ZnO Nanostructure Alignment on Alumina Surface by Carbon Seeding
A. Marcu, L. Trupina, T. Yanagida, C. P. Lungu and T. Kawai

Abstract: ZnO nanostructures were grown on alumina substrate by Pulsed Laser Deposition (PLD) and Vapor-Liquid-Solid (VLS) technique using Au catalyst. While the catalyst disposal on the substrate surface had a random distribution, we were trying to align the grown nanostructures by controlling nucleation process by additional seedings. While pressing substrate surface with a carbon contaminated aluminum foil, a weak tendency of nanowire alignment on parallel lines could be observed on some substrate areas. More evident results were obtained for ZnO nanobelts growing case. We interpret nanostructure lining as preferential interaction of the vicinal plane edges with the contaminated foil and respectively ZnO preferential nucleation on the vicinal planes edges, after interaction with the foil surface.

Keywords: ZnO nanowires, Nanostructure alignment, Carbon seeding

I. INTRODUCTION

Zinc Oxide (ZnO) is a direct band-gap (Eg = 3.37 eV) semiconductor with a large excitation binding energy (60 meV), exhibiting near UV emission, transparent conductivity and piezoelectricity [1]. Thus, ZnO nanomaterials are promising candidates for nanoelectronic and photonics. Compared with other semiconductor materials, ZnO has higher excition binding energy, is more resistant to radiation, and is multifunctional with uses in the areas as a piezoelectric, ferroelectric and ferromagnetic. ZnO-based semiconductor and nanowire devices are also promising for the integration on a single chip. So far, the various applications of ZnO nano materials such as UV detectors [2-5], chemical sensors [6-8] and FED [9-11] are under way. Moreover, ZnO is biocompatible and can be used for biomedical applications without coating so biosensors are also a promising opportunity for the ZnO nanostructures.

Nano-devices fabrication involve a precise control of nanostructure morphology, properties and spatial positioning. In applications as microfluidics or surface acoustic sensors (SAW), the structures alignment is crucial for the device performances. Even if the nanostructures fabrication is more and more effective using so called Bottom-UP techniques as vapor-liquid-solid (VLS) for structure growing, the precise positioning of the catalyst on the substrate surface is still a challenge. The best performance in catalyst positioning still belongs to the Top-Down techniques by using beam lithography which is in many cases not an affordable option. There are also non-lithographic techniques for structure alignment involving growing the structures using templates [12-15] or various

This work was supported in part by a grant of the Romanian National Authority for Scientific Research, CNCS – UEFISCDI, project number PN-III-IDPCE- 2011-3-0522 and PN-III-ID-JRP-RO-FR-2012-0160

A.Marcu* and C.P. Lungu are from National Institute for Laser Plasma and Radiation Physics, Bucharest-Magurele, 077125, Romania, Tel/Fax: +40 21 457 4027, e-mail*: aurelian.marcu@infiph.ro
L.Trupina is from National Institute for Material Physics, Atomistilor 405 bis, P.O.Box MG7, Magurele, Romania
T.Yanagida and T.Kawai are from Institute of Scientific and Industrial Research, Osaka University, 8-1 Mihogaoka, Ibaraki, Osaka567-0047, Japan

II. EXPERIMENTAL SYSTEM

Our experimental system consist of a Pulsed Laser Deposition (PLD) using an Lambda Physics ArF excimer laser. We have gown ZnO nanostructures based on the Vapor-Liquid-Solid (VLS) technique using Au catalyst on (11-20) Al2O3 substrate. Some special plume filtering techniques are necessary for growing ZnO nanowires using our experimental system [20-21]. By considering plume interaction with obstacles [22,23], we opted in this experiment for the axe-off system geometry (Fig. 1) filter technique, and a variable offset ‘h’ of the substrate surface ax from the plume central horizontal propagation plane. The ‘h’ value control would help as controlling the plume filtering efficiency and respectively the plume particle fluency. We used a sintered ZnO target for the ablation process and a single crystal alumina substrate. Ambient oxygen pressure was 1 Pa and substrate temperature about 800°C.

For the disposal of the seeds over the substrate surface, we were using an aluminum (flat) foil heaving a carbon contaminated surface. Such a foil was placed on the alumina substrate and pressed against the deposition surface (Fig. 2), in order to transfer the carbon contaminant on the substrate surface.

---

*This work was supported in part by a grant of the Romanian National Authority for Scientific Research, CNCS – UEFISCDI, project number PN-III-IDPCE- 2011-3-0522 and PN-III-ID-JRP-RO-FR-2012-0160
A.Marcu* and C.P. Lungu are from National Institute for Laser Plasma and Radiation Physics, Bucharest-Magurele, 077125, Romania, Tel/Fax: +40 21 457 4027, e-mail*: aurelian.marcu@infiph.ro
L.Trupina is from National Institute for Material Physics, Atomistilor 405 bis, P.O.Box MG7, Magurele, Romania
T.Yanagida and T.Kawai are from Institute of Scientific and Industrial Research, Osaka University, 8-1 Mihogaoka, Ibaraki, Osaka567-0047, Japan
III. RESULTS

For the case of the optimal system parameters, and respectively for appropriate plume filtering and particle fluency, corresponding in our system to a 5 cm target-substrate distance and about 5 mm ‘h’ off-ax distance, vertical ZnO nanowires (Fig. 3 a) could be obtained on the several square millimeters (11-20) alumina substrate as could be seen in a scanning electron microscopy (SEM) image in Fig. 3a. However, while reducing the plume filtering efficiency and increasing the fluency, (in our case by decreasing ‘h’ with few millimeters) the grown morphology would change from nanowire to nanobelts with no preferential orientation and a top view image of the substrate surface is presented in Fig. 3 b. For such experimental conditions, previous investigations proved that by sputtering carbon seeds on the substrate surface we could still grow nice and vertical nanowire [19] but with no preferential alignment of the grown structures over the substrate surface. In this experiment, by pressing the substrate surface instead of sputtering the carbon seeds the nanowire growing enhancement was also obtained. However, unlike for the carbon sputtering case, a weak tendency of linear alignment of the grown structures could be noticed. In figure 4 are presented a top view SEM image of ZnO nanowires on alumina substrate surface and respectively a 45° angle view image.

By further decreasing the ‘h’ offset value, the plume filtering get worse and the particle fluency increase. Even by using carbon seeds, in this case, ZnO grown morphology would be a mix of nanowire and nanobelts. Interesting fact is that the grown structures where having a more evident alignment tendency and SEM images of such a substrate surface are presented in Fig. 5. The ZnO structures are still grown vertical on the substrate surface but tend to form parallel lines. The distance between the alignment lines is of the order of tens of nanometers. The alignment tendency is visible on areas of square micrometers order or more, but without covering uniform the hole substrate area.

Fig. 2 Substrate contamination using a carbon contaminated aluminum foil

Fig. 3 ZnO nanostructures growing in a) optimal conditions and b) non optimal conditions

Fig. 4 ZnO nanowire alignment tendencies on alumina substrate a) top view and b) 45° view
An atomic force microscopy (AFM) investigation was used to compare the substrate surface in different stages of the sample preparation. We started with a clean 11-20 alumina surface. In order to see the vicinal plane edges, the alumina substrate was initially thermally treated [24] and an AFM image of the 11-20 alumina surface is presented in Fig. 6a. The substrate vicinal plane edges could be clearly seen and it is interesting to notice that the distances between the plane ages is of the order with the ZnO aligned nanoblets inter-space. After the gold catalyst deposition, the substrate was heated up to the deposition temperature (800°C) and kept for several minutes in order to form the catalyst droplets, but no alignment of gold catalyst could be observed Fig. 6b. After pressing the surface with the contaminated aluminum foil surface no differences from the initial surface could be traced by AFM. EDX techniques could not detect traces of carbon presence either. However, the carbon seeds disposed by sputtering, even if they were also experimentally confirmed as enhancing the growing process they were also no traceable. By transferring more carbon the changes could become traceable by both AFM and EDX investigations (Fig. 6c) but this case is far from the optimal seeding condition. Thus, we could only conclude that that we do transfer traces of carbon using this technique, but the amount of transferred material could not be detected with our methods.

Fig. 5 ZnO nanobelts alignment tendencies on alumina substrate a) top view and b) 45° view

IV. RESULTS INTERPRETATION AND DISCUSSIONS

Fig. 6 AFM images of the : a) 11-20 alumina surface, b) gold catalyst after being heated at the working temperature (800°C) and c) EDX pattern of over-contaminated surface with AFM surface image inlet (inset SEM image of the scanned area)
A transmission electron microscopy (TEM) image of a ZnO structure is presented in Fig. 7a. Since the gold droplet is still on the top of the structure it means that the VLS mechanism is still the leading process of the nanostructure growing. This is sustained by the previous observation that, generally, no nanostructure growing could be observed in the absence of gold catalyst. However the triangular membrane growing process, between the nanowire and the substrate, does not seem to be related with the VLS process. Thus, in Fig. 7b, we can see SEM images of a ZnO nanowires having a triangular membrane which are not up the nanowire tip. Furthermore, in Fig. 7c we can see not only nanowires growing together with nanobelts, but nanowire grown through a membrane of a different wire suggesting that the nanowire and the nanobelt growing processes are independent processes which do not actually affect each other. However, the ZnO membrane alignment has to be related with the carbon contamination technique since no alignment could be observed while using carbon sputtering. Taking also into consideration that the distance between aligned structures is comparable with the distance between substrate vicinal plane edges and that the surface 'steps' and defects are also known to work as seedings [25-27], we can came to the conclusion that, in our experiment, the membrane growing is related with the ZnO preferential nucleation on the vicinal surface edge. If the assumption is true, the vicinal surfaces edge has to be particularly affected by the interaction with the carbon contaminated aluminum foil, in spite of the fact that these modifications were untraceable within our investigations. Thus, a preferential seeding on the vicinal plane edges seems effective for booth nanowire and nanobelts samples. The assumption is a reasonable one since for a ‘plane-plane’ interaction, the contact between surfaces would take preferentially place between the peak zones, which in our case correspond to the edges of the vicinal planes. However, the interaction between substrate surface and the foil seems to have rather critic parameters for observing this phenomena, since the alignment of the grown structures could be observed only on some of our investigated samples and only over square millimeter order areas at most.

Fig. 7 Microscopy images of ZnO nanobelts: a) TEM image of a ZnO nanostructure, b) SEM image of an incomplete ZnO membrane and c) SEM image of a nanowire grown through a membrane
VI. REFERENCES


