materials so as to expand the exhaustion regions. We know the extremely small size of these particles will result in quantum confinement of the photo-generated electron-hole pair leading to a blue shift in the absorption spectrum. Research studies are done on the doped nanocrystalline II-VI semiconductors to improve their emission activity[1-3].

Copper bismuth sulphide ($CuBiS_2$) V-VI class of materials find special applications in photoelectrochemical cells, solar absorber coatings, thin film lithography as its forbidden energy gap is 1.65 eV [4]. Chemical deposition of copper bismuth sulphide thin films has been reported using different sulphur releasing sources such as sodium thiosulphate, thiourea, and thioacetamide [5] with different structural, optical and electrical properties. The effect of deposition time of $CuBiS_2$ thin films has been studied and grain sizes were reported in our previous studies [6]. Pawar et al [4] reported acidic aqueous deposition of $CuBiS_2$ thin films with polycrystalline crystal structure in acidic-aqueous medium using spray pyrolysis method.

In this study, CBD was used to deposit nanocrystalline $CuBiS_2$ thin films onto glass substrates. The $CuBiS_2$ thin films were charecterised using photoluminescence (PL). The temperature dependence of the PL intensity and deposition time dependence of the PL intensity results for the $CuBiS_2$ are reported.

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## 2. Material and methods

The film preparation was previously described in our previous paper [6]. Thin film samples are prepared on to well cleaned glass substrates with different bath temperatures ($40^0$C, $50^0$C, $60^0$C & $70^0$C) and deposition time periods (1hour, 3 hours and 5 hours). A photoluminescence (PL) spectrum of the films was recorded using a Cary Eclipse instrument in fluorescence emission scan mode with excitation wavelength of 209 nm.

## 3. Results and discussion

The chemically deposited $CuBiS_2$ thin films were uniform and consisted of small nanocrystalline grains. The preparation of $CuBiS_2$ thin films by CBD is governed by the chemical reaction within the solution of reactants. It was reported that at lower temperatures the surface of the CBD $CuBiS_2$ thin films is rough, but as the temperature continues to increase (at 60°C), the film surface becomes more uniform [5].

Fig.1-12 shows the photoluminescence spectra of $CuBiS_2$ thin films of different bath temperature and different deposition time periods. PL emission intensity increases with bath temperature (up to $60^0$C) and deposition time period. After attaining the bath temperature $60^0$C, intensity decreases (Fig.4). There is blue shift in the PL spectrum of $CuBiS_2$ thin films (Fig.1-6) which is corresponding to defect related luminescence emissions. The emission and absorption peaks occur at wavelengths 419 nm, 456 nm, 486 nm & 209 nm. The strong emission and excitation wavelengths were 419 nm and 209 nm. This effect may be related to the quantum effects. Fig.13 -16 show the temperature dependence and time dependence of PL intensity for emission and excitation wavelengths.

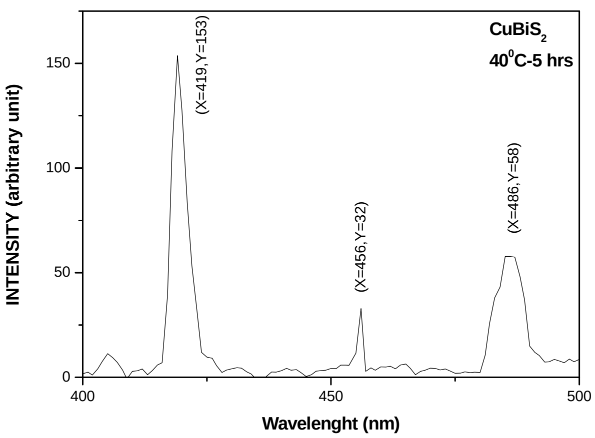


*Fig.1. Photoluminescence Spectra of $CuBiS_2$ thin film with bath temperature $40^0$C (Emission Wavelength 419 nm and Deposition time period 5 hours)*

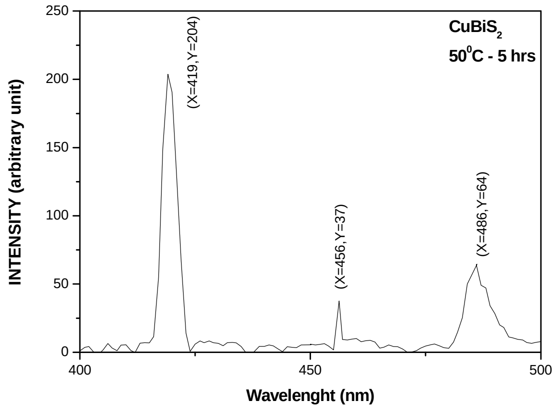


*Fig.2. Photoluminescence Spectra of $CuBiS_2$ thin film with bath temperature $50^0C$ (Emission Wavelength 419 nm and Deposition time period 5 hours)*

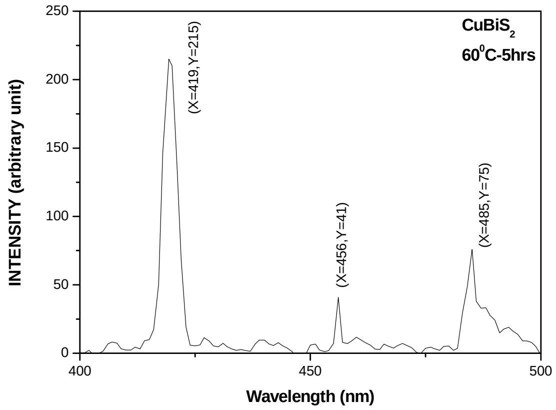


*Fig.3. Photoluminescence Spectra of $CuBiS_2$ thin film with bath temperature $60^0C$ (Emission Wavelength 419 nm and Deposition time period 5 hours)*

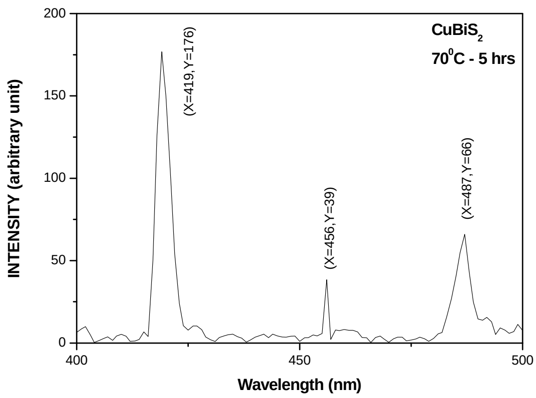


*Fig.4. Photoluminescence Spectra of $CuBiS_2$ thin film with bath temperature $70^0C$ (Emission Wavelength 419 nm and Deposition time period 5 hours)*

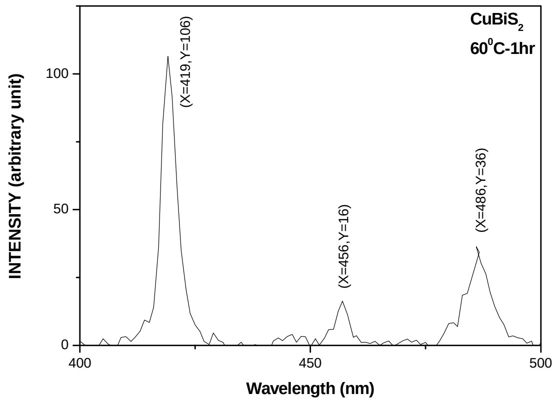


*Fig.5. Photoluminescence Spectra of $CuBiS_2$ thin film with Deposition time period 1 hour (Emission Wavelength 419 nm and bath temperature $60^0C$)*

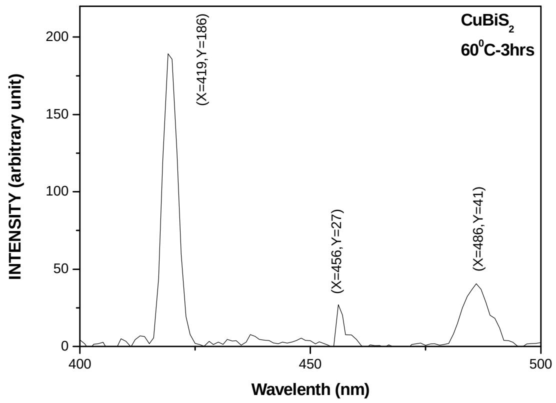


*Fig.6. Photoluminescence Spectra of $CuBiS_2$ thin film with Deposition time period 3 hours (Emission Wavelength 419 nm and bath temperature $60^0C$)*

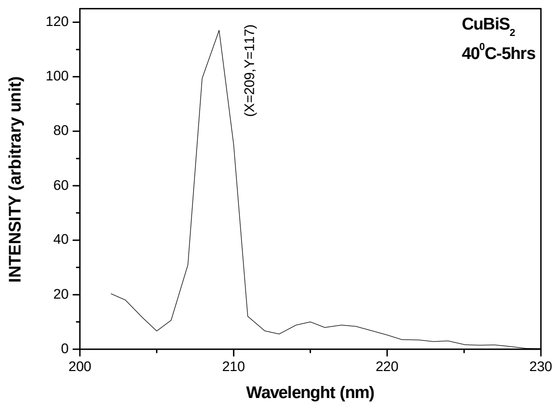


*Fig.7. Photoluminescence Spectra of $CuBiS_2$ thin film with bath temperature $40^0C$ (Excitation Wavelength 209 nm and deposition time period 5 hours)*

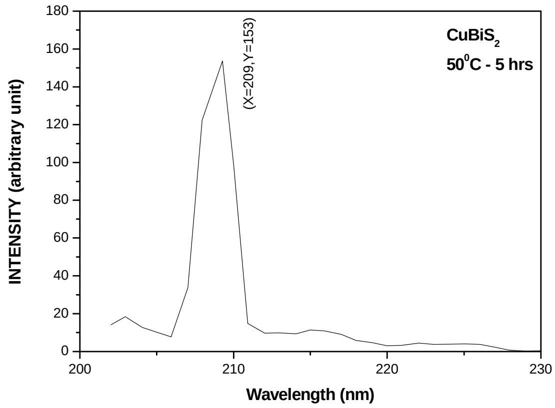


*Fig.8. Photoluminescence Spectra of $CuBiS_2$ thin film with bath temperature $50^0C$ (Excitation Wavelength 209 nm and deposition time period 5 hours)*

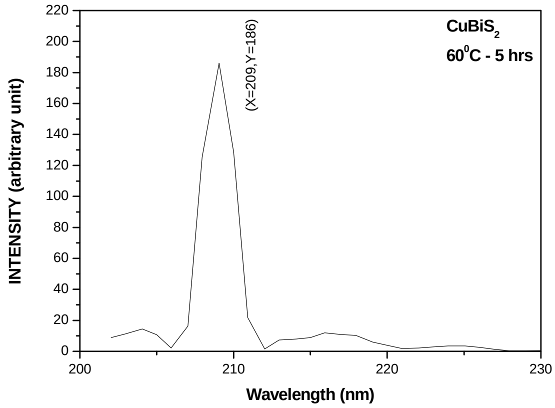


*Fig.9. Photoluminescence Spectra of $CuBiS_2$ thin film with bath temperature $60^0C$ (Excitation Wavelength 209 nm and deposition time period 5 hours)*

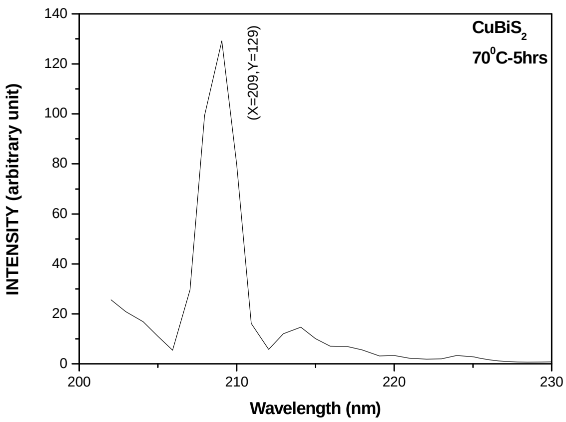


*Fig.10. Photoluminescence Spectra of $CuBiS_2$ thin film with bath temperature $70^0C$ (Excitation Wavelength 209 nm and deposition time period 5 hours)*

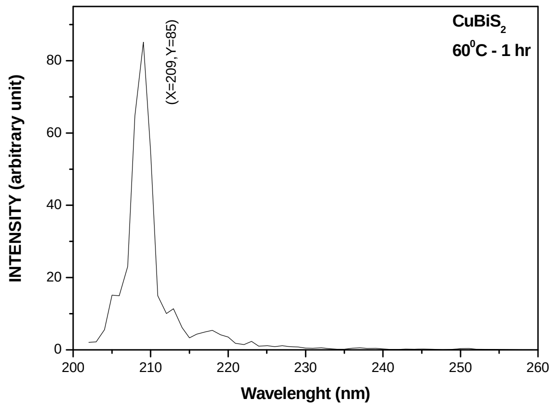


*Fig.11. Photoluminescence Spectra of $CuBiS_2$ thin film with deposition time period 1 hour (Excitation Wavelength 209 nm and bath temperature $60^0C$)*

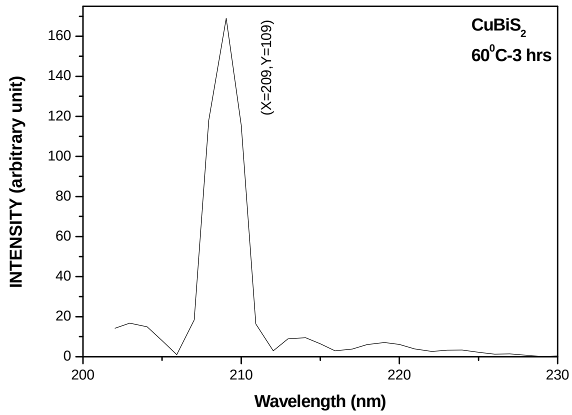


*Fig.12. Photoluminescence Spectra of $CuBiS_2$ thin film with deposition time period 3 hours (Excitation Wavelength 209 nm and bath temperature $60^0C$)*

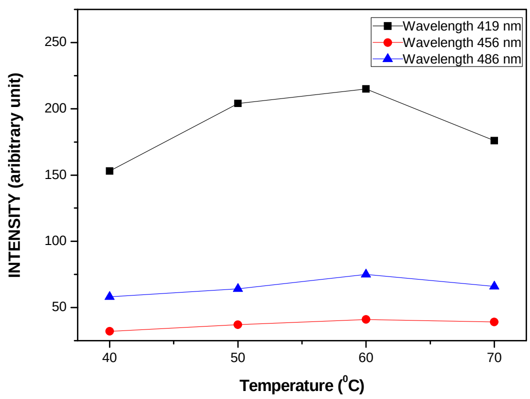


*Fig.13. The temperature dependence of the PL intensity of the $CuBiS_2$ thin film prepared for 5 hours (Emission wavelength 419 nm).*

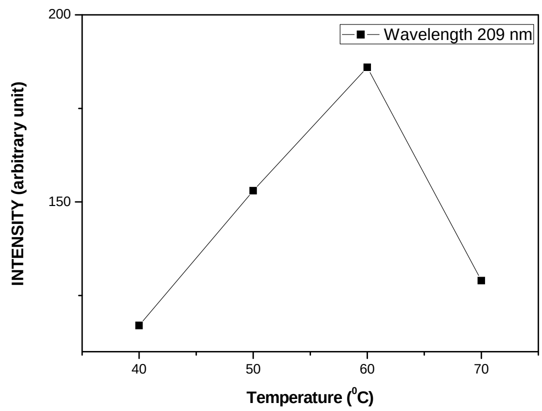


*Fig.14. The temperature dependence of the PL intensity of the $CuBiS_2$ thin film prepared for 5 hours (Excitation wavelength 209 nm).*

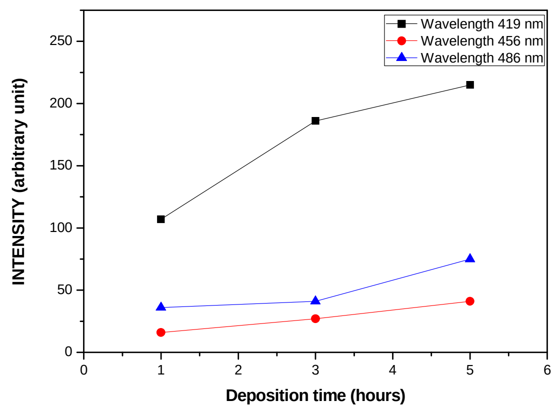


*Fig.15. The deposition time dependence of the PL intensity of the $CuBiS_2$ thin film prepared for $60^0C$ (Emission wavelength 419 nm).*

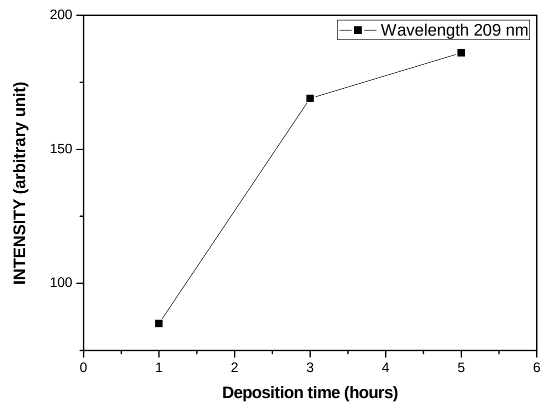


*Fig.16. The deposition time dependence of the PL intensity of the $CuBiS_2$ thin film prepared for $60^0C$ (Excitation wavelength 209 nm).*

The emission peaks occur at higher wavelength than that of absorption peaks. In fact, the peak emission wavelength is invariably shifted towards red end of the spectrum compared to the peak of the absorption spectrum. This phenomenon is known as the Stoke's shift, which finds commercial application in the fluorescent lamps [7]. The luminescence increases with the bath temperature and deposition time period due to the improved crystallinity of the films. The peak intensity in the case of higher temperature films (up to $60^0C$) is much higher compare to that of lower temperature films. This could be due to shape effect. The shape of the materials has an important effect on the PL intensity [8]. All the emissions are associated with defects emerging during the growth of crystallites and are related to deformation of crystallanity due to dislocations and large vacancies [9].

## 4. Conclusions

A strong emission peak is observed at 419 nm. The excitation wavelength was 209 nm. PL emission intensity increases with bath temperature up to $60^0C$ and deposition time period. The emission peak occurs at a higher wavelength than that of the absorption peaks. In fact the peak emission wavelength is invariably shifted towards red end of the spectrum compared to the peak of the absorption spectrum. This phenomenon is known as the Stokes shift.

## References

[1] Y.Chen, D.Bagnall, T.Yao, Material Science and Engineering, **B 75**, 190 (2000).
[2] P.Kumbhakar, D.Singh, C.S.Tiwary, A.K.Mitra, Chalcogenide Letters, **5** (12) 387-394 (2008).
[3] P.Sharma, K.Sreenivas, K.V.Rao, Journal of Applied Physics, **93**, 3963 (2003).
[4] S.H.Pawar, A.J.Pawar, P.N.Bhosale, Bulleten of Materail Science, **8** (3) 423 (1986).
[5] P.S.Sonawane, P.A.Wani, L.A.Patil, Tanay Seth, Materials Chemistry and Physics, **84**,221-227 (2004).
[6] V.Balasubramanian, N.Suriyanarayanan, S.Prabahar, S.Srikanth, Chalcogenide Letters, **8** (10) 637-648 (2011).
[7] J.J.Zhu, X.H.Liao, J.Wang, H.Y.Chen, Mater.Res.Bull. **36** 1169 (2001).
[8] J.Wilson and J.F.B.Hawkes, Optoelectronics-An Introduction II Edition, Prentice Hall of India Publication, New Delhi **113** (1999).
[9] Yongbin Xu, Zhongming Ran, Guanghui Cao, Weill Ren, Kang Deng, Yunbo Zhong, Cyst.Res.Technlol. **44** 851 (2009).