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Synthesis and photoluminescence property of nanostructured sol–gel antimony tin oxide film on silica glass

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ABSTRACT

Sol–gel based spin coated nanostructured films of tetragonal phase of antimony (10 at%) doped tin oxide (ATO) were prepared on silica glass. XRD and TEM images identify the crystallite size lying in the range, ~3.4–9.8 nm. Quantum confinement was observed in the nanoclusters. Evaluated band gaps at 3.62 eV correspond to the transition for bulk ATO and 4.51 eV, 5.26 eV for excitons and oxygen deficiency. Schemes have been proposed for absorption and photoluminescence excitation (PLE). Two excitonic transitions were observed at 275 nm and 310 nm for different nanocluster sizes. Evaluation of mean free path and Fermi energy correspond to ionized scattering and degeneracy of the ATO films.

1. Introduction

Quantum confinement effect of semiconductors [1–5] has been focused recently to the development of pure or doped nanoparticles/nanoclustures, close to the size of Bohr radius [1] either in powder or in the form of thin film. These materials have potential application in photonic devices [6,7] due to their non-linear optical (NLO) properties. Transparent conducting oxides (TCO) can be promising for NLO materials if their nanoclusters are suitably confined to generate excitons by the combination of electron and hole on exposure to electromagnetic radiation. An added advantage of these materials is its visible transmissivity due to their wide band gap property [8], which are of much interest for blue and ultra-violet (UV) optical devices [9], such as light-emitting diodes and laser diodes. As a wide band gap semiconductor, SnO_2 and doped SnO_2 may have potential applications in the areas of solar cells, chemical sensors for their transparency in the visible region and electrical properties. But for photonic applications, attention is presently being paid to study the photoluminescence (PL) properties of nanostructured SnO_2 [7,10,11] for the quantum confinement effect in nanoclusters in presence of electromagnetic radiation. Oxygen deficiency can also give rise to PL property. To obtain the high performance NLO properties in SnO_2 film, modulation of the band gap is required by making the film material in nanostructured form having size close to Bohr radius provided the lattice constants of clusters would not vary [12] with the size. In addition, binding energy of exciton should be relatively high. In the case of nanoclustered films of undoped and doped SnO_2 this property [13] has been observed. The NLO property is very much dependent on the formation of electron hole pair i.e., exciton in the nanoclusters by the interaction of electromagnetic wave. Accordingly PL intensity would increase for the population inversion of excitons which may exist as free state or bound state. The bound state occurs only when the excitons are trapped in the potential well of defect centers [14,15]. Emissions for both bound and free excitons would occur if $E_{ex} > <E_g$ [16,17] while if the excitation energy (E_{ex}) be equal to the band gap (E_g) of exciton, then emissions for only bound excitons will appear. It is observed in nanoclustered ITO system that the PL intensity for free exciton is relatively high if $E_{ex} > E_g$ [17]. Hence, detection of E_{ex} in doped SnO_2 nanoclusters is an important objective for obtaining relatively high population inversion of free excitons having considerable binding energy. Therefore the present objective is to find out nanoclustered doped SnO_2 system for the generation of high quantum of free exciton at ambient temperature overcoming the PL arising from the defect centers. Attempt has been made by various research groups to study nanosized SnO_2, prepared by different methods such as chemical vapor deposition (CVD) [18], magnetron sputtering [19] but this type of study was not done at all for sol–gel based product. We have followed sol–gel processing, as it is a simple technique for the preparation of chemically homogenous, high-purity nanoclustered films of multicomponents. In addition, this report is also the first step to explain the origin of the PL of the defect centers.

2. Experimental

Sol (L1) corresponding to 6 wt% equivalent SnO_2–Sb_2O_3 maintaining Sn:Sb atomic ratios as 90:10 were prepared in alcoholic medium. The required amount of recrystallized hydrated stannic chloride (Loba Chemie) was dissolved by a few ml of ethyl alcohol

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(dehydrated, Bengal Chemicals and Pharmaceuticals Ltd., India) and 1-propanol (E-merck India Ltd., for synthesis) solvent mixture (1:1, by volume) and stirred for 15 min. Similarly, required amount of Antimony (III) chloride (E-merck, India, purity ~98%) was dissolved and stirred separately for 15 min in the same solvent mixture. Next, the antimony chloride solution was added to the tin chloride solution slowly and 2–3 drops of 10.5 (M) HCl was added to the mixture in order to increase the solubility of antimony chloride and to prevent the precipitation of antimony oxy chloride. The solution was stirred for 1 h and aged for 48 h for coating. Films (L11A, L12A, L13A) of (953–1714) ± 3 Å thickness (measured by Autogain L116B ellipsometer) was developed on Heraus make (Germany) Suprasil grade pure silica glass by the spinning technique (Convac, 1001) in 10 000 class clean air room equipped with 100 class work station. The spinning rpm was 1500. After each deposition the films were cured in a closed chamber at 480 °C for 0.5 h. The surface morphology and the cluster size distribution of nanostructured antimony tin oxide film were studied by transmission electron microscopy (TEM) [(Jeol 2110), and (Tecnai G^2 30.S-Twin, FEI company, Netherlands)]. Carbon coated 300 mesh Cu grid was used for TEM images. Crystalline phase was identified by XRD pattern obtained from an X-ray diffractometer [Philips PW-1730 (Ni-filtered Cu K_α radiation)]. UV–vis absorption and photoluminescence (PL) spectra were recorded using Shimadzu UV–vis–NIR model (3101PC) spectrophotometer and Perkin Elmer fluorimeter (LS55) respectively. Hall mobility (μ), free electron carrier concentration (N) and resistivity (ρ) in a magnetic field of 0.51T (Tesla) of the samples were measured at room temperature by HEM 2000 (EGK Corporation, Korea) using four probe van der Pauw method.

3. Results and discussion

On the basis of our previous work [20] it is known that there is always a loss of antimony in the film during the sol to oxide layer transformation due to sublimation effect of Sb-components. We

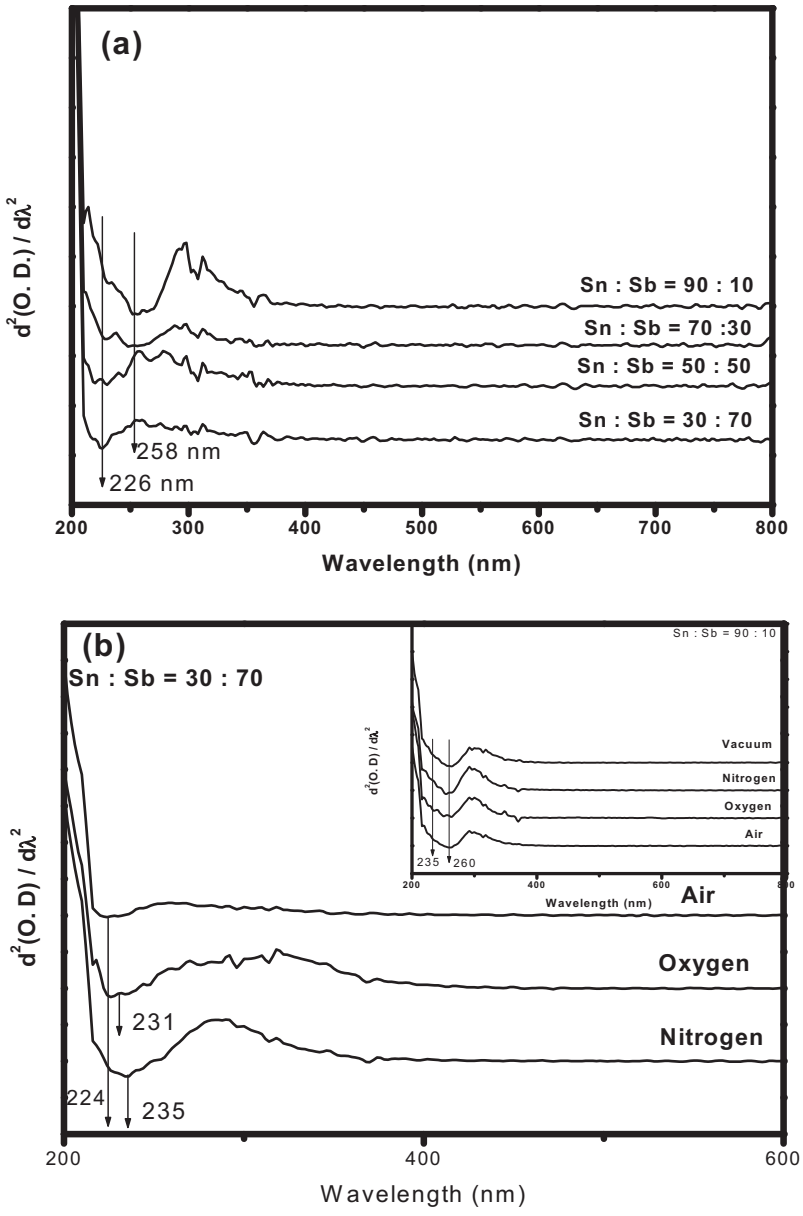

Figure 1. 2nd derivative of absorption spectrum of (a) different tin content film cured in air and (b) low tin content (Sn:Sb = 30:70) cured in different atmospheres (inset, 2nd derivative of absorption spectrum of high tin content film (Sn:Sb = 90:10) cured in air).