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Controlling the photoluminescence of ZnO:Si nano-composite films by heat-treatment

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ABSTRACT

Nano-composite thin films of silicon and zinc oxide were deposited on glass substrates using thermal co-evaporation. On heating the films at different temperatures and different atmospheric pressures, the photoluminescence (PL) emission spectra become broad, giving emissions in UV-Blue, Green and Red region. Analyses reveal that defect-dominated structure of ZnO contributes to the broad PL spectra observed. X-ray diffraction and Raman spectra analysis show that the defects caused by oxygen vacancies decrease with heating which is accompanied by a competing process of decrease in grain size made possible by surrounding silicon reacting at the surface of the ZnO nano-cluster grains giving new bonds, possibly O–Si–Zn bonds. Crystallinity of nano-grains and defects contribute different emission peaks that depending on relative contributions can give comparable peaks resulting in broad emission spectra. The study shows that simple post-deposition process can lead to fabrication of white light emitting devices based on these nano-composites. Best emission spectra are obtained by heating at a temperature of 250 °C in low vacuum.

1. Introduction

Recent research in Material Science has been directed in developing white light emitting diodes. Higher efficiency at lower energy requirement makes LEDs an environmentally friendly candidate. Basic efforts in this quest have been directed towards the study of zinc oxide in the nano-regime. Zinc oxide has stood out as a promising candidate since it is a direct band-gap semiconductor whose band-gap lies in the UV region [1,2], however, it also emits various wavelengths on excitation due to the energy levels appearing within the band-gap due to defects, etc. Emissions from UV to yellow region by ZnO have been reported [3–9]. However, a notable omission from the visible spectra is the wavelengths in the red region. To this effect, materials in the nano-regime hold promise where the band-gap's dependence on crystal size implies one can obtain emissions of different wavelengths by controlling the cluster sizes. Silicon in nano-regime emits in the red region [10,11]. Trivial logic argues that a mixture consisting of both ZnO and silicon (such that their individual emission properties are retained and if possible new lines are emitted) can develop as a candidate for future white light LEDs.

Back in 2003, Liu et al. [12] reported that it was difficult to fabricate ZnO nano-crystals embedded in a solid matrix. Concerted efforts led to recent success, where composite films of ZnO and silicon were fabricated. In this direction, Pal et al. [13] did interesting work. They sputtered films on substrates using ZnO and silicon targets simultaneously, where ZnO targets were placed on silicon targets. While the emission spectrum became broad, it was clear that more sustained and systematic work was required. Klason et al. [14] grew n-ZnO films on p type silicon wafer and developed hetero-junction LEDs that on forward biasing emitted near white light. Singh et al. [15] presented interesting results where the grain size of ZnO grains was controlled by controlling the size of voids in the porous silicon substrate. On comparing the emission spectra reported by the three groups, as well as on the basis of simplicity of fabrication, Pal et al. results seem to be the best. However, more work has to be done to optimize the conditions of material manipulation in terms of grain size and ratio of ZnO and silicon in the nano-composite.

We also believe that similar results could be obtained by thermal co-evaporation of ZnO and silicon. This would make the fabrication method simple and cost-effective. The preliminary results of our work were reported [16]. The as-grown films showed prominent green emission line other than the 365 nm and 620 nm lines due to ZnO and silicon respectively with a faint peak at 410 nm for some samples. The green emission lines obtained were essentially due to defects that resulted in during film fabrication. It is clear from our initial experience [16] that material engineering would be required for obtaining our objective of getting broad emission spectra from ZnO:Si nano-composites. We believe this

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can be achieved either by (pre-fabrication) varying the ratio of the starting material (namely ZnO and Si), doping or varying substrate temperature or (post-fabrication) by heating the sample in vacuum or air at different temperatures for different durations. In this manuscript we discuss our results of controlling emission spectra of ZnO:Si nano-composites by post-fabrication heat-treatment.

2. Experimental

ZnO:Si nano-composites were fabricated by evaporating a mixture of powdered ZnO and n-silicon mixed in a proportion of 1:2 (by weight). For preparing our starting material, highly pure (99.99%) ZnO in powder form was obtained from Merck (Mumbai). Silicon powder was obtained by crushing a silicon wafer. Since manufacturers of silicon wafers protect the same by growing a passivisation layer of SiO_2, we placed the wafers in HF acid to etch off the oxide layer. The mixture of ZnO powder with crushed and powdered Si was pelletized so that the powdered starting material would not fly off on heating the boat for evaporation. The films were grown in vacuum higher than 10^{-6} Torr using JEOL, JEE 4X vacuum evaporation unit. The films were deposited on microscopic glass slide substrates maintained at room temperature. In this study we have used films of 600 Å (labeled G4) and 900 Å (labeled G7) thickness. The as-grown samples of G4 and G7 were heated in vacuum at 250 °C at regular intervals of 30 min to a maximum of 2 h. Similarly, the samples were heated in air at 400 °C to investigate the effect of oxygen. The samples have been labeled for easy identification. The as-grown G4 sample has been labeled as (a), G4 sample heated at 250 °C in vacuum for 2 h as (b) and G4 heated at 400 °C in air as (c). The G7 as-grown sample is labeled (d), G7 heated at 250 °C in vacuum for 1 h as (f) and G7 heated at 250 °C in vacuum for 2 h as (h). These labels have been maintained throughout this study.

The structural studies were carried out using X-ray Diffractometer (Philips PW 3020). The film structure and defects were further investigated using Raman spectra and photoluminescence. The Raman spectra and photoluminescence were recorded using Renishaw's "Invia Reflex" Raman spectroscope and Jobin Yuon's PL-1039 PL spectroscope respectively. The photoluminescence spectra were recorded at room temperature using 270 nm and 390 nm excitation wavelengths using a 450W Xe lamp source. X-ray Photo-electron spectroscopy (XPS) was used to analyze the chemical composition of our samples. XPS measurements were carried out on a Perkin-Elmer X-ray Photo-electron Spectrometer (Model 1257) with Al Kα (1460 eV) X-ray source. The film's surface morphology and texture were studied using the Scanning Electron Microscope (SEM) JEOL (JSM)-840. In the following sections we enlist the results of the various analyses done on our samples.

3. Results and discussion

3.1. X-ray diffraction and morphological studies

Without exception, all the diffractograms of the 600 Å thick films were unmarked, i.e. the X-ray diffraction of our nano-composites did not show prominent peaks. This was expected as seen in our previous study [16], very thin films failed to give X-ray diffraction peaks. As can be seen from Fig. 1, even after annealing the films, peaks representing crystallinity do not appear. However, the broad hump evident in all three cases (as grown, heated in vacuum and in air) is indicative of the short-range ordering of silicon atoms [16,17]. A comparison of the three diffractograms and the hump therein shows that on heating in air, the hump diminishes in terms of both intensity and width. This suggests either a reduction in ordering or formation of new bonding with heating.

Also, the lack of ZnO peaks that were expected to exist in nano-particle state may be because either their species were low in number or their cluster size was too small. We ruled out the possibility of no ZnO being present in the sample based on evidences gathered from other analytical techniques. Hence to resolve the aspect of zinc oxide's cluster size, we studied our samples under the Electron Microscope. The scanning electron microscopy (not shown here) failed to reveal any granularity at the surface of the films. This would suggest that the films were either amorphous in nature or that the ZnO grains were too small.

Since the structural and morphological analysis of G4 was quite inconclusive, providing information only of the grain size of ZnO clusters at the film surface, we focused structural studies on the thicker G7 samples. Fig. 1 shows even the as-grown samples were crystalline with a lone peak. This lone peak at $\sim 2\theta = 35.7^\circ$ corresponds to the (1 0 1) peak of ZnO (ASTM card No. 36-1451). The nano-clusters of ZnO hence exist with wurtzite structure. Comparing the three diffractograms of Fig. 1, one can see that the XRD peaks are considerably broadened and become broader with heating. This is indicative of very small size particles and in turn existence of nano-crystals whose size decreases with heating. The average crystallite size of the particles in the film can

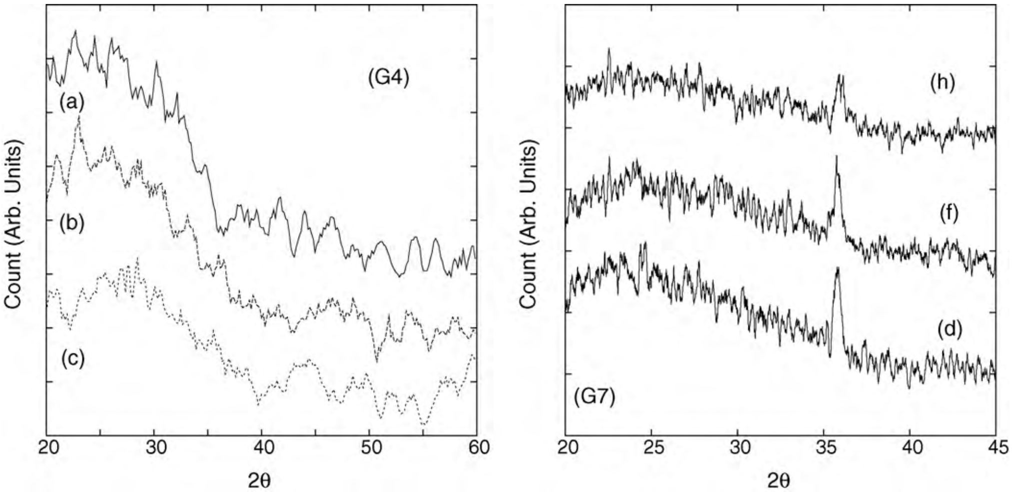

Fig. 1. The XRD diffraction patterns of the (a) as-grown G4 sample, (b) G4 sample heated at 250 °C in vacuum for 2 h and (c) G4 heated at 400 °C in air. Also, shown is the XRD diffractograms of (d) G7 as-grown sample, (f) G7 heated at 250 °C in vacuum for 1 h and (h) G7 heated at 250 °C in vacuum for 2 h.