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Structural and optical properties of Sb—Al co-doped ZnO nanowires synthesized using Nanoparticle Assisted Pulsed Laser Deposition (NAPLD) with Sb as catalyst

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ABSTRACT

The paper deals with study of Sb—Al co-doped ZnO nanowires synthesized using Nanoparticle Assisted Pulsed Laser Deposition (NAPLD). The nanowires were synthesized by using ZnO:Al as target and Sb coated Si as substrate. At a growth temperature of 750 °C, random oriented high density nanowires with a diameter of about 1 μm and a length up to a few tens of micro meters were synthesized. The samples were annealed at 450, 550 and 650 °C. The Sb—Al co-doped ZnO nanowires annealed at 650 °C showed a significant change in lattice constant of 0.06° from XRD and widening of lattice fringe spacing of 0.56 nm from TEM. From the XPS analysis, a peak at 539.5 eV a near binding energy of Sb—O bond and peak at 76.2 eV corresponding to Al—O bonds confirms the penetration of oxygen. The suppression of A_1T modes and $E_1(LO)$ modes from Raman spectroscopy confirms the depletion of oxygen vacancies. Thus resulting in a strong improvement in UV emission and reduction in visible emission as observed from room temperature PL.

1. Introduction

Quasi-one-dimensional ZnO nano materials such as nanowires, nanorods and nanobelts have attracted much attention due to their remarkable morphology dependent properties and potential applications in nano-optoelectronic devices [1–3]. One dimensional ZnO nanostructures posses a wide band gap (3.37 eV) and large exciton binding energy (60 meV) at room temperature [4–6], which make 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. Doping of ZnO nanostructures can be tailored for specific desired applications, among them p-type doping of ZnO is of particular interest [7–9].

It is well known that the most suitable dopant for p-type doping in ZnO are the group-V atoms (N, P, As and Sb) substituting for O [10,11]. Several recent experiments have shown successes in doping p-type ZnO by using large radius group-V element such as P and As [12,13]. In addition to single element doping, a donor–acceptor co-doping method has been also proposed to realize heavy p-type doping [14–16]. The deliberate co-doping of donors with acceptors is essential for the enhancement of the solubility of the acceptors with the stabilization of the ionic charge and distributions and the reduction of acceptor binding energies. The co-doping methods simultaneously using group-V acceptors (N and P) and group-III reactive donors (Al and In) were also proposed to increase the solubility of acceptors in ZnO [17–19]. Al:As co-doped ZnO thin film synthesized using magnetron sputtering and Sb:Al co-doped ZnO thin films synthesized using sol–gel also confirms the p-type doping of the samples [20,21]. In addition annealing of these co-doped thin films will lead to significant change in their structural, optical and electronics properties [22]. However there are limited on reports in synthesizes of co-doped ZnO nano structures and characterization of their properties towards functional device applications. Hence this paper is focused towards synthesize of Sb—Al co-doped Zno nanostructures using NAPLD (Nanoparticle Assisted Pulsed Laser Deposition) and the characteristics of the nano structures at different annealing conditions has been experimentally analyzed to investigate the mechanism.

In this study, ZnO:Al is used as a target and Si coated with Sb is used as the substrate. The NAPLD experiments were performed at different temperature condition matching with the melting temperature of Sb so as to initiate the growth of the nanowires. The synthesized Sb—Al co-doped ZnO nanowires were annealed at different temperature conditions. The surface morphology of the

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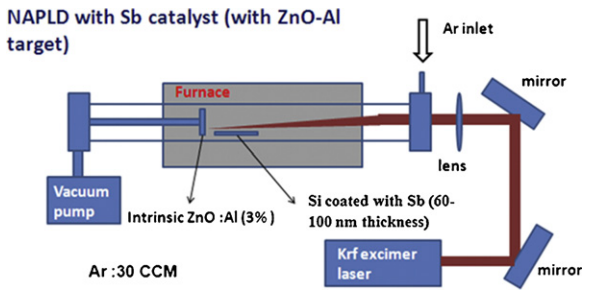

Fig. 1. Schematic layout of NAPLD experimental setup.

samples was investigated through SEM. The composition analysis of the samples was investigated through XPS. The structural properties of the nano wires were analyzed through XRD, TEM, and Raman spectroscopic analysis. The optical properties of the samples were investigated through room temperature PL.

2. Experimental investigation

Fig. 1 shows the schematic layout of NAPLD experimental setup. Sintered intrinsic ZnO:Al target was used as source material to synthesis nanowires. Intrinsic Si wafer (~15 mm × 15 mm) coated with Sb to a thickness of 60–100 nm using thermal evaporation method was used as a substrate. The substrate was mounted on a layer of SiC and inserted into the horizontal quartz tube chamber. The target to substrate distance was 15 mm. For one growth run 36000 KrF excimer laser pulses with 20 Hz repetition frequency were applied. The laser energy density on the target was about 3 J cm^{-2} in the presence of argon gas at a pressure of 100 Torr and a constant flow rate of 27.5 SCCM. The Sb—Al co-doped ZnO nanowires were synthesis at a growth temperature of 750 °C with growth duration for period of 20 min. After synthesis, to activate the dopant, the samples were post annealed for a period of 30 min at different temperatures in the ambient condition.

The surface morphology of the Sb—Al co-doped nanowires was observed by a scanning electron microscope (SEM) (Keyence VE-7800). To investigate the influence of annealing temperature towards structural and optical properties of the samples. The structural characteristics of the samples were analyzed through X-ray diffraction (XRD), TEM (JEM-1300NEF, JEOL Ltd.) and Raman spectroscopic system (HORIBA LabRAM ARAMIS). The composition analysis of the samples was investigated through XPS (XPS ESCA 5800 ULVAC-Phi Inc). 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.

3. Results and discussion

To investigate the mechanism of growth initiation of the nanowires from the Sb coated substrate, the experiments were performed at different temperature conditions ranging from 550 to 750 °C which is slightly higher than the melting point of Sb. The representative morphologies of as synthesized samples grown at different temperature conditions are revealed by SEM images. Fig. 2(a) shows the cluster formation of Sb on the surface of Si, when the samples are kept at a growth temperature of 550 °C. These clusters act as a seed to initiate the growth of nanowires. When the growth temperature was increased to 650 °C, initiations of nanowires from the clusters were observed as shown in Fig. 2(b). When the growth temperature was increased to 750 °C random oriented high density nanowires with a diameter of about 0.75 μm and a length up to a few tens of micro meters were observed as shown in Fig. 2(c). When the growth temperature was increased beyond 850 °C density of the nano wires were considerably decreased.

To investigate the annealing behavior of the Sb—Al co-doped nano wires. Three set of nanowire samples synthesized at 750 °C were prepared and annealed at 450, 550 and 650 °C in air. The annealed samples were analyzed through XRD to investigate the structural characteristics.

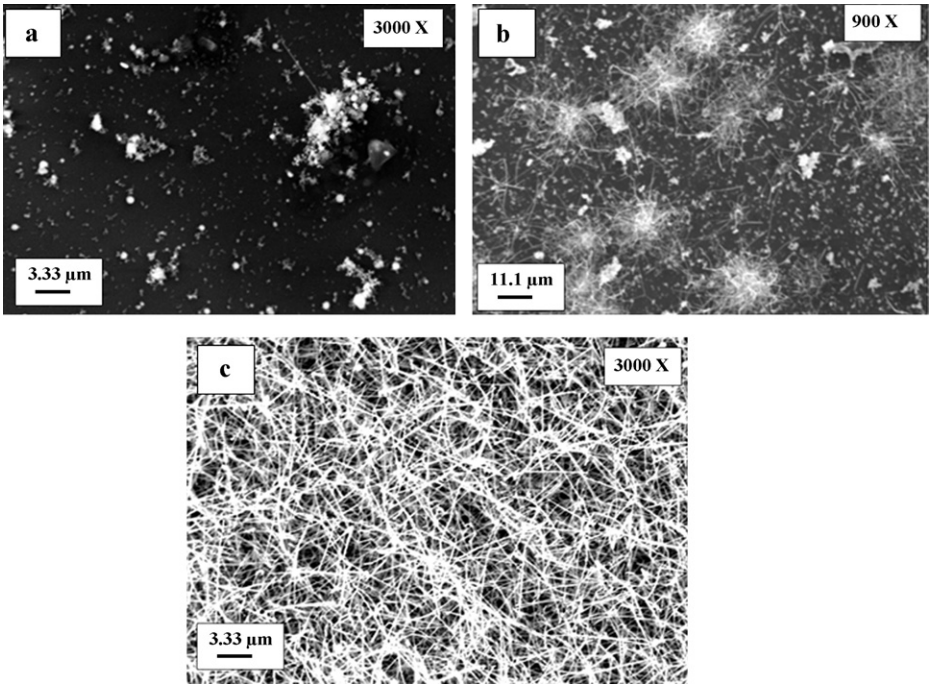

Fig. 2. SEM micrograph representing (a) formation of droplets from Sb coated substrate at 550 °C, (b) Growth initiation of Sb—Al co-doped ZnO nanowebs from Sb coated substrate at 650 °C and (c) Synthesize of high density Sb—Al co-doped ZnO nanowebs at 750 °C.

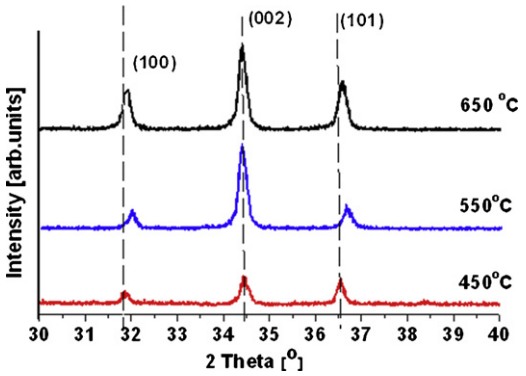

Fig. 3. XRD patterns of Sb—Al co-doped ZnO nanowebs at different annealing temperatures.

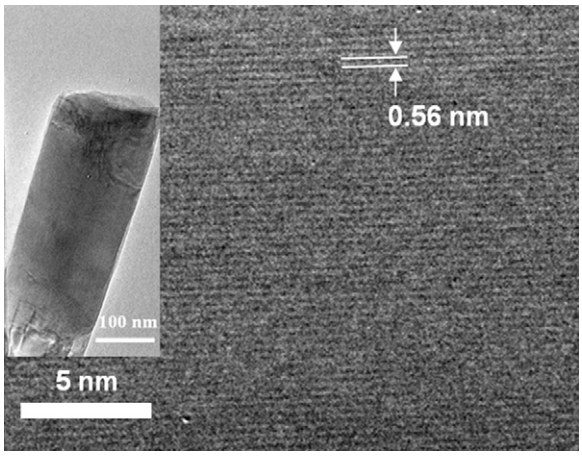

Fig. 4. TEM analysis of Sb–Al co-doped ZnO nano wire (a) low-magnification and (b) high resolution taken from the side of the nanowires.

Fig. 3 shows the XRD characteristics of the annealed Sb—Al co-doped ZnO nanowires. As indexed in figure, diffraction peaks are basically attributed to the wurzite structure of ZnO (JCPDS 76-0704). No extra peaks due to the Zinc antimony or Zinc aluminum phase are observed in the XRD, this confirms that the dopants would have substituted in the Zn site without change in the wurzite structure. With increase in annealing temperature from 450 to 650 °C, the (0 0 2) peaks enhances significantly as compared with the other two peaks (1 0 0) and (1 0 1). Also, the intensity of all diffraction peaks enhances at higher annealing temperature, because higher temperature provides more energy to enhance the atom mobility resulting in an improvement in the quality and crystallinity of the nanowires. With increase in annealing temperature the Sb—Al co-doped ZnO nanowires showed a significant change in the lattice constant resulting in lower angle shift of the peaks [23–26]. The nanowires annealed at 650 °C and 550 °C showed a measurable lower angle shift of about 0.06° in the (1 0 0) and (1 1 0) peaks compared to the nanowires annealed at 450 °C. In order to go for a detail investigation, the nanowires annealed at 650 °C were investigated through TEM.

Fig. 4 shows high magnification TEM images of the Sb—Al co-doped ZnO nanowires and low magnification image in the inset. It was observed that the nanowires are structurally uniform with a lattice fringe spacing of 0.56 nm this is slightly wider than the pure ZnO. The wider lattice fringe spacing is due to the influence of Sb and Al in ZnO lattice [27]. In order to understand the origin of the chemical environment and content of Sb and Al. The co-doped ZnO nano wires annealed at 650 °C were analyzed through X-ray photo electron spectroscopy (XPS).

Fig. 5(a) shows the XPS analysis on the content of Sb. Two $Sb_{3d3/2}$ bands are observed at a binding energy of 536.9 and 539.5 eV respectively. The 536.9 eV is close to binding energy of metal Sb, and the 539.5 eV is near binding energy of Sb—O bond. From the XPS it is clear that the deducted Sb posses two kinds of chemical environment, one is metal Sb, which locates at grain boundaries of the ZnO and another substitution Sb at Zn site (Sb_{Zn}). Based on Fig. 5(a) the Sb content is estimated to be 0.9% in a form of Sb and 4.5% in the form of Sb_{Zn}. This proposed that Sb would substitute for Zn(Sb_{zn}) instead of oxygen in the Sb-doped ZnO and then produce two corresponding Zn vacancies (V_{Zn}), which forms a Sb_{Zn}–$2V_{Zn}$ complex acceptor [28].

Fig. 5(b) corresponds to the $Al_{2p3/2}$ core level and the fraction of Al is estimated to be around 0.56%. The $Al_{2p3/2}$ peaks at 76.2 eV are possibly related to Al—O bonds, supporting the fact that Al-induced donors are presented in the co-doped films [29]. In order to investigate the secondary phase segregation and the influence of impurity doping on the lattice fringe property of the Sb—Al co-doped ZnO nanowires, Raman spectroscopic analysis were performed on the Sb—Al co-doped ZnO nanowires annealed at 450 and 650 °C.

Fig. 6(a) shows the Raman spectroscopic analysis of the Sb—Al co-doped ZnO nanowires annealed at 450 °C. Dominant peak at 332, 380 and 556 cm^{-1} was observed. Fig. 6(b), shows the Raman spectroscopic analysis annealed at 650 °C and the dominant peaks are observed at 310 and 439 cm^{-1}. The 522 cm^{-1} corresponds to the crystalline silicon substrate peak. The peak at 332 cm^{-1} in Fig. 5(a) and 439 cm^{-1} in Fig. 6(b) corresponds to E_{2H}–E_{2L} and E_2H modes of non polar optical phonon respectively. These two peaks confirm that the Sb—Al co-doped ZnO nanowires posses' good crystal structure [30–33]. The peak at 380 cm^{-1} corresponding to the A_1T modes. This is not observed on Sb—Al co-doped samples annealed at 650 °C, instead a peak at 310 cm^{-1} peak corresponding to the lattice deformation induced by the presence of Sb in the ZnO lattice [34]. A small peak suppressed at 556 cm^{-1} attributes to the $E_1(LO)$ modes which are associated with the structural defects related to oxygen

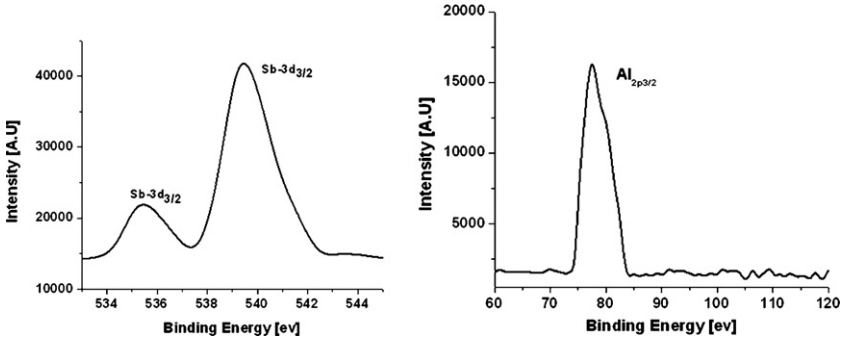

Fig. 5. (a) $Sb_{3d3/2}$ and (b) $Al_{2p3/2}$ narrow scan XPS spectra of Sb—Al codoped ZnO nano wires annealed at 650 °C.

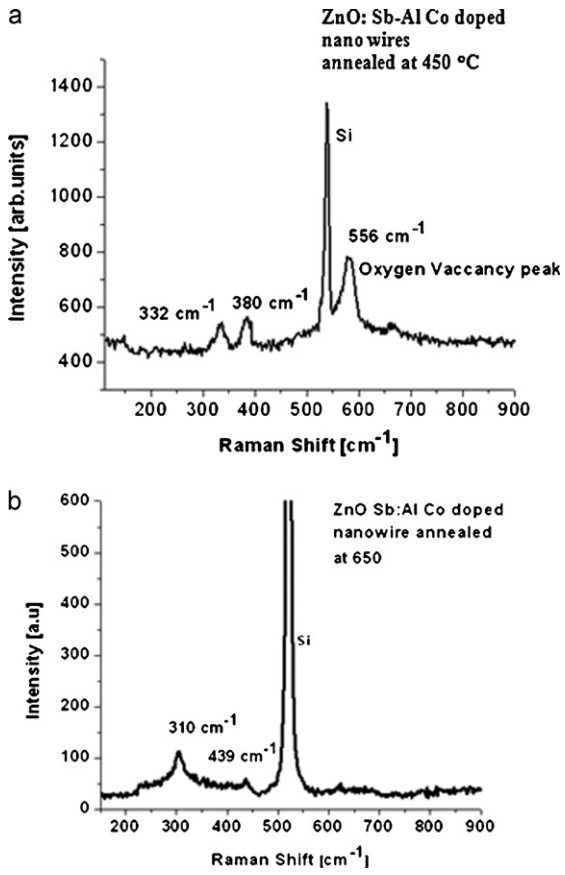

Fig. 6. Raman spectra of Sb—Al co-doped ZnO nanowires annealed at (a) 450 °C and (b) 650 °C.

vacancies [35]. The optical properties of the Sb—Al co-doped ZnO nanowires were investigated for different annealed samples using room temperature PL.

Fig. 7 shows the room temperature PL spectrum of Sb—Al co-doped ZnO nano wires. The PL spectra of the ZnO nano wires annealed at 450 °C exhibits weak 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. With increase in annealing temperature to 650 °C, increase in intensity of the UV emission was observed. Thus the formation of the single ionized oxygen vacancies has been considerably reduced [36,30].

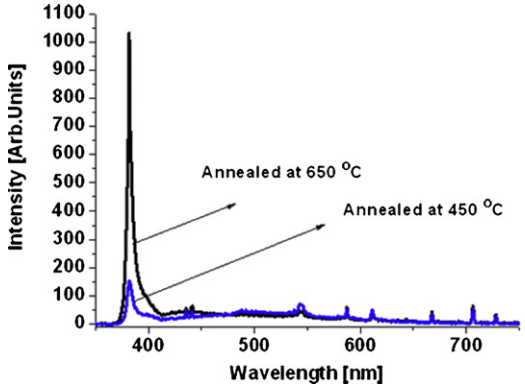

Fig. 7. Room temperature PL spectroscopic analysis of Sb—Al co-doped ZnO nanowires annealed at 450 °C and 650 °C.

The experimental results discussed in detail, throws a light on the mechanism of Sb—Al co-doped nanowires. The Sb coated on the Si substrates has helped to initiate the growth of nanowires. During the growth and on further annealing to a higher temperature of around 650 °C has lead to the diffusion of the dopant in the ZnO lattice. This has been confirmed by the change in the lattice constant from XRD and widening to lattice fringe to 0.56 nm from TEM.

From the XPS analysis it is clear that the presence of Sb 539.5 eV is near binding energy of Sb—O bond, confirming that the Sb would substitute for Zn(Sb_{Zn}) instead of oxygen in the Sb-doped ZnO and then produce two corresponding Zn vacancies(V_{Zn}), which forms a Sb_{Zn}–$2V_{Zn}$ complex acceptor[37]. The presence of $Al_{2p3/2}$ peaks at 76.2 eV are possibly related to Al—O bonds leading to excess of oxygen neutralizing the oxygen vacancies [38].

The annealing of these Sb—Al co-doped samples also has their own influence in the depletion of oxygen vaccines. This has been confirmed from the Raman spectroscopic analysis The suppression of A_1T modes at 380 cm^{-1} and $E_1(LO)$ modes at 556 cm^{-1} are observed in the Sb—Al co-doped nanowires annealed at 650 °C as compared to the samples annealed at 450 °C. The A1 T modes corresponds to lattice irregularities such as oxygen defect or the dopant atom along the *c*-axis and $E_1(LO)$ modes are associated with the structural defects related to oxygen vacancies [39]. The suppression of these models will lead thus leading to reduction in visible emission and improvement in UV emission as observed in room temperature PL [40,41,36].

4. Conclusion

Sb—Al co-doped ZnO nanowires has been successfully synthesized using Nano particle Assisted Pulsed Laser Deposition (NAPLD), by using ZnO:Al as target and Sb coated on Si as substrates. At a growth temperature of 750 °C, random oriented high density nanowires with a diameter of about 1 μm and a length up to a few tens of micro meters were synthesized. To investigate the annealing behavior of the Sb—Al co-doped nano wires. Three set of nanowires samples synthesized at 750 °C were annealed at 450, 550 and 650 °C. The nanowires annealed at 650 °C and 550 °C showed a measurable lower angle shift of about 0.06° in the (1 0 0) and (1 1 0) peaks compared to the nanowires annealed at 450 °C. In support to the XRD analysis, a wider lattice fringe spacing of 0.56 nm was observed from TEM. The suppression of A_1T modes and $E_1(LO)$ modes from Raman spectroscopy confirming that depletion of oxygen vacancies. XPS analysis confirming that the Sb would substitute for Zn(Sb_{Zn}) instead of oxygen Al—O bonds leading to excess of oxygen, neutralizing the oxygen vacancies. Thus Sb—Al co-doped nanowires annealed at 650 °C showed a strong UV emission and reduction in visible emission as compared to the Sb—Al co-doped nanowires annealed at 450 °C.

As a conclusion the Sb—Al co-doped ZnO nanowires annealed at 650 °C posses high stoichiometric nature, good structural and optical properties, hence it is highly suitable for light emitting device applications.

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