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MODIFICATION OF STRUCTURAL AND PHOTOLUMINESCENCE PROPERTIES OF ZrO_2 THINFILMS BY COPPER (Cu) DOPING

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Homogeneous and transparent Cu doped ZrO_2 thin films were prepared by sol–gel dipcoating method. Theundoped film have mixed phase of tetragonal and monoclinic.When the films doped with Cu there is only Monoclinic phase was observed. The grain sizes of the films were increased with increasing Cu dopant.The PL intensity of ZrO_2 thin films increased with increase in Cu concentration. Doping with cations (Cu^{2+} ions) withavalencelowerthanZr^{4+} can createoxygen vacancies inthecrystallatticeduetothenecessityofcharge balance. Hencetheprepared Cudoped ZrO_2 thin films canbeappliedinnanoscalephotonicdevicessuchaslenses,switches,waveguidesetc.

Keywords: **Zirconia, dip coating, Copper -doped zirconia, Thin films, Sol–gel, Photoluminescence**

1. INTRODUCTION

Zirconia (ZrO_2) is widely used as an essential material in the optical fields including broadband interference filters and active electro-optical devices due to its excellent optical properties, such as high refractive index, large optical band gap, low optical loss and high transparency in the visible and near infrared region. It has wide band gap andshort wavelength photoluminescence (PL) emission property[1-3].

Pure ZrO_2 usually contains various intrinsic defects such as Zr vacancies, interstitial Zr, O vacancies and interstitial O [4]. These intrinsic defects form either acceptor level or donor level in the band gap that would greatly affect the luminescent properties of ZrO_2. It is now well known that the metal doped ZrO_2 has the high potential for fabricating novel nanoelectronics and optical devices with enhanced performance. The metal ions used as dopants are generally of smaller size and lower valence (thanZr^{4+}ions) that may result in a decrease in the unitcell volume and generation of positive holes with lattice deffects (oxygen vacancies).The size of ionic Cu is small (ionic radius 73Å Cu^{2+}), compared with the ionic size of Zr^{4+}(ionic radius 80Å for Zr^{4+}). It is well known that chemical doping greatly influences the structural,electronic and optical properties of ZrO_2. By introducing extrinsic dopant Cu, the defect environment is changed whether the Cu atom substitutes the zirconia atom or it occupies the interstitial site. Control of defects is, therefore, vital in achieving viable applications of ZrO_2. Therefore, it would be worthy to investing at the doping effect on the luminescent properties of Cu doped ZrO_2.

In this study, Cu -doped ZrO_2 thin films with Cu (1&3%) molar concentrations were prepared by sol–gel method. The aim of the investigation was to find the influence of Cu incorporation on the structure, optical and luminescence properties of ZrO_2 thin films.

2. EXPERIMENTAL DETAILS

In the present study, inorganic precursor route was chosen for the fabrication of nanocrystalline transparent zirconia thin films. Zirconium oxy chloride octahydrate ($ZrOCl_2.8H_2O$) (Sigma-Aldrich 99.5%) was used for the preparation of the precursor solution. A homogeneous solution (2wt%) of zirconium ox chloride octahydrate in 1-butanol and ethanol (in the ratio 1:1) was prepared, by mixing 1mol of zirconium oxy chloride octahydratein $^1/_2$ of the total volume of mixed 1-butanol and ethanol. The solution wasstirred for 45 minutes using magnetic stirrer. The water for hydrolysis, nitric acid for oxidation and acidic acid for stabilization in the ratio of, Water: $HNO_{3:}$ Acidic acid = 20: 0.4: 3 were then added to the salt-alcohol solution. Subsequently, the rest of 1-butanol and ethanol mixed with the required amount of acetic acid and Cu (for1-3mol% of Cu) was added under vigorous stirring in a controlled manner. The stirring was continued for another 90 minutes to get a clear transparent sol-solution. The precursor solution thus prepared was deposited on clean glass substrate susingalocally-built dip-coating apparatus.

The dip coating parameters were optimized depending on the viscosity and concentration of the precursor solution at 5cm/min lifting speed and 90^0 vertical lifting. The dipcoated films were dried at room temperature and then heated to 100^0C attherateof4^0C/min in air.Films were maintained at this temperature for 1h for the evaporation of moisture and organic impurities. This process of coating and drying was repeated 8times to obtain films of appropriate thickness for X-raydiffraction(XRD) analysis. Then the films were annealed at 500^0 C for crystallization. The structural and Photoluminescence characterizations of these annealed films were then performed.

3. RESULTS AND DISCUSSION

3.1. Structural analysis

Fig. 1.1 shows theXRDpatternoftheundopedZrO_2 film. The XRD pattern revealed a mixed phase of tetragonal and monoclinic ZrO_2 with preferred orientations along T(111)and M(−111). Figure 1.2 shows the Cu doped (1 and 3%) ZrO_2 thin films annealed at 500 °C.The XRD pattern revealed only the monoclinic phase of ZrO_2 with preferred orientation along M (111) plane. No metallic characteristic peaks have been detected.The grain size (D) of the nanocrystalline films were calculated fromthe FWHM of XRD using Scherrer equation [6]

$$D = \frac{k\lambda}{\beta cos\theta}$$

Where D is the grain size, K = 0.9 a correction factor, β the full width at half maximum (FWHM) of the most intense diffraction peak, λ thewavelength of X-ray and θ, the Bragg angle. Table 1 summarizes the diffraction angle, crystalline phase, d- spacing and grain size of undoped and Cu doped Zirconia thin films. The grain sizes werefound to increase from 10.3 nm to 71.2 nmwith increase in Cu doping. This is due to the agglomerationof the grains of ZrO_2around the dopant.Generally the addition of a catalyst stops isotropic agglomeration ofparticles; instead anisotropic agglomeration occurs resulting in growthof particles in certain direction [7].The change in stress of the films is owing to the change in boundaries between grains and the crystalline phase completely transformed into monoclinic.

Table 1

Sample	Diffraction angle2θ	Crystalline phase	d-spacing[Å]	Grain size (nm)
undoped	30.29	T(101)	2.9	
	31.6	M(111)	2.86	10.3
Cu doped 1%	31.64	M(111)	2.8	65.0
Cu doped 3%	31.55	M(111)	2.82	71.2

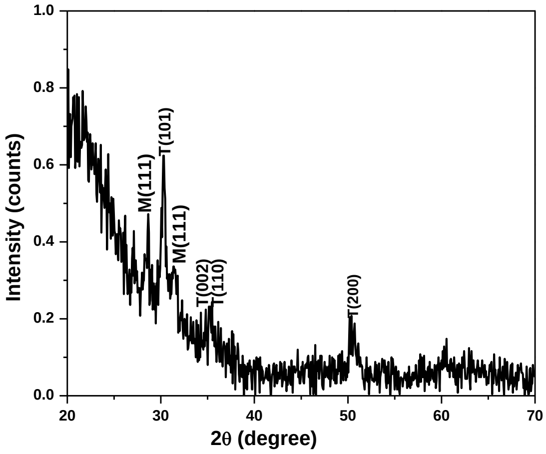

Fig .1.1 XRD Pattern of undoped ZrO$_2$ thin films annealed at 500^{0}C

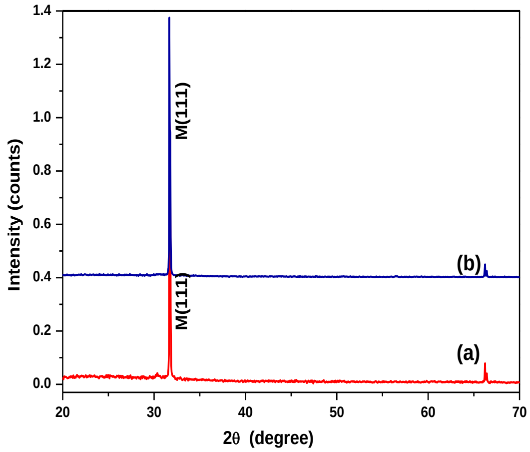

Fig .1.2 XRD Pattern of (a) 1% and (b) 3% Cu dopped ZrO$_2$ thin films annealed at 500^{0}C

3.2. PHOTOLUMINESCENCE STUDY

Fig. 2.1 shows the photoluminescence (PL) spectra of the undoped ZrO_2 thin film annealed in air at 500 °C. All the films were excited with 243nm. The energy gap of tetragonal ZrO_2 phase is greater than 5.5 eV. Monitoring the 390 nm emission band [9] has revealed that the excitation at 243 nm (5.11 eV) produced a large intensity. The excitation band at 243 nm corresponds to energy near the energy gap of ZrO_2 tetragonal phase and has been assigned to grain boundary defect states, that are an inherent aspect of the nanocrystallinity [10]. The PL spectrum of undoped zirconia thin film (Fig. 2.1) exhibits an intense near band edge emission peak at 392 nm.The intense zirconia emission peak at 392 nm in the ZrO_2 thin film can be due to the ionized oxygen vacancies (F and F^+centers) from the conduction band. Generally UV emission can arise as a result of the radiative recombination of a photo generated hole with an electronoccupying the oxygen vacancy[3]

Figure 2.2(a) & (b) shows the PL spectra of 1% and 3% Cu doped ZrO_2 thin films. An additional emission peaks in the range of 350–550 nmhave been observed in the prepared1% Cu doped ZrO_2 thin film. The PL peaks were located around 411, 433 (blue) and 460 nm(blue) respectively. These peaks were due to the redox properties of various valence state of Cu in ZrO_2. The blue emission in the wavelength range of 440–500 nm arised from the singly ionized associated oxygen vacancy defects (AOD^+ centers) [11]. From the observations, we conclude that the AOD^+ centers formed by the substitution of Cu^+ along with Cu^{2+}. At the temperature of 500 °C, the oxidation is low when compared to the high temperature. It is noted that, the associated oxygen vacancies have been created due to Cu^{2+} doping, and it is more dominant than that of temperature effect. Figure 2.2 (b) reveals the blue emission increases with the increase in Cu dopant. At these points, it should be noticed that this type of luminescent materials can be applied in electroluminescent flat panel displays, color plasma display panels, fluorescent lamps, and cathode ray tubes. In our previous studies [3], when the ZrO_2 thin films doped with Al and annealed at high temperature, the intensity of this (4.07 eV) peak increased, which is related to the trapped positive charge in the metal dioxide. In Cu doping in ZrO_2 film, due to the redox properties of various valence states of Cu in ZrO_2, the amount of trapped positive charges changed.

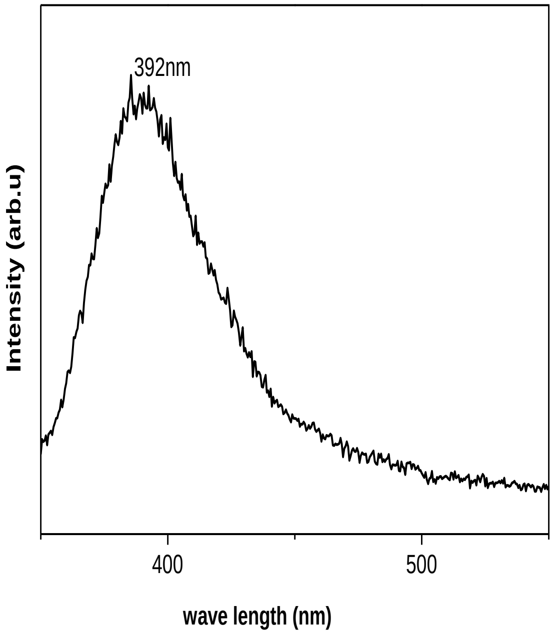

Fig 2.1 Photoluminescence of undoped ZrO_2 thin film

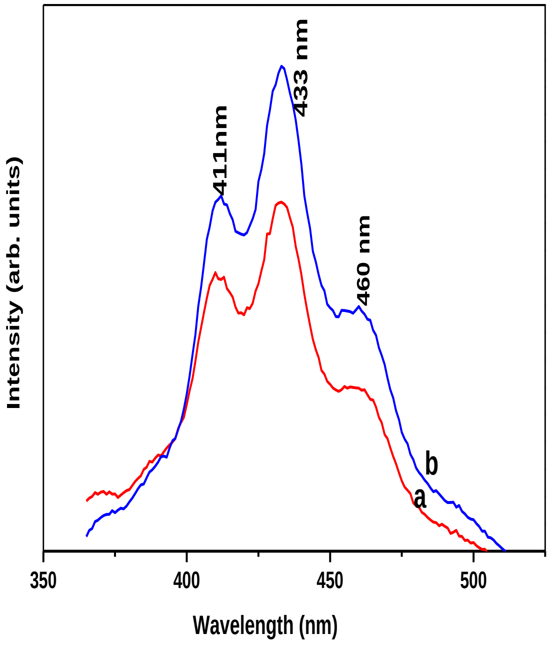

Fig 2.2 Photoluminescence spectra of Cu doped (a) 1% and (b) 3% ZrO_2 thin films

IV. CONCLUSION

Homogeneous and transparent undoped and Mn doped ZrO_2 thinfilms were prepared by sol–gel dip coating method. The XRD pattern ofthe undoped ZrO_2 thin film revealed a mixed phase of tetragonal andmonoclinic ZrO_2 with preferred orientations along T(111) andM(111). The films doped with Cu the monoclinic phase was stabilised. The PL peaks were observed for Cu doped ZrO_2 located at 411, 433 (blue) and 460 nm(blue)due to the redox properties of variousvalence states of Cu in ZrO_2. Thus Cu doped ZrO_2 materialscan find wide applications in optoelectronic devices, electroluminescentflat panel displays, color plasma display panels, fluorescent lamps,cathode ray tubes, etc.

REFERENCES

[1]I.JohnBerlin,J.S.Lakshmi,S.SujathaLekshmy,G.P.Daniel,P.V.Thomas,K.Joy, J. Sol–Gel Sci.Technol.58(2011)669.

[2]I.JohnBerlin,V.S.Anitha,P.V.Thomas,K.Joy,J.Sol–Gel Sci.Technol.64(2012) 289.

[3]I.JohnBerlin,L.V.Maneeshya,K.T.Jijimon,P.V.Thomas,K.Joy,J.Lumin.132 (2012)3077.

[4]I.JohnBerlin,S.Sujathalekshmy,P.V.V.Thomas, Ganesan,K.Joy,ThinSolid films 550(2014)199.

[5] I.JohnBerlin,K. JoyPhysicaB457(2015)182–187

[6]B.D. Cullity, S.R. Stock, Elements of X-ray Diffraction, third ed. Prentice Hall, Upper

[7] Saddle River, 2001. 388.M.K. Hossain, S.C. Ghosh, Y. Boontongkong, C. Thanachayanont, J. Dutta, J. Meta. Nanocryst.Mater.23 (2005) 27.

[8] D. Kohl, M. Henzler, G. Heiland, Surf. Sci. 41 (1974) 403.

[9] J.S. Lakshmi, I. John Berlin, Georgi P. Daniel, P.V. Thomas, K. Joy, Physica B 406 (2011) 3050.

[10] K. Joy, L.V. Maneeshya, K.T. Jijimon, P.V. Thomas, Thin Solid Films 520 (2012) 2683.

[11]Z. Wang, B. Yang, Z. Fu, W. Dong, Y. Yang, W. Liu, Appl. Phys. A 81 (2005) 691.