

Facile Synthesis of Vertically Aligned ZnO Nanowires on Carbon Layer by Vapour Deposition

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Abstract—A facile vapour deposition method of synthesis of vertically aligned ZnO nanowires on carbon seed layer was developed. The received samples were investigated on electronic microscope JSM-6490 LA JEOL and x-ray diffractometer X'pert MPD PRO. The photoluminescence spectra (PL) of obtained ZnO samples at a room temperature were studied using He-Cd laser (325 nm line) as excitation source.

Keywords—ZnO nanowires, vapor-phase deposition, Ni catalytic layer, facile method of synthesis, carbon catalytic layer, the photoluminescence spectra, X-ray spectrum.

I. INTRODUCTION

At present zinc oxide due to unique physical characteristics is becoming the important material for application in short-wave light-emitting diodes, detectors, piezoelectronic devices, power electronics etc. [1].

Alongside with using ZnO in the form of monocrystals and thin films, the increasing number of potential applications is offered for the aligned nanowire arrays, for example, for piezogenerators [2], solar elements [3], gas gauges [4], etc. Therefore, the synthesis of high-quality ZnO material with controlled microstructure for optoelectronic and electronic devices is a very important topic.

To use aligned high-quality ZnO nanowire (NW) arrays with controllable microstructure, various techniques for ZnO film growth have been developed [5-8]. In most studies, aligned ZnO NWs were grown by surface catalyzed vapor-

phase deposition. The aligned growth upon the epitaxial orientation relationship between the ZnO NWs and substrate was achieved on various single crystal substrates including sapphire, GaN, SiC, etc. When synthesizing the ZnO NWs a catalytic layer is pre-deposited on the surface of the substrate.

The gold [6], silver and palladium [7], as well as iron [8] and copper [9] nanoparticles are used for this purpose.

Amorphous substrates such as quartz, glass etc., and cheap catalysts, for example, carbon or ZnO seed layer, etc. have much higher commercial potential.

In this work, aligned ZnO NWs were prepared on Si and SiO₂/Si substrates with a carbon seed layer. The NWs were grown by surface catalyzed vapor-phase deposition process. The crystalline structure, orientation, micro-morphology and photoluminescence spectra of the obtained ZnO films were studied. The physical mechanism of carbon seed layer influence on the ZnO NWs growth was discussed.

II. EXPERIMENT

The ZnO NWs were grown by vapor transport method with a Zn source. The ZnO layers have been synthesized by a simple vapor transport system, consisting of alumina tube furnace with internal diameter of 20 mm and length of 480 mm, forepump and gas supply system.

The granulated metal zinc with cleanliness of ~99.998 % was used as a Zn source. Three substrates were usually used for this experiment. The first of them was located on distance about 5 mm from a Zn source, the second - 20 mm and the third - 40 mm. The source of zinc was situated in the maximal temperature field, and substrates - in the field of a temperature gradient. The furnace was sealed and pumped out. After pumping out the gas-carrier was moved into the furnace at the fixed ratio of partial pressure of atmospheric air and argon as 2:1. The total pressure was as variable parameter and it varied within the limits from 300 torr up to 30 torr.

It was revealed, that at pressure higher up to 300 torr, zinc almost stops evaporating, and the growth of ZnO layer does not occur. It provides a way to fix the time of synthesis of structures, therefore the heating of substrates was carried out at pressure 300 torr. When required temperature (550-650°C)

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was achieved the pressure quickly decreased up to the chosen value. And synthesis was carried out during short (it's usually 10-20 minutes) time. After it the pressure was increased up to 300 torr and furnace was cooled down.

The (100) - or (111) -oriented polished silicon wafers with thickness 300 micron and with in size $\sim 3 \times 10$ mm were used as substrates. The substrates were carefully cleared, degreased, washed out in ethyl spirit and twice-distilled water and dried in a drying box before ZnO layer growth.

In this work the pure silicon substrates as well as substrates with thin layers of nickel, zinc or carbon were used. The Ni or Zn layer thickness of 50 nanometers was created by thermal deposition in the vacuum. Two methods of creation of thin carbon layers have been applied. First, the thin layer of amorphous carbon was created by wetting the substrate with alcoholic solution of polymer. As polymer the polyelectrolyte-surfactant complex (PSC) was used. The PSC have been prepared by the dropwise addition of a cellulose-based polycation solution (N, N, N-trimethylammonium derivatized hydroxyethyl cellulose JR-400) to anionic (sodium salt of dodecylbenzenesulfonate) surfactant solution. The PSC formed very uniform and thin film on Si substrate surface after drying at room temperature. It is obvious, that pyrolysis of the polymer film takes place during increase of temperature up to 550-600°C and a carbon thin film is formed instead. The estimation for thickness of the carbon layer with taking into account concentration of polymer gives value as low as several nanometers. The thin graphite layers were also pulled out from graphite onto silicon substrate by the known Scotch tape technique.

III. EXPERIMENTAL RESULTS

The morphology of the sample obtained at temperature 600°C within 20 minutes and pressure at 180 torr is shown in Fig. 1. The areas consisting of structures in the form of hexahedral rods with identical sizes were found out. Underside ends of these rods were fixed on a substrate. However the areas consisting of identical rods did not cover the whole surface of the substrate but settled down as the separate spots.

To obtain the samples with uniform arrays of the NWs, the substrates with pre-created zinc (or nickel or carbon) seed layer were applied. The Zn or Ni seed layer allows to obtain homogeneous monocrystalline ZnO NW layers oriented by (002) plane parallel with substrate. The morphology of ZnO sample which has been grown up on nickel layer is shown in Fig. 2 as an example.

It was found that carbon seed layer deposition enhances dramatically the growth of ZnO NWs. In Fig. 3 the boundary of carbon seed layer (at the left) and a clean surface (on the right) of a sample after vapor-phase deposition process at 550°C/90 torr/15 min are shown. Apparently, nucleation and growth of ZnO NWs do not occur on a clean surface. Only the ZnO NWs nucleated in a gas phase and then precipitated on the clean surface of Si substrate, are observed.

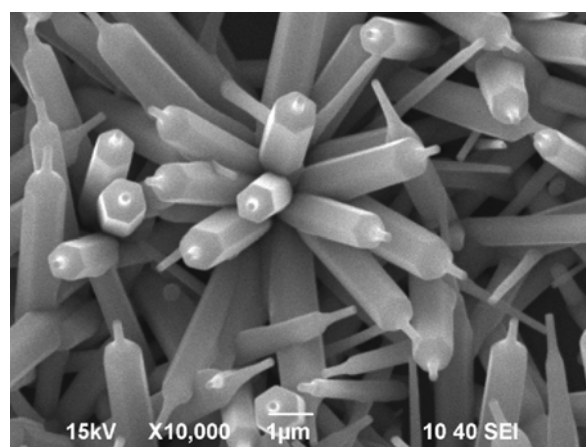
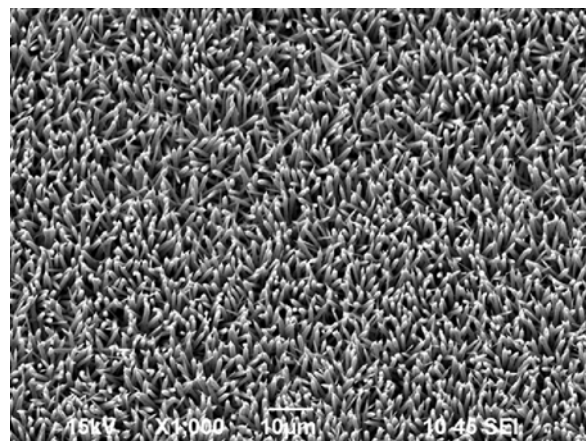


Fig. 1 Morphology of ZnO layer received on a clean silicon substrate during 20 minutes synthesis at 600°C and pressure at 180 torr

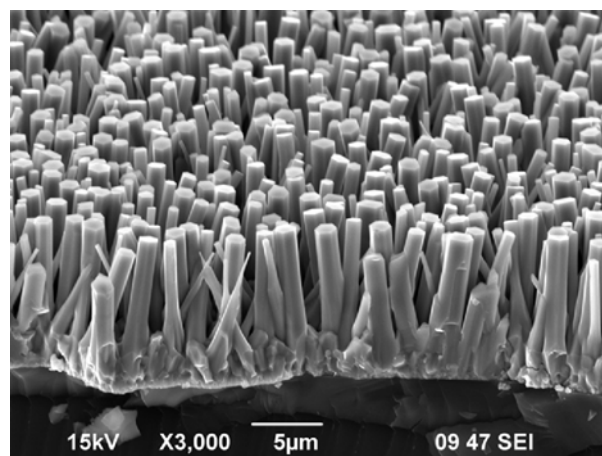
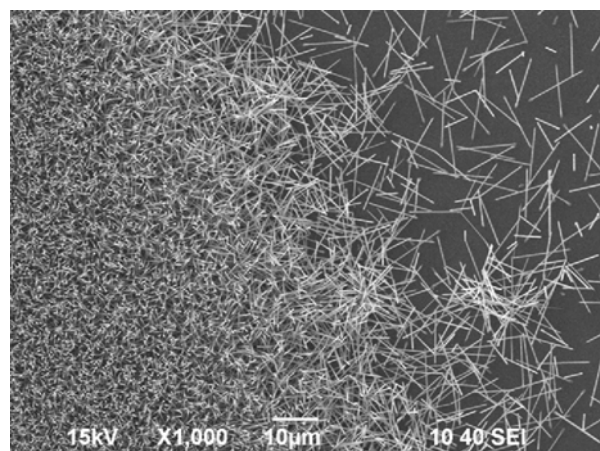


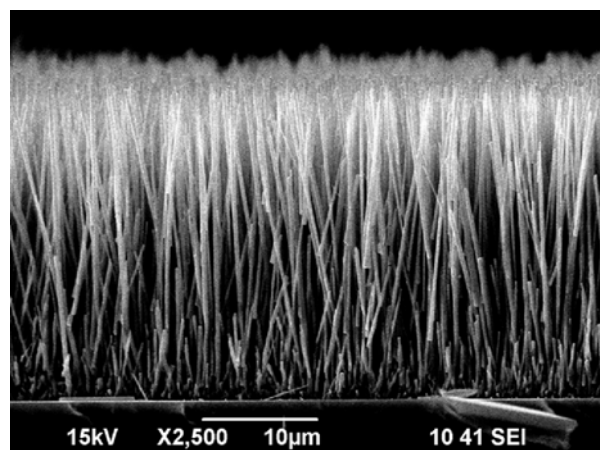
Fig. 2 Morphology of ZnO layer obtained on silicon substrate with Ni catalytic layer

The NWs grow via the vapor-liquid-solid (VLS) mechanism by the self-catalyzed growth [10]. At the same time ZnO NWs layer synthesized on substrate covered by C seed film, was synthesized via a vapor - solid (VS) mechanism. The carbon layer provides presence of nucleation

points. It drastically increases the growth rate on substrate surfaces.



a



b

Fig. 3 Morphology of ZnO layer deposited on a silicon substrate with the carbon seed layer. a - a boundary of carbon seed layer (at the left) and a clean surface (on the right), b - a cross-section view of a sample with ZnO NWs grown on carbon seed layer

XRD data of samples are resulted in Fig. 4 and show presence of the basic reflexes (002) and (004), it testifies to a high degree of ordering of ZnO rods. Reflexes from a silicon substrate were not observed because of the large thickness of a ZnO layer.

The photoluminescence spectra (PL) of obtained ZnO samples at a room temperature are studied using He-Cd laser (325 nm line) as excitation source (Fig. 5). While the energy of PL band in ultra-violet area 3.23 eV (half-width is 150 meV) is close to ZnO energy gap (3.37 eV at 300 K) and this is a result of free exciton recombination, the green band with energy around 2.5 eV is attributed to lattice defects formed in the host such as ionized oxygen vacancies.

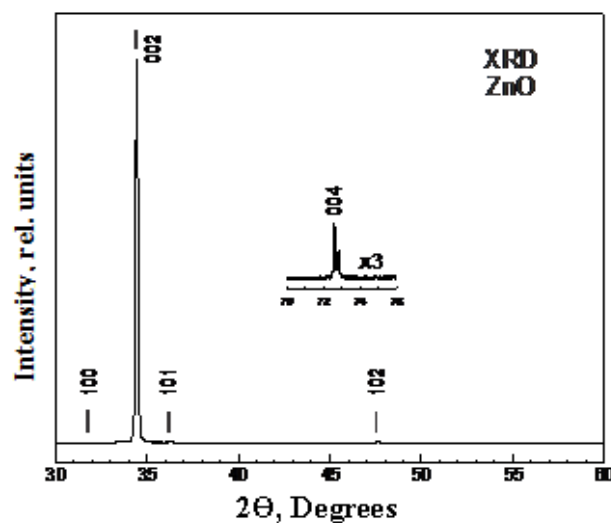


Fig. 4 XRD data of ZnO layer received on a silicon substrate with the putted carbon layer

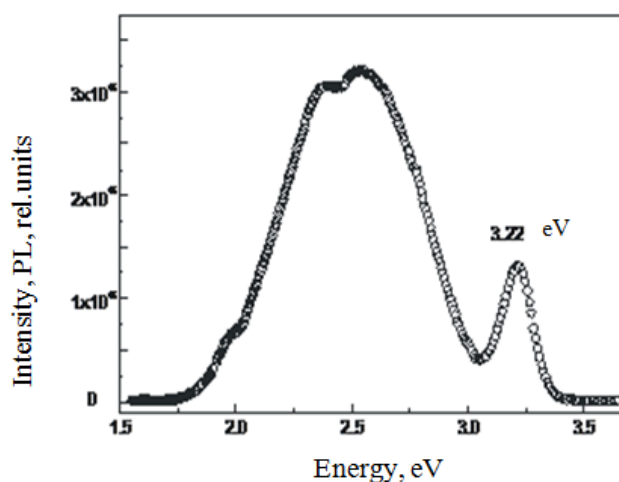


Fig. 5 PL spectrum of ZnO NWs grown on carbon seed layer on the substrate surface

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