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Fechete, A., Wlodarski, W., Holland, A., & Kalantar-Zadeh, K. (2006). Growth of indium oxide nanostructures by thermal evaporation. *Proceedings of the 2006 International Conference on Nanoscience and Nanotechnology*, 138–141. <https://doi.org/10.1109/ICONN.2006.340570>

Published Version: <https://doi.org/10.1109/ICONN.2006.340570>

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Growth of Indium Oxide Nanostructures by Thermal Evaporation

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Abstract — In this work, we report the synthesis and characterization of indium oxide nanostructures grown by thermal evaporation on silicon substrates with and without the presence of gold catalysts in the temperature range of 600 to 900°C. These structures are in the form of nanobelts and nanorods with dimensions from a few micrometers in length and less than 200 nm in width. The growth processes involved in the formation of the nanostructures are the vapor-solid (VS) and vapor-liquid-solid (VLS) mechanisms where the former is responsible for growth when Au catalyst is used. Scanning Electron Microscopy was employed to characterize the morphology of nanostructures.

Keywords - Nanobelts, Nanorods, InO_x , Thermal evaporation, Vapor-transport techniques, Gold catalyst.

I. INTRODUCTION

The fabrication of one-dimensional nanostructures of semiconducting metal oxides such as nanorods, nanowires and nanobelts has recently attracted much attention. These nanostructures show novel physical and chemical properties and have potential applications in the development of electronic and optoelectronic devices [1, 2]. Additionally, the application of these structures in the sensor field is very promising due to their large surface to volume ratio [3]. Recently many researches have focused their attention on the fabrication of semiconducting oxide nanostructures with wide-bandgaps, such as indium oxide (direct bandgap energy in of 3.55~3.75 eV). Indium oxide (InO_x) is an important transparent conducting oxide (TCO) material with many applications such as: window heaters, solar cells and flat panel displays [4]. It is also an insulator in its stoichiometric form, whereas in its non-stoichiometric form it behaves as a semiconductor material [5]. There are many reports on the synthesis of InO_x nanostructures in different dimensions and forms such as: nanowires [6] and nanobelts [7] using various methods. These include: physical evaporation [8], laser ablation [9], carbothermal reduction reaction [10] and a template-assisted approach using mesoporous silica [11]. Sensors based on field effect transistors with high sensitivity using InO_x nanowires for toxic gas detection have also been fabricated [12].

In this paper, we report the synthesis and characterization of indium oxide (InO_x) nanobelts and nanorods grown by thermal evaporation through vapor-solid (VS) and vapor-liquid-solid (VLS) growth processes on polished silicon

substrates. Synthesis was conducted with and without the presence of a gold catalyst.

II. EXPERIMENTAL PROCEDURE

The indium oxide nanorods and nanobelts were synthesized by thermal evaporation using 99.995% pure In_2O_3 powder as a source material (purchased from China Rare Metal Material Co. Ltd.). Approximately 3-5 g powder was loaded on an alumina boat and positioned in the central part of a 50 cm long horizontal quartz tube in a furnace (Fig. 1).

Figure 1. Schematic of the experimental apparatus used for the growth of InO_x nanostructures.

Samples of one side polished silicon substrates with and without a Au catalyst layer were placed at distances of 7 cm (labeled as NSiAu for the sample with gold catalyst and for blank sample NSi), 10 cm (MSi and MSiAu) and 15 cm (FSiAu and FSi) from the source material in the tube. A thin layer of Au catalyst was deposited using a DC sputterer, which generated a green surface. During the thermal evaporation process a constant flow of pure Ar gas was maintained at 0.5 l/min. The temperature of the furnace was rapidly increased with a heating rate of 50°C/min. and held for 30 minutes. The deposition temperature was varied from 600°C to 900°C.

The dissociation process occurs at the constant flow of pure Ar when the heating of the In_2O_3 powders starts, thus the In vapors are carried to the sample regions where they condense forming nanorods or nanobelts. After cooling to room

temperature, light yellow layers were found on the inner wall of the quartz tube. The growth mechanism of these nanostructures will be discussed later. The morphology and structure of the product was examined using a Philips XL30 scanning electron microscope (SEM).

III. RESULTS AND DISCUSSION

For temperatures below 650°C no nanostructure growth was observed. The nanostructures were discernable at temperature above 700°C.

Figures 2a and 2b show the SEM micrographs of the synthesized nanobelts at different magnifications obtained at the deposition temperature of 750°C on a blank silicon substrate (sample MSi). Randomly arranged nanobelts with a localized dense distribution can be seen with some of them appearing to be bent. The lengths of the nanobelts are of a few micrometers and have widths between 10 and 200 nm.

Figure 2. SEM micrographs of InO_x nanobelts on a silicon substrate (without Au catalyst) deposited at 750°C. Different magnifications of the MSi sample show: (a) the size, and (b) the shape of the nanobelts.

The nanostructures have a sparse distribution on the silicon substrate in some areas where they are formed in agglomerations with different geometrical shapes and dimensions. Figure 3a and 3b shows nanobelts forming “nano-squares” with dimensions up to several tens of micrometers.

Figure 3. (a) and (b) SEM micrographs of InO_x nanobelts on a silicon substrate (without Au catalyst) deposited at 750°C. Different magnifications of the MSi sample show different shapes of the nanobelts.

The formation of nanobelts without the use of a gold catalyst is believed to be due to the vapor-solid growth mechanism [13].

A possible explanation of the vapor-solid (VS) growth process of the nanobelts is given by Z. R. Dai *et al.* The source material is assumed to vaporize in molecular species at high temperature and is composed of stoichiometric cation-anion molecules. At lower temperatures the molecules will condense onto the substrate forming small nuclei. The newly arriving molecules will continue to deposit on the nuclei, while the surfaces that have lower energy start to form as side surfaces. As the low-energy surfaces tend to be flat due to high mobility of the molecules, more molecules will be deposited in the growth front resulting in the fast formation of nanobelts [14].

The surface energy minimization can play an important role in the formation of nanowires and nanobelts [15]. It can be said also that the size of the nanobelts is determined by the growth temperature and kinetics of the crystal growth (supersaturation ratio). These are the two dominant processing factors in controlling the morphology of the products in the VS growth process [14]. Also it is well known that defects such as: dislocations, kinks, vacancies, scratches, grooves and ledges are favored sites that improve nucleation which results in the formation of nanostructures such as nanowires [16].

Figure 4 shows SEM micrographs of the indium oxide nanostructures obtained for the samples which have a very thin Au catalyst layer. In this case, the growth process involved is the vapor-liquid-solid (VLS) mechanism, which is also called catalysis growth [13]. In this mechanism, proposed for first time by Wagner and Ellis [16], the anisotropic crystal growth is guided by a droplet of liquid alloy. The droplet surface has a higher sticking coefficient and therefore a preferred absorption site for the vapor reactant. As the droplet becomes more saturated with the vapor reactant, different nanostructured growth will begin by the precipitation process of the reactant. The role of the liquid droplet in the growth process is similar to that of a catalyst in chemical reaction; the Au nanoparticle serve as the catalyst between the vapors feed and solid growth and influences the nanostructures' direction and diameter.

As can be seen from Fig. 4a, at 750°C In_2O_3 crystallites are formed around the Au particles, which agglomerated in clusters with dimensions larger than 1 μm . When samples were located further from the In_2O_3 source, the formation of both nanorods and nanobelts around crystallites could be observed, however they have a random distribution (Fig. 4b).

At 900°C the formation of nanorods around Au particle were observed. The diameter of these nanorods is dependent on the gold particle diameter, which is less than 250 nm. The crystallites were homogenously scattered on the surface with distances between clusters being approximately 1 μm (Fig.4c).

Figure 4. SEM micrographs of In_2O_3 nanostructured thin films on silicon (with Au catalyst) deposited at: (a) 750°C for MSiAu sample, (b) 750°C for FSiAu, and (c) 900°C for MSiAu sample.

IV. CONCLUSIONS

In this work we presented In_2O_3 nanostructures obtained by thermal evaporation at different deposition temperatures with and without a gold catalyst layer.

The SEM analysis revealed the growth of nanobelts that were approximately 10-200 nm wide and a few micrometers long at 750°C when no catalyst was used. When a gold catalyst was used, homogenously scattered nanorods were obtained at 900°C.

Work is presently in progress to optimize the deposition conditions and to further characterize these structures using transmission electron microscopy (TEM), X-ray diffraction (XRD) and to obtain a denser distribution of these nanostructures on the entire surface of the substrate for gas sensing applications.

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