White and UV emission from swift ion irradiation modified zinc oxide-porous silicon nanocomposite through cathodoluminescence spectroscopy

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Abstract

Modifications in the optical properties of the porous silicon (PS) nanocomposites with zinc oxide after the swift ion irradiation with Nickel ion of 130 MeV are reported. For the first time the PS/ZnO optical properties were studied with cathodoluminescence and the evolution of white PL along with UV emission is being reported after irradiation. The white light emission has been explained with the help of an increase in the deep level defects in the zinc oxide layer after irradiation.

Introduction

Porous Silicon (PS) has been considered as one of the important Si-based luminescent materials since Canham presented the first observation of efficient photoluminescence from PS at room temperature [1]. Its open structure and large surface area, combined with unique optical and electrical properties, make it a good option for templates [2, 3]. In general, the emission energy of PS layers increases with decreasing silicon crystallite size, covering the entire visible spectrum from red to blue [4, 5] and the red-emitting PS can be obtained easily. If the red emission from PS layers could be combined with a blue-green emission from a ZnO film, it would be possible to obtain white light. This combination opens a possible route for a white LED, which is important for display technology. In 2007 and 2009, our group [6-8], reported the white luminescence from the nanocomposites of ZnO-PS deposited by solgel spin coating technique. The origin of the luminescence was discussed by developing a flat band energy diagram, suggesting the basis of electron tunneling between the interface of ZnO and PS through the siloxane structure formed at the interface of Zinc oxide and PS. Recently Kayahan [9] also reported the white luminescence from thin films of zinc oxide deposited onto the n-type macroporous silicon surface by rf-sputtering. The broadband PL spectra were discussed using oxygen bonding model for the PS and the native defects model for ZnO. Apart from that, many groups [10-13] have reported the UV light emission from modified PS. In particular, couple of works by Qin el al. group [10] has reported UV emission from thermally oxidized PS with the peak wavelength of 340 to 370 nm. It was concluded that the luminescence centers in silicon oxide are responsible for UV emission from oxidized PS and SiO_2 powder.

Experimental Details

PS samples were fabricated by wet electrochemical etching [15] of boron doped, (100) silicon wafers with resistivities in the range 0.8 to 1.2 ohm-cm. The anodization was carried out using solution of HF: Ethanol = 1:1 (by volume) under constant current of 30mA/cm^2 and time 429 s. The thickness of the sample was kept 9 micron. After the fabrication, the samples were rinsed by ethanol and dried in pentane. The ZnO films were deposited on microporous substrate using RF magnetron sputtering. The PS substrate temperature was kept at 300 °C during the deposition of ZnO. For the deposition of ZnO film, first the deposition chamber was evacuated to a pressure of ~9x10^{-6} torr by turbomolecular pump backed by scroll pump. The films were deposited in Argon gas atmosphere at a base pressure of ~9x10^{-3} torr during the deposition. The

RF power was 150 watts and deposition was carried out for 30 minutes for these samples. After the deposition the samples were annealed at 700 °C in argon environment.

The annealed film were also irradiated with 120MeV Ni ions using the15UD Pelletron Accelarator at Interuniversity Accelerator centre (IUAC), New Delhi. The samples were mounted on a rectangular shaped ladder and were irradiated in high vacuum (HV) chamber. The focused ion beam of constant current of about ~ 1.5 pnA - was scanned over an area of 1x1 cm^2. The above sample was irradiated with fluence of $1x10^{13}$ ions/cm^2. The PL properties were studied using Varian Fluoroscence spectrophotometer (Cary Eclipse) under the excitation by 325 nm photons using 500 W Xenon lamp. Cathodoluminescence (CL) spectroscopy was done using Jeol JSM 5300 scanning electron microscope using electron beam energy of 15keV. The PL properties were studied using Varian Fluoroscence spectrophotometer (Cary Eclipse) under the excitation by 325 nm photons using 500 W Xenon lamp. Cathodoluminescence (CL) spectroscopy was done using Jeol JSM 5300 scanning electron microscope using electron beam energy of 15keV. CL measurements were performed at 100K in the UV-visible spectral range using Hamamatsu R928P photomultiplier. A SPEX 340-E computer controlled monochromator was used for the spectral analysis. The structural properties of the PS and nano composites were analyzed using high resolution field emission SEM (JSM-7401F).

Results and discussion

The cross sectional view of the composite ZnO-PS structure just after annealing (Figure 1) reveals the overall thickness of PS of approximately 8 µm along with ZnO layer of 450 nm on the top. A close investigation of the structure reveals the microporous (with pore size less than 5nm) morphology of the PS layer (well known in 0.8 to 1.2 ohm cm resistivity) and a well defined interface.

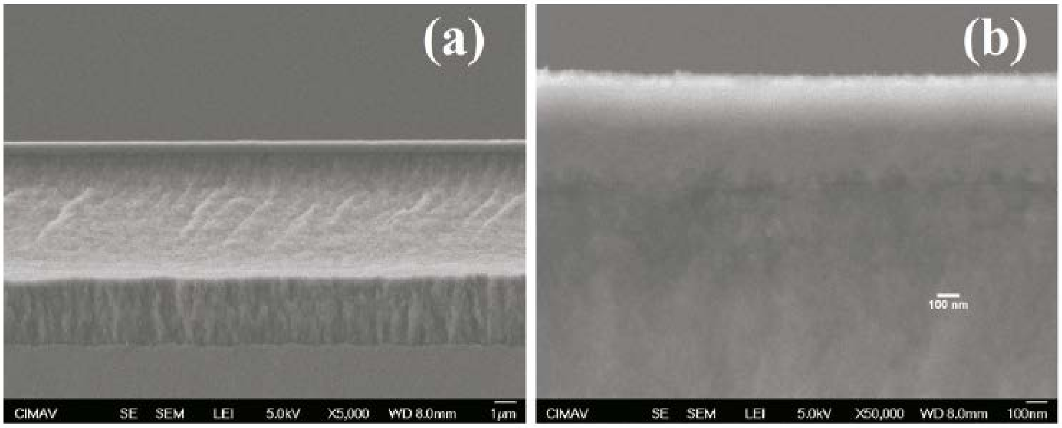

Figure 1: SEM images of ZnO/PS film after annealing at 700 ^{0}C for 1hr showing the cross- sectional view with ZnO layer at the top. (a) ZnO over the PS layer of almost 8 microns (b) a closer view of the zinc oxide layer and the PS –ZnO interface.

Room temperature PL spectrum of the annealed ZnO-PS composite structure (shown in Figure 2a) reveals two dominating peaks centered at 3.17 and 1.7 eV. The PL peak around 3.17 eV could be attributed to the excitonic emission of ZnO [16] and the emission band at 1.7eV is due to PS [1]. A relatively small contribution of different defects in the green blue region has also been observed. In general, for understanding the emission mechanism of the PS/ZnO nanocomposites, we should try to understand the individual contribution of PS and different defect states of ZnO. In ZnO, usually two peaks are most common: (a) a narrow UV emission at around 3.26 eV, due to exciton emission and (b) a broader emission band located in the green part of the visible spectrum. The presence of the green emission has been the subject of investigation and is still not very clear. It could be due to copper/sulfur impurities or intrinsic defects like interstitial zinc ions / oxygen vacancies which could be possible recombination centers. In the recent past oxygen vacancies have been considered the most important factor for the recombination centers involved in the visible luminescence of ZnO.

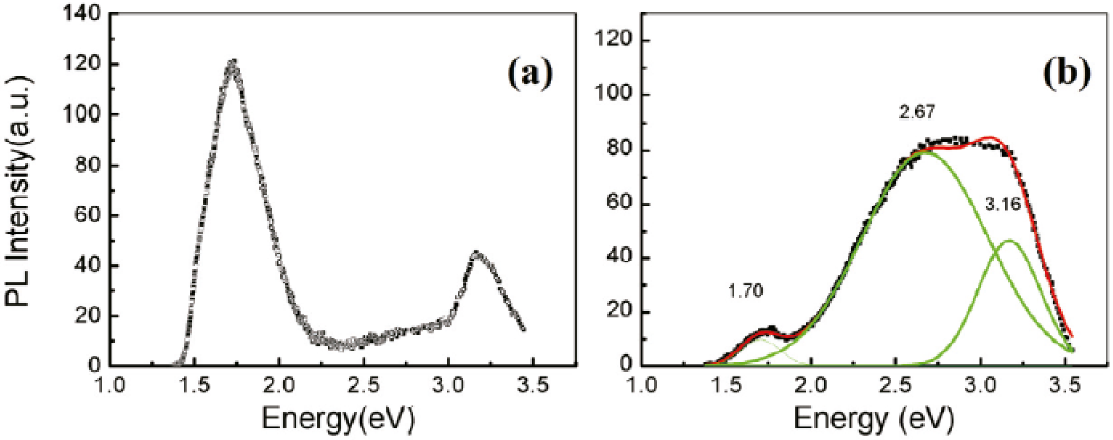

Figure 2: PL spectra of ZnO/PS composite before and after irradiation with130 MeV Nickel ions (a) Pristine: The peak emission at 1.7 eV and 3.2 eV of energy are considered to be due to PS and ZnO respectively. A small contribution of defects from ZnO can be seen in the range 2.2 eV to 3.0 eV (b) after irradiation with 1x10^{13}ions/cm^2 fluence, the contribution due to PS was decreased to 84 % of its original luminescence.

Recently, Dijken et al.[17] have shown the visible emission due to a transition of a photo-generated electron from a shallow level, close to conduction band edge, to deeply trapped holes (a Vo** centre). The surface trapped hole can tunnel back and recombine with an electron in an oxygen vacancy (Vo*), leading to the creation of a Vo** centre, which is a recombination centre for the visible emission.

Now coming back to the understanding of PL mechanism, the changes in the relative intensities of the above mentioned peaks will be analyzed after irradiating the sample (Figure 2b) with 1x10^{13} ions/cm^2 fluence of 130MeV of Nickel ions. After irradiation, the evolution of the broad peak in the visible region can be deconvoluted into two peaks, one centered at 2.67 eV and the other at 3.16 eV. The peak around 2.67eV can be attributed to the transitions generated by amorphous SiO_x formed on PS as previously reported by Arakaki et al [18], (although some works have also attributed such peaks to the transitions between Zn_i states and VZ_n / conduction band to V_{zn} or oxygen vacancies (V_0) [19, 20]. The peak intensity corresponding to 2.67eV has been observed to be increased by 80 % with respect to the pristine sample where the presence of defects is almost insignificant. On the other hand, no significant change in the peak intensity corresponding to excitonic emission (3.16eV) was observed. The peak at 1.70 eV which corresponds to PS has been decreased significantly by 83% and this is in accordance with the results previously reported by Singh et al. [8].

In order to understand the contribution and the evolution of the defect related PL results, CL measurements were taken before and after the irradiation at 100K. Figure 3 shows CL spectra acquired before and after the irradiation with a broad band white light emission from 1.75 to 4.0 V generated from the ZnO film and PS. CL spectra reveals some similarity with the PL spectra (discussed above) with an exception of the evolution of the UV emission peak. The CL spectra shows several well defined shoulders that permitted a deconvolution using Gaussian curves to find four components centered at 2.0, 2.68, 3.24 and 3.8 eV. Similar to the PL spectra, the CL component at 3.24 eV is assigned to the ZnO band edge emission and the component at 2.0 eV is the well-known ZnO-defect related yellow band [21,22]. As mentioned before during the PL discussion, the UV and blue components of 3.8 and 2.68 eV, have been previously reported by Arakaki et al. [18] and have been attributed to the amorphous SiO_x formed on PS. The formation of oxygen vacancies and impurities in the oxidized silicon has been proposed previously as the origin of these two bands [23, 24]. However, the formation of an intense blue band centered at 2.78 eV has been reported more recently by Zhang et al in ZnO films grown on SiO_2 substrates (Corning 7059) [25], and was assigned to electron transitions from shallow levels generated by oxygen vacancies or interstitial zinc to valence band. Moreover, this blue band has also been found in ZnO-SiO_2 nanocomposites [26, 27] and their origin has been attributed to point defects generated at the ZnO/SiO_2 interface [28]. The blue emission has also been found in ZnO nanostructures by other authors, suggesting that it is produced by point defects type oxygen vacancies or interstitial zinc [29, 30]. The formation of point defects associated to this blue band at the interface ZnO/SiO_2, generated onto PS, could explain the behavior of this emission in our samples. Particularly, the CL measurements recorded more clearly the presence of this emission from the non-irradiated sample that PL measurements [Figs. 3(a) and 2(a) respectively], apparently due to the higher penetration of the electron beam, which excited the radiative-centers present at the interface ZnO/SiO_2/PS. The high sensibility of the CL technique to recorded emissions generated by point defects or impurities in semiconductors could explain this behavior [31, 32].

For the irradiated sample, the PL measurements recorded a strong increase of the blue emission [Fig. 2(b)], which reveals the formation of point defects associated to this emission. We suggest that these point defects were formed in the ZnO film and in the interface ZnO/SiO_2, due to the penetration depth of the ions is upto 9 μm. CL measurements revealed also an increase in the relative intensity of the blue emission from this irradiated sample [Fig. 3(b)], recording a change to the I_{band}-edge / I_{blue} ratio from 1.97 to 1.50 in the CL spectra acquired before and after irradiation. This increase in the intensity is attributed to the generation of point defects related with this blue emission in the ZnO film and at the ZnO/SiO_2 interface.

Conclusion

Simultaneous observation of white light and UV emission have been reported on the zinc oxide-PS nanocomposite through photoluminescence and Cathodoluminescence spectroscopy. The two luminescence measurement techniques have been found to complement each other and CL is found to provide more information on the defects related luminescence. Defects have been shown to increase after modifying the structure through irradiation.

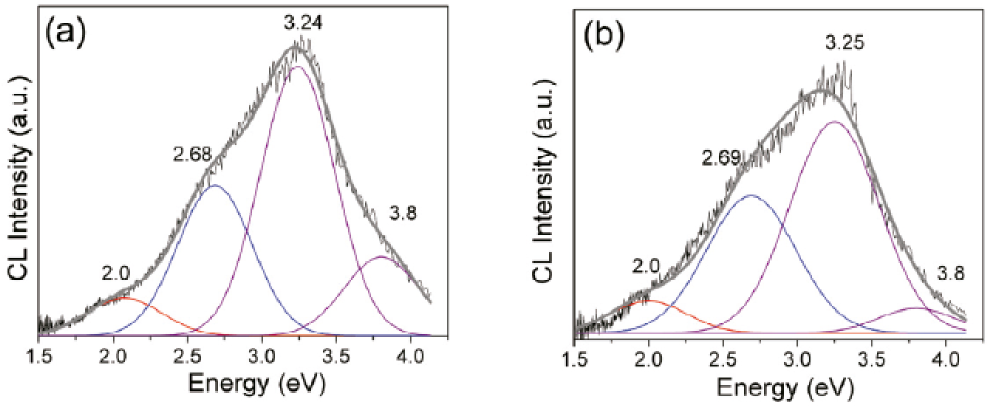

Figure 3: Cathodoluminescence spectra at 100 K (a) pristine (b) after irradiation.

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