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Growth and Characterization of Nickel Catalyzed Gallium Oxide Nanowires on Sapphire Substrate

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Beta gallium oxide (β-Ga_2O_3) nanowires (NWs) were synthesized via chemical vapor deposition in argon atmosphere using gallium as a precursor and sapphire substrate coated with ultra thin film of nickel (Ni). In this report, we report the growth of β-Ga_2O_3 NWs as a function of deposition time. The structure and morphology of grown NWs were characterized by X-ray diffraction (XRD), energy dispersive X-ray spectroscopy (EDS) and scanning electron microscopy (SEM). The results revealed that single crystal growth of the NWs and their crystallinity improved with the increase in the deposition time. The diameter of β-Ga_2O_3 NWs varied in the range between 40-80 nm and their length was observed up to many micrometers. The optical property of NWs was determined using UV-visible spectrophotometer and the bandgap of β-Ga_2O_3 NWs was found to be about 4.30 eV.

Keywords: Gallium oxide, Nanowires, Nickel, SEM, XRD.

PACS numbers: 78.40.Fy, 78.67.Bf, 78.67.Uh

1. INTRODUCTION

It is well known that one dimensional (1-D) semiconductor nanostructures (NS) including nanowires (NWs), nanobelts (NBs), and nanorods possess unique electrical, optical, and mechanical properties. These properties in many cases are superior to their bulk materials. The reduced dimensionalities of 1-D nanostructure make defect free, high quality material with high surface-to-volume ratio (aspect ratio). Over the last decade, an intensive research has been carried out on nanostructures based binary semiconductors such as ZnO, TiO_2, SnO_2 and Ga_2O_3 [1] because of their wide bandgap nature. The wide bandgap nature makes these semiconductor nanostructures for the potential applications of optoelectronic nanodevices from the wavelength range ultraviolet (UV) to red [2, 3].

Gallium oxide has wide bandgap of about 4.2-4.9 eV [4-6] at room temperature (RT). Beta form of gallium oxide is thermally and chemically most stable form from RT to melting point (1800 °C) [7]. β-Ga_2O_3 has monoclinic lattice structure with lattice parameters $a = 12.23$ Å, $b = 3.04$ Å, $c = 5.80$ Å, and $\beta = 103.7°$. Generally, Ga_2O_3 is n type due to slight oxygen deficiency and these oxygen vacancies act as shallow donor with ionization energy of 0.03-0.04 eV. β-Ga_2O_3 has potential application in solar energy conversion devices, flat panel display, optical limiter for ultraviolet and high temperature gas sensor [8, 9].

In literature, few reports have described the growth of Ga_2O_3 NWs using Ni as a catalyst. Chun et al. [10] reported growth of Ga_2O_3 nanowires using Ni as catalyst where they used 0.01 M ethanol solution of $NiCl_2.6H_2O$ to form Ni nanoparticles on alumina substrate. Chang et al. [11] also reported synthesis of Ga_2O_3 nanowires using Ni as a catalyst. They have used 0.01 M ethanol solution of $NiNO_3$ to form Ni nanoparticles on silicon substrate. Here in this paper, we have synthesized Ga_2O_3 NWs using Ni as a catalyst. We have shown the formation of Ni nanoparticles by thermal evaporation technique. We observed that NWs crystallinity improved with increasing deposition time. The structural, morphological and optical properties of the grown NWs were investigated by X-ray diffraction (XRD), scanning electron microscope (SEM), elemental composition by energy dispersive X-ray spectroscopy (EDS) and UV-vis. spectrophotometer.

2. EXPERIMENTAL

2.1 Sample Preparation

An ultra thin film of nickel (2 nm) was deposited on the sapphire (c-plane) substrate at 10^{-5} Torr by thermal evaporation technique. Further, we have annealed the samples at 650 °C for 1 h in order to form nanoparticles. In our approach, Ga metal with a purity of 99.999 % (Aldrich) was taken as the precursor. About 0.5 g of Ga metal was placed in a quartz boat and Ni-coated substrates were clipped over the boat. The total system was loaded at the center of a quartz tube. The quartz tube was placed inside a tubular furnace at a temperature 900 °C for 2 h, 4 h, and 6 h. A constant flow of argon (Ar) gas was maintained in the quartz tube. The ramp rate of furnace was 10 °C min^{-1}. After the completion of process, the CVD system was cooled down naturally. A white wool-like product was collected over the substrate.

2.2 Characterization

The as-synthesized products were characterized and analyzed by different characterization techniques. For the structural studies, X-ray diffractometer (Philips Xpert Pro) using CuK_α ($\lambda = 1.5405$ Å) radiation in 2θ range 20-80° was used. Scanning electron microscopy images of NWs and Energy dispersive X-ray spectros-

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copy were obtained using Zeiss (Model EVO-50). The optical properties were measure using UV-visible spectrophotometer (Hitachi-U-3900H).

3. RESULTS AND DISCUSSION

3.1 Morphology of Nanoparticles and NWs

Fig. 1 (a)-(d) show the Ni nanoparticles distribution and nanowire morphology. Fig. 1a reveals that nanoparticles are distributed over the sapphire substrate that serves as nucleation sites for the nanowires growth. The average size of Ni nanoparticles is 50 nm. Fig. 1 (b)-(d) show the β-Ga_2O_3 NWs for 2 h, 4 h, and 6 h, respectively. It can be seen from Fig. 1(b) that NWS are at beginning stage. The length of the NWs is in the range of 300-500 nm because the growth process ends at the stage where the gallium metal supply ends. The vermicular NWs are spread over the entire substrate [Fig. 1(c) and (d)]. The average diameters of NWs are 40 nm and 80 nm for 4 h and 6 h, respectively. The length of NWs in both case (4 h and 6 h) are up to many microns.

As we can see clearly from SEM images that morphologies of NWs changes with deposition time. An increment in diameter as well length was observed.

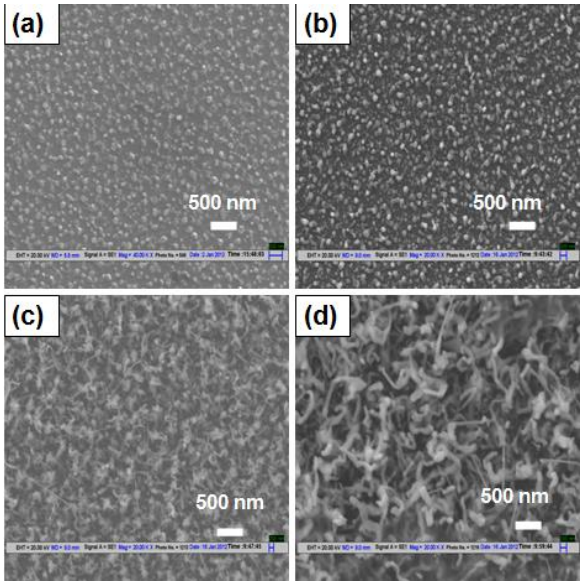

Fig. 1 – SEM images of Ni nanoparticles (a), β-Ga_2O_3 NWs at different deposition time 2 h (b), 4 h (c), 6 h (d)

3.2 Structural Analysis

Glancing angle X-ray diffraction spectra of β-Ga_2O_3 NWs are shown in the Fig. 2. In the diffractograms of the NWs XRD peak at $2\theta = 31.68°$ and $d = 2.82$ Å corresponding to (– 202) or (002) planes is observed to be the most prominent peak. Other peaks at $2\theta = 69.62°$, $d = 1.34$ Å, $2\theta = 72.47°$, $d = 1.30$ Å, $2\theta = 77.97°$, $d = 1.22$ Å and $2\theta = 35.15°$, $d = 2.55$ Å corresponding to (– 420), (– 204), (603) and (111) planes, respectively, are also observed. These peaks matched well with the value for the monoclinic β-Ga_2O_3. The exact 2θ value corresponding to (– 202) or (002) is 31.73°. This slight shifting is occurred because of the existence of the strain. All the diffraction peaks indexed in the Fig. 2 are in good agreement with those of the monoclinic β-Ga_2O_3 with lattice parameters $a = 12.23$ Å, $b = 3.04$ Å, $c = 5.80$ Å and $\beta = 103.7°$ (JCPDS Card No.43-1012). It is observed that crystallinity improved with increasing deposition time. Recently, Shi et al [12] reported the influence of reaction time on the properties of GaN NWs and they have observed that crystalline quality increased with reaction time.

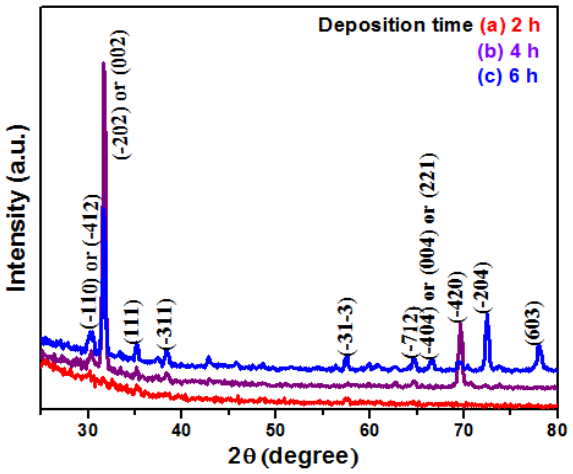

Fig. 2 – XRD patterns of β-Ga_2O_3 NWs for different deposition time 2 h (a), 4 h (b), 6 h (c)

3.3 Compositional Analysis

The compositional analysis of β-Ga_2O_3 NWs was carried out using energy dispersive X-ray spectroscopy (EDS).

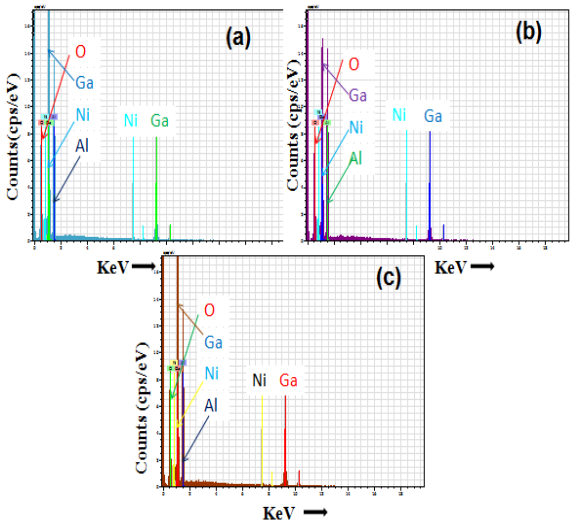

Fig. 3 – EDS spectra of β-Ga_2O_3 NWs for different deposition time 2 h (a), 4 h (b), 6 h (c)

Fig. 3 (a) – (c) shows the EDS spectra and it reveals that NWs mainly comprise of Ga and O, while tip of nanowire consists of Ni particle. The other elements such as Al are also observed due to sapphire substrate. The calculated value of molecular concentration of Ga and O is matched well with powder value of Ga_2O_3.

3.4 Optical Properties

The optical properties of the β-Ga_2O_3 NWs were measured using UV-vis. spectrophotometer. For bandgap determination, a plot of $(\alpha h\nu)^2$ versus photon energy was made. The bandgap of β-Ga_2O_3 NWs was found to be 4.30 eV for 4 h and 6 h. For the first time, Kuo et al. [13] have discussed diffuse reflectance spectrum of Ga_2O_3 NWs and nanobelts. They have reported bandgap of Ga_2O_3 NWs near about 4.56 eV.

In literature, the bandgap of Ga_2O_3 is reported between 4.2-4.9 eV [4-6]. The reason for this uncertainty (variation in bandgap) may be anisotropy of monoclinic structure or difference in preparation condition.

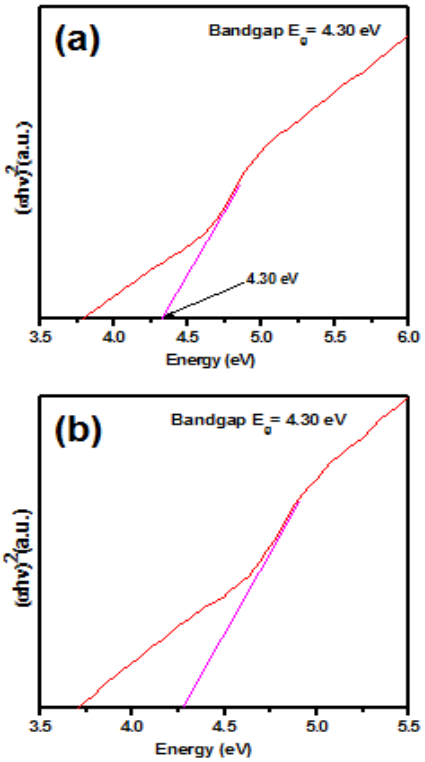

Fig. 4 – Plot of $(\alpha h\nu)^2$ versus photon energy of β-Ga_2O_3 NWs for 4 h (a), 6 h (b)

4. CONCLUSIONS

We have successfully synthesized β-Ga_2O_3 NWs using Ni as a catalyst by chemical vapor deposition method. The morphology of NWs was vermicular and the diameter of the β-Ga_2O_3 NWs in the range between 40-80 nm. The crystalline quality β-Ga_2O_3 NWs improved with the increase in the deposition time. The nanowire mainly consists of Ga and O elements. The bandgap of NWs was found to be 4.30 eV.

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