Analysis of Structural & Optical Properties of Aluminium Nanoparticles decorated on SiO$_x$ Nanowires by GLAD Technique

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Abstract — In this paper, Glancing angle Deposition (GLAD) Technique have been employed for the growth of Al Nanoparticles (NPs) decorated SiO$_x$ Nanowires (NWs) using e-beam evaporation system. The FE-SEM and HR-TEM results reveal the successful growth of Al NPs and SiO$_x$ Nanowires above the buffer layer of In$_2$O$_3$ TF. The measured length of SiO$_x$ NWs is ~ 450 nm and the thickness of In$_2$O$_3$ TF (buffer layer) is ~100 nm. The EDAX analysis confirms the presence of Oxygen (O), Aluminium (Al), Silicon (Si), and Indium (In). The SAED analysis shows the polycrystalline nature of In$_2$O$_3$ and Al which is correlated to the XRD peaks. Also, XRD result confirms the amorphous nature of SiO$_x$ NWs. The optical absorption of In$_2$O$_3$ TF/SiO$_x$ NWs/Al NPs is found to be ~1.3 fold compared to In$_2$O$_3$ TF/SiO$_x$ NWs, which may be due to the Surface Plasmon Resonance (SPR) effect of Al NPs on the sample. The PL analysis also reveals the photon emission enhancement from the sample with Al NPs. Therefore, this growth technique which enhanced the optical properties may be applicable in a wide range of optoelectronic applications.

Keywords — Aluminum Nanoparticle; GLAD; Nanowires; SiO$_x$

1. INTRODUCTION
Nanostructures of metal-oxide semiconductors have grabbed attention due to their large number of novel phenomena at the nanoscale dimensions and have found for electronic, optoelectronic, electrochemical and electromechanical devices. Vertically-aligned amorphous SiO$_x$ nanowires have been reported for the optoelectronic devices due to their stable blue light emission [1-3]. GLAD is a physical vapor deposition technique which offers the nanostructure films for a wide range of optical applications [4]. As the physical properties of nanostructures including size, shape, and structure can be altered or manipulated easily and so as the optical characteristics are influenced. Enhanced optical absorption in spherical metal nanoparticles (NPs) is being found due to Surface Plasmon Polaritons [5] because light does not couple to surface plasmons [6]. The incident light excites the outer electron of nanoparticles which oscillates at the resonant frequency and depending on the dielectric environment surrounding the particle light is either absorbed or scattered [7]. So, for obtaining the plasmonic effect throughout the UV-vis-near-IR spectrum can be tuned by tuning the geometry parameters of NPs such as particle shape and diameters. On the premature stage of the plasmonic effects research, the noble metals [8, 9] such as Ag and Au have been fully analyzed but in recent trends Al NPs have boomed in research market not only because of its low cost, and easy manufacturing but also due to its higher plasma frequency which makes the aluminium permissible for the ultraviolet region responses [10].

In this paper, we have reported the fabrication of In$_2$O$_3$ TF/SiO$_x$ NWs/Al NPs and In$_2$O$_3$ TF/SiO$_x$ NWs on the glass and Si (p-type) substrate through e-beam evaporation technique. The structural and optical properties are investigated...
in details for potential photodetector application. The morphology and structural properties of In$_2$O$_3$ TF/SiO$_x$ NWs/Al NPs were characterized through Field Emission-Scanning Electron Microscope (FE-SEM), High Resolution-Transmission Electron Microscope (HRTEM) and X-ray Diffraction (XRD) analysis which manifests the SiO$_x$ amorphous nature. The optical properties for In$_2$O$_3$ TF/SiO$_x$ NWs/Al NPs were investigated using UV/Vis Spectrophotometer and photoluminescence (PL) analysis.

2. EXPERIMENTAL PROCEDURE

SiO$_x$ nanostructures have been fabricated with the help of GLAD technique by evaporating pressed and sintered SiO$_2$ pellets using electron-beam evaporator (HHV, 15F6). Here, the pellets preparation is adopted similar to the process reported in the literature [11]. Briefly, SiO$_2$ pellets were obtained from pure SiO$_2$ powder (99.99% pure, MTI, USA) by using the preparation conditions such as by hydraulic press under a pressure of 3000 kilos/cm$^2$ and then sintered in air at 850$^\circ$C for 1 hr. The Si and glass substrates (1 cm x 1 cm) were cleaned properly by acetone, methanol and distilled water prior to deposition. Substrates were transferred to the substrate holder which was kept at the distance of 24 cm from the source material with 120 rpm azimuthal rotation and 85$^\circ$ orientation with respect to the perpendicular line between the source and substrate holder [12]. SiO$_x$ NWs (450 nm) were deposited on the substrate coated with In$_2$O$_3$ TF (100 nm). The In$_2$O$_3$ TF was deposited using In$_2$O$_3$ pellets (99.999% pure, MTI, USA). The TF deposition was deposited through the normal growth. The base pressure ranging from 1 x $10^{-5}$ to 1 x $10^{-6}$ mbar were maintained during the whole deposition process. A low deposition rate was maintained ~1.2 Ås$^{-1}$ during both SiO$_x$ NW and In$_2$O$_3$ TF deposition. The chamber temperature reached up to 51$^\circ$C during the deposition. The vacuum pressure was continuously monitored by pirani and penning gauge.

The work has been done to show the influence of the optical characteristics by introducing the aluminum NPs on SiO$_x$. The crystallographic structure of SiO$_x$ NWs with and without Al NPs was characterized by XRD using X-Pert Pro Pan Analytical with Cu K$_\alpha$ ($\lambda = 1.54056$ Å$^\circ$) radiation. The FE-SEM (Carl Zeiss, Merlin, 5 kV) and HR-TEM (JEOL, JEM 2100, 200 kV) with SAED and EDAX analysis were carried for the surface and structural morphology. The optical measurement of sample deposited on the glass substrate was analyzed through the UV-Vis near-infrared Spectrophotometer (Lambda 950, PerkinElmer) for the wavelength range of 350 nm to 900 nm. The PL analysis was recorded using xenon lamp (ELICO, SL 174) for the excitation wavelength of 270 nm.

3. RESULTS AND DISCUSSIONS

3.1 Structural and Morphological Characteristics

At the very beginning of the experiment, SiO$_x$ NWs were fabricated on bare Si substrate, during this deposition the chamber temperature reach up to 43 $^\circ$C. And the GLAD films were sparkling and got bubbled kind structure after a month shown in Figure 1 (a). Also, the growth of nanowires was found inappropriate through FESEM analysis. Thereafter, SiO$_x$ NWs were fabricated on the substrate coated with In$_2$O$_3$ TF shown in Fig. 1 (b).

Figure 1. (a) SiO$_x$ NWs deposited on Si substrate without buffer In$_2$O$_3$ TF showing bubbled structure, and (b) SiO$_x$ NWs deposited on Si substrate with In$_2$O$_3$ TF as a buffer layer.

Figure 2 (a) shows the top view of FESEM analysis of as-deposited In$_2$O$_3$ TF/SiO$_x$ NWs/Al NPs which clarifies the successful growth of Al NPs. The top average diameter of Al NPs was found ~ 503 nm from the magnified image.
shown in the inset. The EDAX analysis shown in Fig. 2 (b) shows the presence of Oxygen (O), Aluminium (Al), Silicon (Si) and Indium (In). The spectrum showed the emission from OK, Al K, Si K and In L emissions where the emission from Si K shells was from the Si substrate and SiO\(_x\) NWs both. From the composition table shown in the inset, it is concluded that 55.72 at % of OK would form SiO\(_x\) where x < 2 lies. The chemical mapping shows the presence of Oxygen (grey), Aluminium (violet), Silicon (green), and Indium (yellow) where the composition of oxygen was found more as it is contributed from In\(_2\)O\(_3\) and SiO\(_2\) source materials shown in Fig. 2(c).

Figure 2. (a) Top view of FESEM analysis of Al NPs coated SiO\(_x\) nanowires, (b) EDAX analysis, and (c) chemical mapping.

Thereafter, separated nanocolumns were analyzed through TEM analysis where the bottom part is showing In\(_2\)O\(_3\) TF (100 nm) and the top part is of SiO\(_x\) NWs (450 nm). In\(_2\)O\(_3\) and SiO\(_x\) are easily differentiated by the color contrast where the dark part is indicating In\(_2\)O\(_3\) and light part is indicating SiO\(_x\) shown in Fig. 3(a). The measured diameter of SiO\(_x\) NWs is nearly equal for the top to bottom which is of ~ 235 nm. HRTEM of Al NPs is shown in Figure 3(b) from where the d-space are measured in the range of 0.121 nm to 0.128 nm which corresponds to the d-space of Al NPs obtained from XRD. The SAED analysis shown in the inset is obtained for the In\(_2\)O\(_3\) and Al and manifests their polycrystalline nature from the bright spot ring patterns which are also being confirmed by XRD analysis later on.
Figure 3. HRTEM image of In$_2$O$_3$ TF/SiO$_x$ NWs/Al NPs (a) separate SiO$_x$ NWs with In$_2$O$_3$ TF at the bottom, and (b) Al NPs showing d-space with SAED (inset).

Figure 4 shows the XRD pattern of as-synthesized In$_2$O$_3$ TF/SiO$_x$ NWs/Al NPs sample deposited on Si. The XRD pattern reveals the amorphous nature of SiO$_x$ NWs [13] due to the low deposition rate of 1.2 Ås$^{-1}$ and lower substrate temperature (i.e. < 200 °C) [14]. The diffraction patterns from the phases (400) and (440) at ~ 34.63° and ~ 50.8° respectively proved the polycrystalline nature of In$_2$O$_3$ [15]. The stronger diffraction peaks observed at ~ 32.89°, ~ 61.59°, and ~ 69.32° is attributed to the Si substrate [16]. The diffraction peak at ~38.9° corresponds to the (111) crystal plane of Al NPs [17] which is very weak due to the low deposition time of ~ 4 min. The crystallite size of Al NPs was found about ~ 76.6 nm using Debye-Scherer’s relation at the crystal plane of (111).

Figure 4. XRD pattern of In$_2$O$_3$ TF/SiO$_x$ NWs/Al NPs sample.

3.2 Optical Characteristics

Figure 5(a) shows UV-Vis optical absorption spectra of the samples In$_2$O$_3$ TF/SiO$_x$ NWs/Al NPs and In$_2$O$_3$ TF/SiO$_x$ NWs deposited on the glass substrate under the wavelength ranging 350 nm to 900 nm. The enhancement of 1.3 fold is observed in the photon absorption for the In$_2$O$_3$ TF/SiO$_x$ NWs/Al NPs sample as compared to In$_2$O$_3$ TF/SiO$_x$ NWs sample. This enhanced photon absorption form the sample with Al NPs may be due to SPR effect of the Al NPs. The enhancement is equivalently found for the UV-visible-near infrared region as far the reason of surface plasmon resonance (SPR) effect [18]. The spectral sensitivity of the detectors enhances from the localized surface plasmon
resonance (LSPR) effects of the Al NPs also the responses are being altered on the diameter size of NPs [19]. Fig. 5(b) shows the tauc plot i.e. $(\alpha h\nu)^2$ versus photon energy $(h\nu)$ of $\text{In}_2\text{O}_3$ TF/$\text{SiO}_x$ NWs and $\text{In}_2\text{O}_3$ TF/$\text{SiO}_x$ NWs/Al NPs samples. The optical energy band gap of the sample are found out to be ~ 2.56 eV for $\text{SiO}_x$ nanostructures and 2.64 eV for $\text{SiO}_x$ nanostructures with aluminum nanoparticles from the intercept on the energy axis as shown in fig. 5(b). The band gap obtained from our samples are corresponds to the reported band gap of $\text{SiO}_x$ in the literature [20]. It is also reported that the band gap of $\text{SiO}_x$ nanostructures optical bandgap are tunable from 1.5 eV to 2.9 eV by varying the concentration of Si [21, 22].

Figure 5. (a) UV-Vis absorption spectrum of $\text{In}_2\text{O}_3$ TF/$\text{SiO}_x$ NWs and $\text{In}_2\text{O}_3$ TF/$\text{SiO}_x$ NWs/Al NPs and $\text{In}_2\text{O}_3$ TF/$\text{SiO}_x$ NWs/Al NPs samples, (b) $(\alpha h\nu)^2$ versus energy plot of the samples, and (c) Photoluminescence spectrum of the samples.

The increase in bandgap is correlated to the presence of Al NPs [23]. The room temperature PL spectra are shown in Fig. 5(c) for the $\text{In}_2\text{O}_3$ TF/$\text{SiO}_x$ NWs/Al NPs and $\text{In}_2\text{O}_3$ TF/$\text{SiO}_x$ NWs samples using an excitation wavelength of 270 nm. The luminescence spectra show emission peaks at ~ 410 nm (3.02 eV) and ~ 412 nm (3.01 eV) with two shoulder peaks at ~ 438 nm (2.83 eV) and ~ 468 nm (2.64 eV). An average of ~1.16 fold emission intensity is observed after the incorporation of Al NPs on $\text{In}_2\text{O}_3$ TF/$\text{SiO}_x$ NWs. The peak at 468 nm corresponds to the energy band gap of 2.64 eV which is correlated to the tauc plot. While the reason for the peak recorded at ~ 410 nm could be the oxygen defects i.e. can be related to the nonstoichiometric composition of silicon dioxide which makes them responsible for the blue emission [24-26]. Murthy et al. reported similar peak at 2.83 eV for the reason of interface between $\text{SiO}_2$-$\text{Si}$ with a shoulder peak at 2.66 eV [27]. The similar band at 2.83 eV observed due to the interface of $\text{SiO}_2$-$\text{SiC}$ [28] so, the peak at 438 nm could be attributed because of the interface of $\text{SiO}_2$-$\text{In}_2\text{O}_3$-$\text{Si}$. Whereas the shift observed from 412 nm to 410 nm is the contribution of Al NPs which can be also observed from the tauc plot.
4. CONCLUSION

In this paper, SiO$_x$ NWs/Al NPs have been successfully fabricated through the GLAD Technique and have shown the influence obtained on the optical characteristics in the presence NPs. Morphology and structural analysis have been done with the help of FE-SEM and HR-TEM, where FE-SEM reveals the growth of Al NPs. HR-TEM analysis shows the length of SiO$_x$ NWs $\sim$ 450 nm and also the thickness of In$_2$O$_3$ TF is $\sim$ 100 nm. The XRD and SAED results confirm the polycrystalline nature of In$_2$O$_3$ TF and Al NPs. And, the amorphous nature of SiO$_x$ NW from XRD result. The decoration of Al NPs on top of In$_2$O$_3$ TF/SiO$_x$ NWs samples gives the enhanced optical absorption and photoluminescence spectrum. The luminescent band obtained are due to the oxygen defects in SiO$_x$ NW and In$_2$O$_3$ TF. This enhanced optical properties makes the device applicable for the optoelectronic applications.

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