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Physical Properties of CBD Based ZnO-SiO_2 Core-Shell Composite Thin Films

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Abstract

Chemical bath deposition was used to fabricate ZnO-SiO_2 composite core-shell thin films for different concentrations at pH 10.8. SEM micrographs of thin film with optimized concentration showed uniform surface coverage and nest like morphology of the crystallites. Absence of impurities in the EDX spectra revealed the formation of good quality ZnO-Silica composite film. FTIR study suggested that linkage between ZnO and silica was improved in the thin film.

Keywords : CBD, Core shell thin film, FTIR, EDX, SEM,

1. Introduction

ZnO nanostructures have gained importance due to their specific properties which may be utilized in many potential device applications. Being cost-effective, zinc oxide may replace very expensive materials in different applications. It is found to be a suitable candidate for optoelectronic devices such as solar cell [1,2], chemical sensor for some gases [3,4] biosensors for detection of biomolecular interactions [5],luminescent and electrical devices, vacuum fluorescent displays(VFD), solid state white light source[6], textiles[7], sun screen due to UV absorption property etc. ZnO is an II-VI semiconductor possessing wide band gap energy of 3.37 eV at room temperature [8]. It may replace toxic CdS buffer layer which is placed between window layer and absorber layer in thin film CuIn(Ga)Se_2 (CIGS) solar cells [9]. Polycrystalline thin films of ZnO can be prepared by different methods such as spray pyrolysis [10], sputtering [11], pulsed laser deposition[12], sol-gel[13], physical vapor deposition[14], chemical bath deposition (CBD)[15] etc. Among these various techniques, CBD is the simplest and the most economical method. In the present study, attempts were made to deposit ZnO-SiO_2 nano composite thin films using CBD in order to improve physical and optical properties of the deposited films as compared to pure ZnO [16]. These films were investigated for the structural and optical properties.

2. Materials and Methods

We report deposition of composite core shell thin films of ZnO-SiO_2 using CBD with Zinc nitrate, HMTA and TEOS as precursors and investigated their structural and optical properties. The deposition was carried out using a two step process i.e. coating of ZnO seeds on the glass substrate and further growth of thin films on the seeded substrate. After cleaning the substrate properly using chromic acid and ethyl alcohol, they were dipped in milliQ water and

ultrasonicated for 15 min. The glass slides were finally dried in hot air at 100°C for 3h. Zinc acetate dihydrate ($Zn(CH_3COO)_2.2H_2O$) was procured from Sigma Chemical Co., USA. Absolute ethanol AR grade was from S.d.fine Chemicals, Mumbai, India. These chemicals were directly used without further purification. For deposition of seed layer[17] on the substrate, 25mM of $Zn(CH_3COO)_2.2H_2O$ in absolute ethanol solution was used. In order to obtain thick dense seed layer, the glass slides were further dipped in the above solution at 65°C for 2 h in an oven, rinsed with distilled water and finally dried at 100°C for 30 min.

For deposition of thin films, a set of four baths were prepared using different concentrations of equal volume of aqueous solutions of $Zn(NO_3)_2.6H_2O$ and HMTA as mentioned in Table No.1,mixing them using an ultrasonicator for 15 min. Based on our earlier findings[18] pH of each bath was adjusted to 10.8 using 1N NaOH. 0.5 ml of tetra ethyl orthosilicate (TEOS) was added to each bath, and was thoroughly mixed for 15 min using an ultrasonicator. The seeded substrates were dipped in the above prepared baths and were kept in an oven at 90°C for 2 hours and were finally air dried. Scanning electron microscopy (SEM, HITACHI model S 3700N) was used to observe the morphology of the particles in the thin films. Elemental phase composition of as deposited films was analyzed using energy dispersive X-ray Spectroscopy (EDX) (HITACHI model S 3700N). FTIR spectra were conducted using Shimazdu IR Affinity-1S.

Table No.1: Growth Parameters for Thin Films of ZnO: SiO_2 deposited at different Concentrations

Sample code	$Zn(NO_3)$Conc.	HMTA Conc.	pH	TEOS (ml)	Deposition Time(hr)	Deposition Temp(°C)
S1	25mM	25mM	10.8	0.5	2	90
S2	50mM	50mM	10.8	0.5	2	90
S3	75mM	75mM	10.8	0.5	2	90
S4	100mM	100mM	10.8	0.5	2	90

3. Result & Discussion

Here $Zn(NO_3)_2.6H_2O$ act as a source of Zn^{2+} ions while HMTA plays a dual role i.e. a weak base as well as a chelating agent thereby inhibiting the rapid precipitation of zinc hydroxide [19,20]. By controlling the pH of the bath and concentration of Zn^{2+} in an oriented manner HMTA promoted heterogeneous growth over homogeneous growth thus avoiding a high ZnO saturation index. Chemical structure of TEOS revealed the presence of an alkoxy silane with four alkoxyl groups, out of which one group may be hydrolysed and thus react with the OH^- group on the hydroxylated ZnO surface under basic conditions[21]. The hydrolysis rate of TEOS was increased with increase in pH and also due to the presence of ammonia released in the bath during decomposition of HMTA. Ammonia also acts as a catalyst besides controlling Zn^{2+} ion

concentration. By increasing the pH above 5 (pI of silica is 2) the –ve charge on silica increases rapidly[22]. This leads to an electrostatic interaction with positively charged ZnO (pI of ZnO is 9.2) and as a result ZnO:SiO_2 composite were formed. Growth parameters of as deposited thin films are mentioned in Table No.1.

3.1 Structural Study

3.1.1 Morphological Study

Figure 1 shows the SEM images of the samples deposited at different concentrations and revealed that only in the sample S4(Figure 1(d)), the substrate has been fully covered with nest type morphology of thin films. This may be due to the reason that with an increase in the concentration, more number of nuclei will be available to grow and hence will improve the rate of deposition. Coverage of the thin film of ZnO nanoparticles with amorphous silica improved the degree of dispersion. Overgrowth of some rod shaped ZnO crystals was observed above the surface indicating typical nature of ZnO. Similar Nanoporous structure with perpendicular pores were also reported in literature[23].

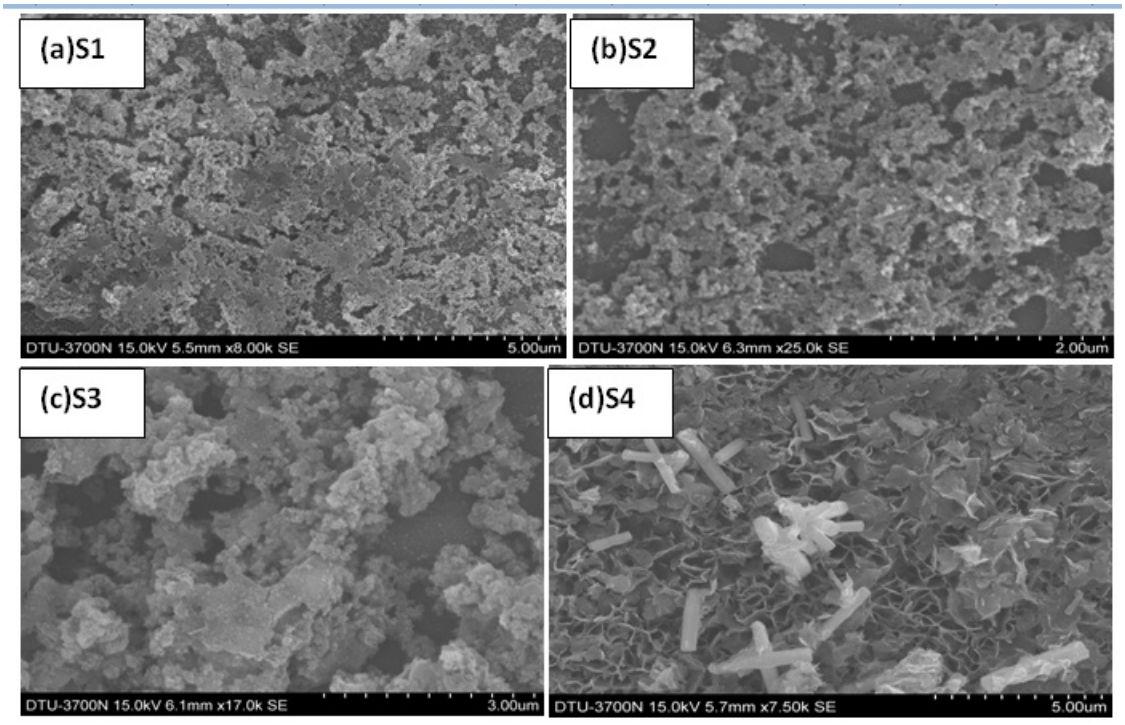

Figure 1: SEM Images of Thin Films of ZnO: SiO_2 at different Concentrations

3.1.2 Elemental Analysis

SEM- EDX was used to confirm the qualitative elemental composition of the thin films prepared at different concentrations. The presence of Zn, O and Si was confirmed by corresponding EDX peaks(Figure 2). The presence of small amount of Ca, Al and K in the EDX spectra of S1, S2 and S3 samples suggests incomplete coverage of substrates. The absence of any other element in the EDX spectra of sample S4 suggested the high purity of the nano-composite thin films. Au peak is from gold coating of the sample.

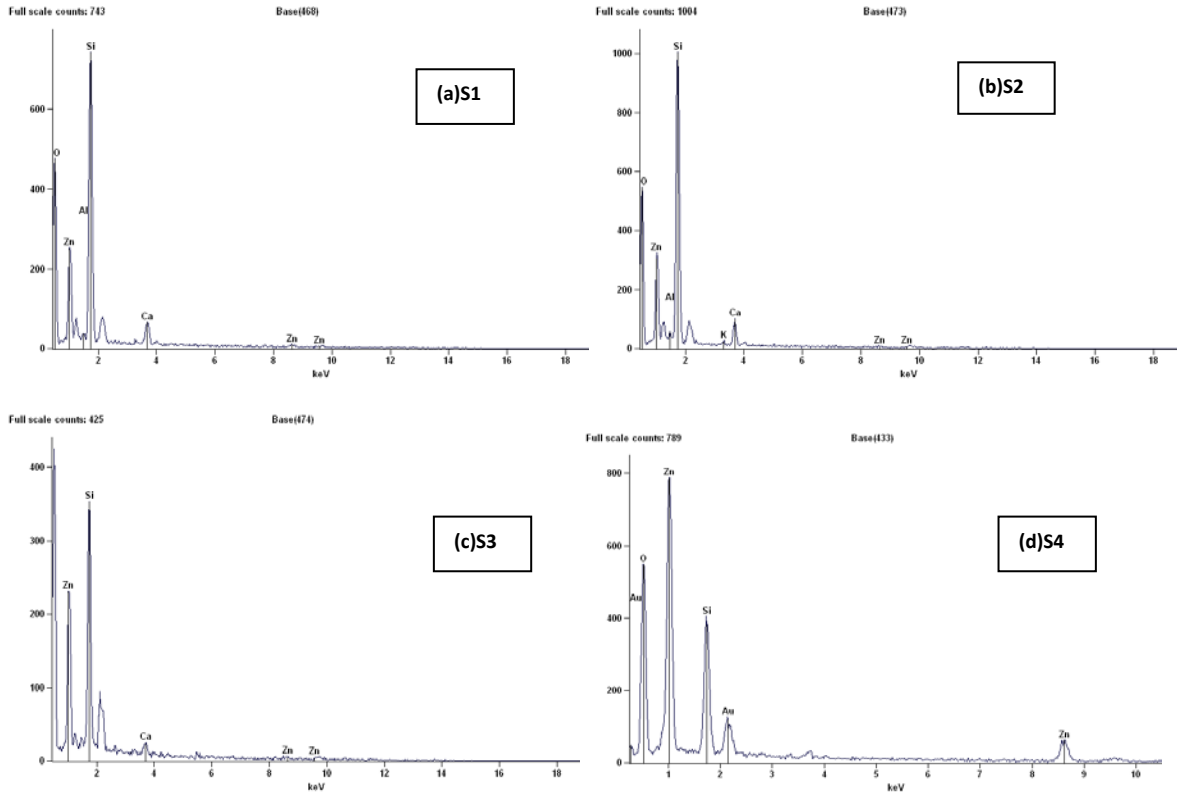

Figure 2: EDX Images of Thin Films of ZnO: SiO_2 at different Concentrations

3.1.3 FTIR Study

IR analysis revealed the presence of an interphase band between ZnO and Silica at 887 cm^{-1} in S4 (Figure3(d)).The shift in the band of silica at 910 cm^{-1} (Figure.3(e)) towards lower wavenumber i.e. to 887 cm^{-1} suggested a change in the local bonding structure of Silica(Fig.3(d))and thus showing the interaction of ZnO with Silica. The weak band around 1350 cm^{-1} and the weak peak at 2330 cm^{-1} in all the samples were assigned to N=O group and carboxylates respectively[24]. A weaker broad band around 3340 cm^{-1} could be assigned to the O-H stretching vibrations in H bonded water on the ZnO surface in sample S1and S2. This band

can be crosschecked through a weak 1635cm^{-1} band due to scissor bending vibration of molecular waterin S1 and S2. Absence of impurities in sample S4 (Figure3(d)) revealed the formation of good quality ZnO-Silica composite film.

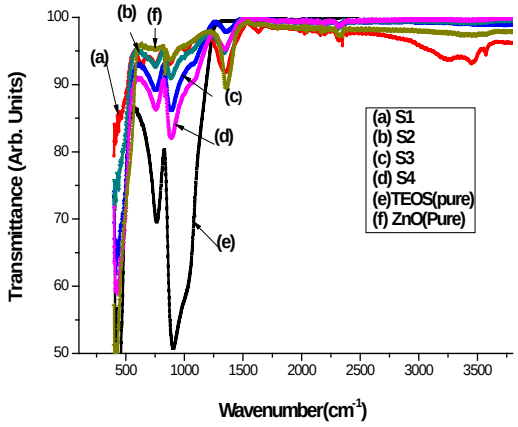

Figure 3: FTIR Spectra of ZnO: SiO_2Thin Film at different concentration

4. Conclusion

Transparent ZnO-SiO_2 composite thin films were successfully grown on seeded glass substrates by chemical bath deposition at different concentrations. It was observed that to obtain good quality thin films, equal volume of equimolar(100mM) aqueous solutions of $Zn(NO_3)_2.6H_2O$ and HMTA mixed with 0.5 ml of TEOS were used in the chemical bath for a deposition time period of 2hours at pH 10.8. The optimized deposition parameters were used for further investigation to fabricate ZnO–SiO_2 composite nano-crystalline films with optimum combination of improved physical and structural characteristics.

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