Influence of ZnO buffer layer on growth of Sb doped ZnO nano wires using nano particle assisted pulsed laser deposition (NAPLD) using Sb as catalyst

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ABSTRACT

Influence of ZnO buffer layer thickness on the structural and optical properties of the Sb catalyzed/doped ZnO nanowires synthesized using NAPLD has been investigated. Buffer layer with a thickness of 100 nm, 800 nm and 1600 nm coated with Sb are used as a substrate and pure ZnO was used as a target to synthesize Sb doped ZnO nanowires. Introduction of the buffer layer lead to the growth of vertically aligned along with horizontally grown ZnO nano wires. With the increase in buffer layer thickness, the core diameter of the vertically grown ZnO nano wires was subsequently increased. Nano wires synthesized with a buffer layer thickness of 1600 nm showed a significant change in the lattice constants, resulting in measurable lower angle of about 0.06º from XRD, widening of lattice fringe spacing of 0.54 nm from TEM and Suppression of A_1T and $E_1(L0)$ modes in Raman Spectroscopic. In addition a strong UV emission with absence of visible emission was observed from the room temperature PL. This confirms the generation of Sb doped ZnO nano wire with high crystal quality. Copyright © 2012 VBRI Press.

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Introduction

One dimensional ZnO nanostructures possess a wide band gap (3.37 eV) and large exciton binding energy (60 meV) at room temperature [1-3]. This makes ZnO an ideal material for studying the transport processes in one dimensionally confined object, which are important for the development of high performance nano devices, including sensors, ultra violet/blue emission devices, field emission devices and so on. However, the difficulty in synthesis of p-type ZnO is hampering [4-6].

To tailor the properties of the 1-D ZnO nanostructures, several doping elements have been used and reported in the literature such as Ga, In, P, Sn and etc, in particular for the p-type doping of ZnO. Among them there are few reports in the literature which demonstrate the growth of Sb-doped ZnO [7, 8]. Most of the Sb-doped nanowires were developed by carbothermal evaporation method by using different metal catalyst such as Au. Co, etc. These catalysts commonly induce extra defects in the product, which confirms that the catalyst used can occupy a space in lattice [9-11]. Usage of solid metallic Sb dopant powders coated on the substrate can also act as a dopant source to synthesize Sb doped nanostructures [12]. Sb doped ZnO nanowires using carbothermal evaporation method and Nano-sheets synthesized using NAPLD, confirms the diffusion of Sb by considering dopant as a self-catalyst [13-16].

However, these synthesizing methods may possess some defects, owing to lattice and thermal mismatches from the substrate [17]. This can be rectified by introducing a pure ZnO buffer layer so as to improve the structural and the optical properties of the ZnO nano structures [18]. Hence this research work, highly focus towards generation of high quality Sb doped ZnO nanostructures by introducing ZnO buffer layer.

In this paper an attempt has been made to synthesize Sb doped nanowires by coating Sb on the ZnO buffer layer and the nanowires were synthesized using pure ZnO target. Horizontally grown nanowires were observed without a buffer layer. Vertically grown nanowires combined with horizontal nanowires were observed. The influence of the buffer layer thickness towards the structural and the optical properties of the synthesized nanowires have been investigated.

The surface morphology of the nanowires was investigated through SEM. The structural properties were investigated through XRD, Raman spectroscopy and TEM. The optical properties of the samples were analyzed using room temperature and low temperature PL spectroscopic analysis.

Experimental

Fig. 1 shows the stages in synthesis of Sb catalyzed/ doped ZnO nano wires using Nano Particle Assisted Pulsed Laser Deposition (NAPLD). In this experiment, a sintered source target of pure ZnO target with 99.99% in purity (Kojundo Chemical Laboratory, Japan) was used for synthesizing buffer layer and nano wires. A silicon substrate (1 cm ×1 cm) was put on a SiC heater in a vacuum chamber and the target substrate distance was set to be 40 mm. The ZnO

target was ablated with the third harmonics of a Q-switched Nd:YAG laser (Spectra Physics, Quanta-Ray, GCR-290) at 355 nm with a repetition rate of 10 Hz and a fluence of about 1.3 J/cm². A ZnO buffer layer was deposited on the sapphire substrate at a background oxygen pressure of 3.3 Pa with a substrate temperature of 650∘C for 1.5 minute for the growth of 100nm, 10 minutes for 800nm thick and 20 minutes for 1600 nm thick. The Si deposited ZnO buffer layer was coated with Sb (99.999% pure (Nilaco corporation, Japan)) to a thickness of 80-100 nm using thermal evaporation method. The ZnO nanowires were continuously grown on the Sb coated ZnO buffer layer at 40 kPa with a substrate temperature of 750∘C for 30 min.

The morphology of the as-deposited products was analyzed by a scanning electron microscopy (SEM) (VE-7800S, KEYENCE). Crystal quality was investigated by a high resolution transmission electron microscopy (TEM) (JEM- 1300NEF, JEOL Ltd.) and an X-ray diffractometer (XRD) (MultiFlex, Rigaku Co.). An analytical Raman microscope system (HORIBA LabRAM ARAMIS) was used to investigate the structural characteristics. The optical properties of the ZnO nanowires were investigated by observing the room temperature photoluminescence (PL) using a He-Cd laser (IK3301 R-G, KIMMON KOHA Co., Ltd., 325 nm) as the excitation light source.
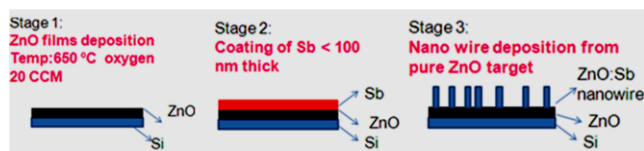

Fig. 1. Stages in synthesis of Sb catalyzed/ doped ZnO nano wires using Nano Particle Assisted Pulsed Laser Deposition (NAPLD).

Results and discussion

Surface morphological analysis

The representative morphologies of as synthesized samples are revealed by SEM images at different experimental conditions. At first, the influence of Sb as a catalyst, in generation of nanowires has been investigated. **Fig. 2 (a)** shows the SEM image of pure ZnO nanoweb like structures synthesized on bare Si substrate using NAPLD. In contrast **Fig. 2(b)** shows the high density random oriented growth of the nanowires synthesized on Sb coated Si substrate. These random nanowires are generated from the droplets of Sb, formed on the substrate during the growth processes.

Fig 3. Shows the influence of ZnO buffer layer at varying thickness in generation of Sb doped ZnO nanowires. Horizontally grown nanowires combined with vertically aligned nano wires were observed from the samples grown on the ZnO buffer layer. To investigate the morphology of the vertically aligned nanowires, SEM micrographs are taken at a tilted angle as shown in F**ig. 3(a)** shows the Sb catalyzed doped nanowires synthesized on a buffer layer of 100 nm thickness. The vertically aligned ZnO nanowire with a length of 200nm and a core diameter of around 100 nm was observed. With increase in buffer layer to 800 nm thickness, the nanowire with slight increase in length and diameter of 0.5 μm and 400 nm respectively. With further increase in buffer layer to

thickness of 1600 nm, increase in core diameter of the nanowires of around 800 nm was observed.

Structural analysis

The structural characteristics of the Sb catalyzed/ doped ZnO nano wire coated on a ZnO buffer layer of 1600 nm thick were investigated through XRD, Raman spectroscopy and TEM analysis.
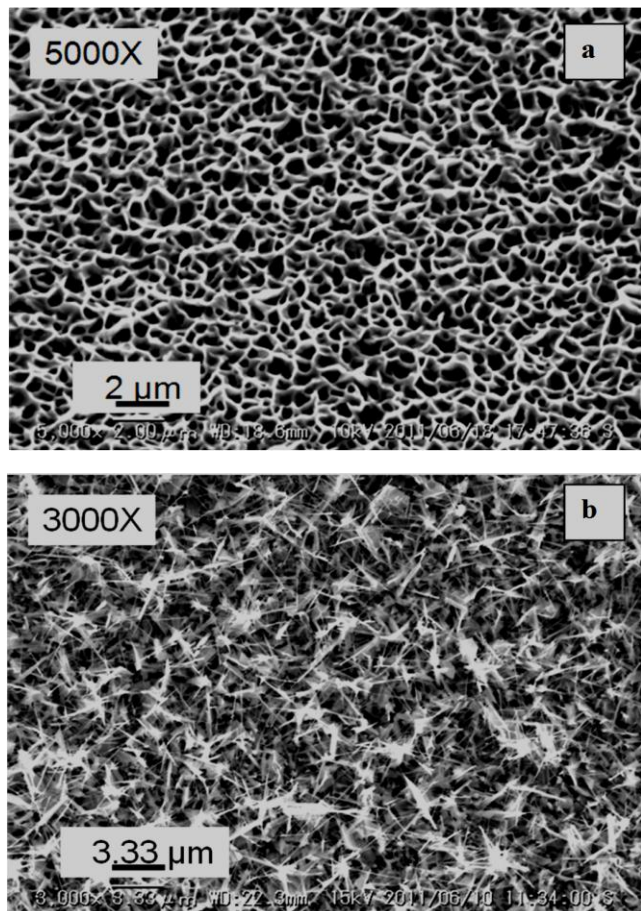

Fig. 2. Surface morphology of ZnO nano structures synthesized on Si substrate using NAPLD a) with no catalyst and buffer layer (tilted view) b) with Sb as catalyst and no buffer layer.
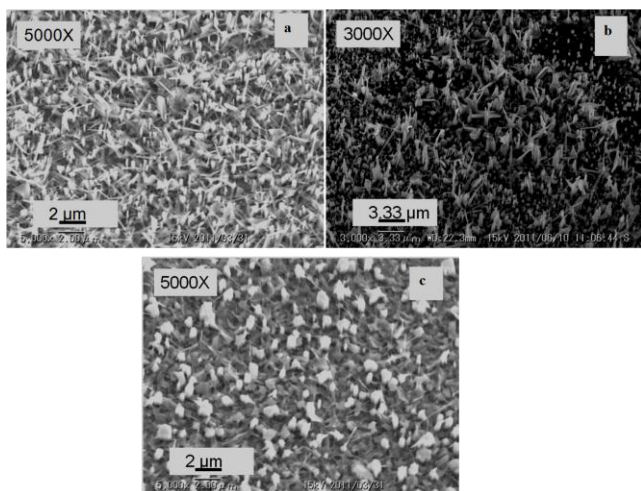

Fig. 3. Surface morphology of ZnO nano structures synthesized at different buffer layer with a thickness of a) 100nm b) 800 nm c) 1600 nm.

The phases of the as-grown nanowires were identified by XRD. The XRD results of the pure ZnO and Sb-doped ZnO are shown in **Fig. 4** for comparison. The XRD pattern of the Sb-doped ZnO indicates that the nanowires have the wurzite structure and no secondary phase was found as compared to the XRD spectrum of pure ZnO. The Sb doping in ZnO causes significant change in the lattice constants, resulting in measurable lower angle shift of about 0.06º in the (100) and (101) peaks as compared to the pure ZnO nano wires [19].
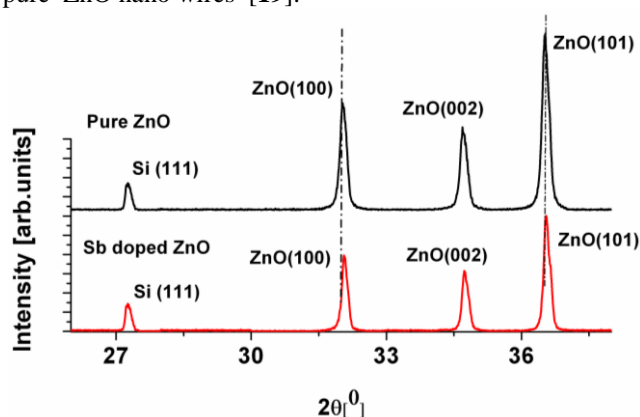

Fig. 4. Xray diffraction analysis of the pure and Sb catalyzed/ doped ZnO nano wires.
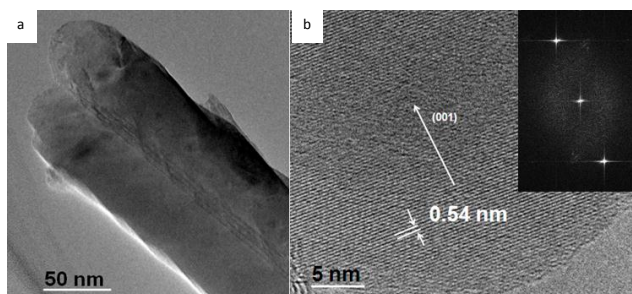

Fig. 5. TEM analysis of Sb catalyzed/ doped ZnO nano wire on 1600 nm buffer layer. (a) low- magnification and (b) high resolution taken from the side of the nanowire. The inset is the corresponding Fast Fourier Transform (FFT pattern).

Fig. 5 shows low and high magnification TEM images of the Sb-doped ZnO nanowire and the corresponding fast Fourier transform (FFT) patterns as in the insets. It was observed that the nanowires are structurally uniform with a lattice fringe spacing of 0.54 nm, which confirms that the grown nano-structure are preferentially oriented in the [0001](c-axis) direction [20]. The wider lattice fringe spacing is due to the incorporation of Sb in ZnO lattice.

Fig. 6 shows the Raman spectrum of the pure and Sb catalyzed/doped ZnO nanowires. The peaks at 332, 380 and 439 cm^{-1} corresponds to the E_{2H}-$E_{2L,}$ A1T and E_{2}H modes of the host ZnO modes respectively. The peak at 520 cm^{-1} is attributed to the Si substrate. The peaks observed in both pure ZnO and Sb-doped ZnO nanowire at 332 cm^{-1} confirms that the ZnO nanostructures are excellent single crystal with hexagonal wurzite structures [21]. While comparing the Raman spectrum of pure ZnO, the peak at 380 cm^{-1} is depressed and hardly observed in Sb-doped ZnO nanowires. For ZnO materials where close-packed layers of zinc and oxygen are stacked alternately along the c axis, the lattice irregularities such as oxygen

defect or the dopant atom along the c-axis would directly affect the displacement of the ions in the A_1T modes. In our experiments, both the O vacancies and the Sb-dopants atoms are responsible for the depressed A_1T modes of ZnO [**22**]. In addition, suppression of peak at 556 cm^{-1} attributes to the $E_1(L0)$ modes which are associated with the structural defects related to oxygen vacancies [**23**] which also supports the Sb diffusion.
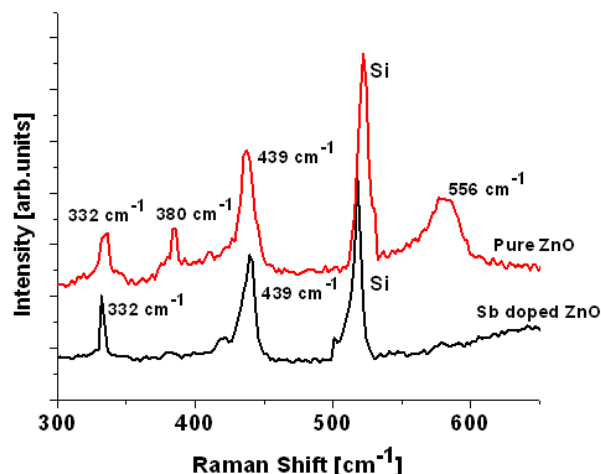

Fig. 6. Raman spectroscopic analysis of a) pure ZnO (buffer layer) (b) Sb catalyzed/ doped ZnO nano wire synthesized on 1600 nm buffer layer.
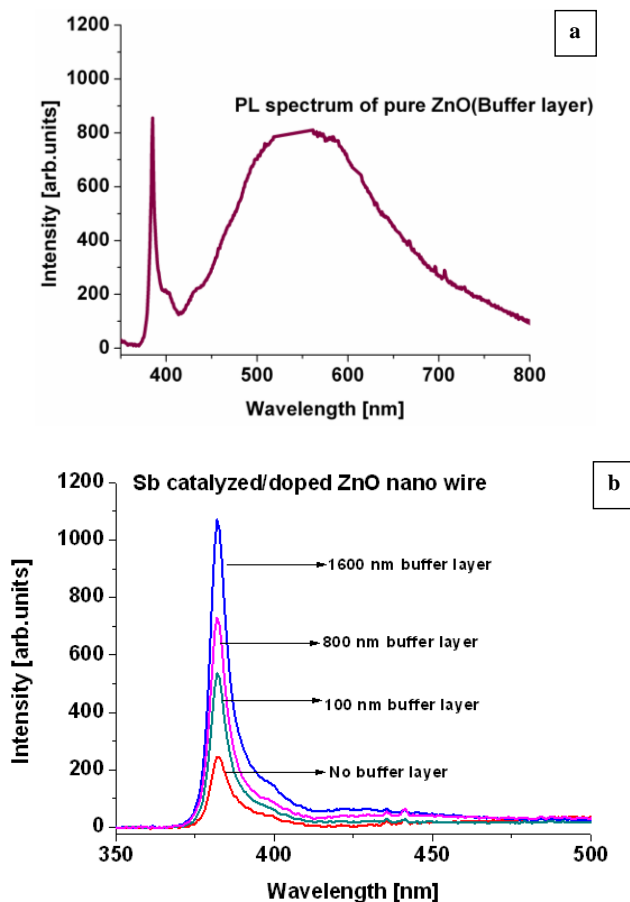
Fig.7. Room temperature PL Spectroscopic analysis of (a) Sb catalyzed/ doped ZnO nano wire at different size of the buffer layer (b) pure ZnO

Optical properties

Fig. 7a shows the room temperature PL spectrum of the pure ZnO thin film which act as a buffer layer The PL spectra of the ZnO film exhibits UV peak emission i.e. the near band edge (NBE) emission at around 380 nm and a broad deep level emission (DLE) corresponding to the visible emission is observed. and **Fig. 7b** shows the Pl spectrum of the Sb catalyzed/ doped ZnO layer synthesized on different buffer layer thickness A sharp UV emission with absence of visible emission peak was observed from the Sb catalyzed/doped ZnO samples. The intensity of UV emission is increase with respect to the buffer layer thickness

The Peak at NBE is attributed to band-to-band transitions, excitonic emissions and donor acceptor pair transitions. The origin of DLE that is the visible emission appeared due to the radial recombination of a photogenerated hole with electron of the ionized oxygen vacancies in the surface lattice of the ZnO [**24**]. It is also considered that the radiative transitions between shallow donors (related to oxygen vacancies) and deep acceptor (zinc vacancies) can create defect in the luminescence spectra [**25**]. Thus the PL visible emission peak at 520 nm originates from the single ionized oxygen vacancies. This is due to the increase of layer defect during nucleation processes [**26, 27**].

This layer defect during nucleation process is completely rectified in the Sb catalyzed/doped ZnO samples synthesized on the e buffer layer, resulting in strong UV emission and absence of visible emission as observed in **Fig. 7b**. In addition the presence 332 cm^{-1} and suppression of peak at 556 cm^{-1} attributes to the $E_1(L0)$ modes which are associated with the structural defects related to oxygen vacancies in Raman spectroscopic analysis from **Fig. 6** . Thus the Sb-doped ZnO nanosheets possess a good crystallization quality and high stoichiometric nature.

Conclusion

In summary, the influence of ZnO buffer layer in synthesis of Sb doped ZnO nanowire by using Sb as catalyst in NAPLD was experimentally investigated. Buffer layer with a thickness of 100 nm, 800 nm and 1600 nm coated with Sb are used as a substrate and pure ZnO was used as a target to synthesize Sb doped ZnO nanowires. Vertically grown nanowires combined with horizontal nanowires were observed with the influence of buffer layer. In addition ZnO nano wire showed a significant change in the lattice constants, resulting in measurable lower angle of about 0.06º from XRD, widening of lattice fringe spacing of 0.54 nm from TEM   this confirms the diffusion of Sb in ZnO lattice. With the increase in buffer layer thickness, the core diameters of the vertically erected ZnO nano wires are subsequently increased. The nano wires synthesized with a buffer layer thickness of 1600 nm showed a strong intensity UV emission with absence of visible emission as compared to the nano wires synthesized at different buffer layer thickness as analyzed room temperature PL. In addition Suppression of A_1T and $E_1(L0)$ modes in Raman Spectroscopic confirms the generation confirms the defect

during nucleation process is completely rectified resulting in generation of high quality Sb doped ZnO nano wires, which can be used for optoelectronic applications.

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