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ZnO nanowire mophology control in pulsed laser deposition

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Nanowire morphology is known to depend in vapor-liquid-solid (VLS) technique on catalyst shape and size. We have investigated nanowire growing by VLS technique using pulsed laser deposition (PLD) approach. Nanostructures morphology has been studied from the laser ablation plume point of view. For the case of ZnO nanowires, plume control proved to have a crucial influence in controlling nanostructures morphology and outside an optimal range, the 'wire shape' is completely destroyed. A comparison between ZnO nanowire morphology obtained at different laser power is presented. Results for 'eclipse' deposition setup with some special masks are also included, together with the interpretation of some morphology results.

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1. Introduction

Nanowires have recently become a very widely investigated area due to the continuous development of nanotechnology and the possibility of using nanowires as "bricks" for nano-devices construction [1-5]. In most of the cases the specific cylindrical shape of the nanowire is mainly interesting only from the reproducibility point of view, but in some particular cases a precise control of shape is desired [6-9]. There are various techniques for nanostructures fabrication generically classified as Top-Down and Bottom-Up approaches. Vapor-Liquid-Solid (VLS) technique represents one of the most promising techniques of the Bottom-Up approach. It was initially developed for chemical-vapor-deposition (CVD) systems, but was later used with various techniques including sputtering and PLD. Nanowire fabrication by PLD/VLS, in spite of the fact that it does not have such a high productivity as CVD/VLS, has some certain advantage regarding nanostructures purity, crystal structures and material properties that for some special purposes might be preferred to other techniques.

Zinc oxide is a wide band gap semiconductor material (3.2 eV) interesting for light emitting diodes, laser diodes [10], chemical sensors [11] and more. Nanostructures fabrication using this material has been approached by many techniques [12-16] including PLD [17-19]. Even if VLS technique brings a better shape and size control and the PLD technique is known as having the best results from the structures purity and crystal structures, PLD/VLS is not a widely used technique for ZnO nanowires fabrication. One of the reasons is that VLS process limitation are not very well understood, particularly for PLD processes and further optimizations are necessary. The aim of this study is to investigate the VLS growing limitations respectively optimizations, from the ablation plume point of view.

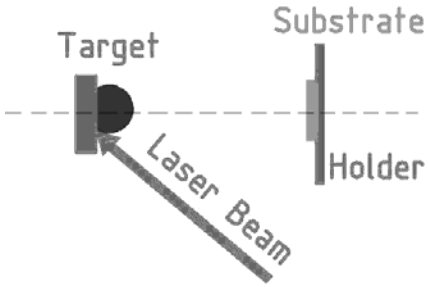

Fig. 1 PLD experimental setup – basic scheme

2. Experimental method

We have grown ZnO nanowires by PLD/VLS with Au catalyst, starting from a classic PLD system with deposition ambient conditions already considered as optimized in previous publications regarding PLD/VLS ZnO nanowires growing, respectively 1 Pa oxygen pressure and 750^0 C substrate temperature. Laser energy was up to 100 mJ/pulse and repetition frequency 10 Hz. Substrate-target distance was 5 cm. A scheme of the basic experimental setup is presented in Fig. 1. The target was obtained by ZnO powder sinterization at 1100^0 C. The substrate was a commercial 0001 single crystal alumina.

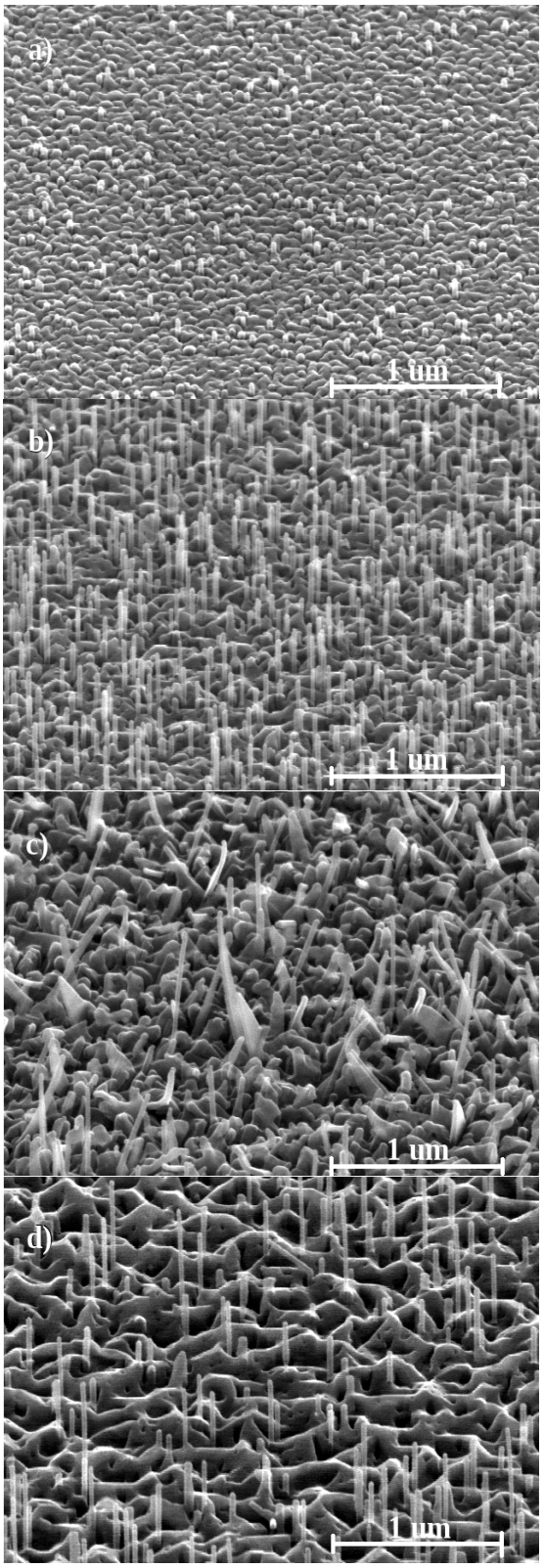

Fig. 2. ZnO gown structures morphology at a) 15 mJ, b) 30 mJ, c) 45 mJ and d) 60 mJ.

3. Results and discussions

For beginning we have investigated the laser pulse energy variation influence on ZnO grown structures. Due to the fact that ZnO plume is strong and fast, the laser power variation is easily reflected in plume size variation and respectively ZnO structures growing rate. For this reason the investigated variation range was limited to 15-60 mJ respectively a power density variation between 0.4-1.6 J/cm^2 . As could be observed from Fig. 2, at 15 mJ pulse energy the ZnO rather tends to form a thin film with some island growing tendencies, suggesting a too low ablation rate. At 60 mJ pulse energy, laser beam seems to ablate to much material exceeding VLS optimal growing rate and producing a porous structure of nanobelts and nanowires. The optimal laser pulse energy seems to be in our case around 40 mJ, where most of the growing structures seem to have cylindrical shape. However, nanobelts, conical wires and island structures are still present and morphology control seems rather poor. We will further keep ambient conditions and consider ablation plume as not optimized for these present conditions. Since our laser pulse energy fluctuations are about 15-20%, a more accurate laser energy tuning would have no meaning In other words, it means that laser energy instability is generating a plume variation outside of VLS optimal growing rate/pulse for these experimental conditions. Thus, as a second step we can try a direct control of the plume using obstacles. First of all we have, as the simplest option, the 'plain mask' (Fig. 3) deposition method (also known as 'eclipse' technique). The plain mask is placed ex centric between target and substrate. By analyzing structures morphology in several places of the substrate surface, significant difference could be noticed between substrates' 'well' covered area (Fig 4 a) and uncovered area (Fig 4 b) of the same sample, deposited under the same experimental condition mentioned above. A 'good' morphology area that could be found in between the two extremes presented above, is shown in Fig. 4 c).

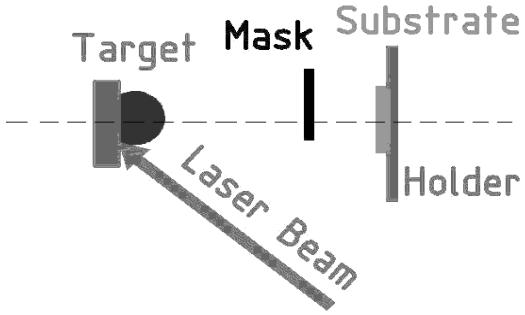

Fig. 3 a) Plane mask - experimental setup.

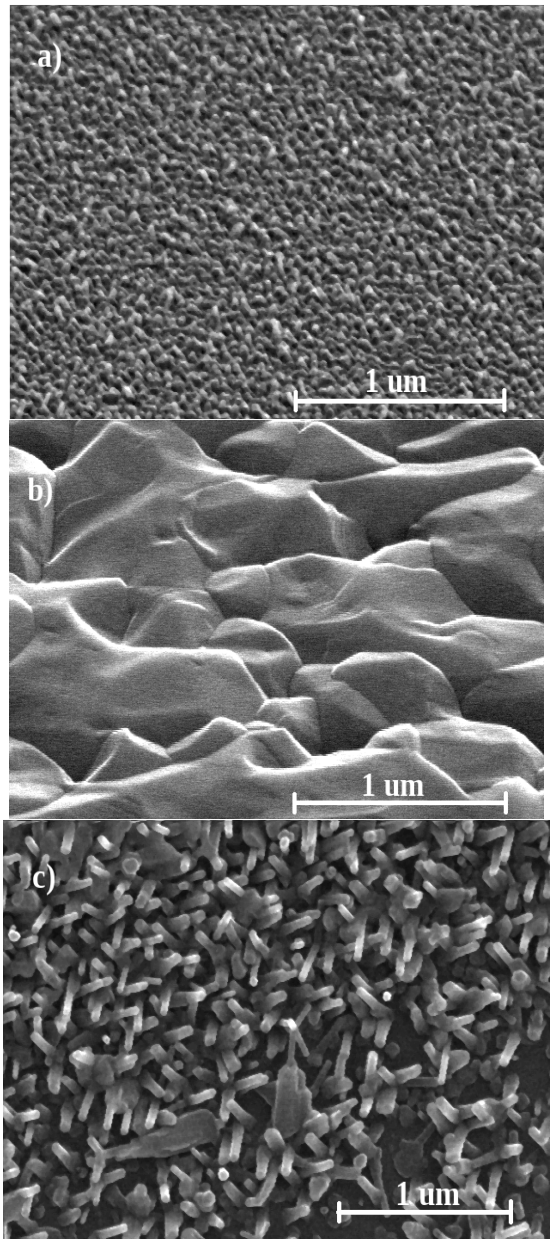

Fig. 4 a) SEM - Substrate morphology under the plane mask b) SEM – Substrate morphology outside the mask are c) SEM – optimal substrate morphology under the plane mask - corresponding to a substrate position in between a) and b).

By using this 'plain mask' setup we were able to obtain good nanowire morphology in some specific and localized areas. This proves that plume control is indeed crucial for a good nanowire morphology, but this experimental setup does not really give the possibility of a good and uniform nanowire morphology for the whole sample. The problem with plume adjustment by using plain mask technique is the fact that, as previously discussed in literature [21-23], the plume is not uniform distributed after the interaction with the obstacle, especially at small distances mask-substrates. Even if the plume reduction is effective and a fine global tuning is possible, the plume spatial uniformity might be a problem when the growing process is so sensitive to the plume. For this reason optimized areas as the one presented in fig. 4 c exist on the substrate but can not be extended for the 1 x 1 cm substrate.

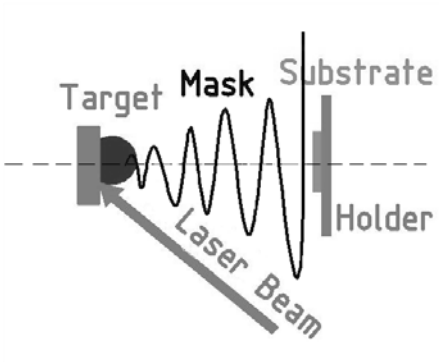

Fig. 5 Helical mask experimental setup

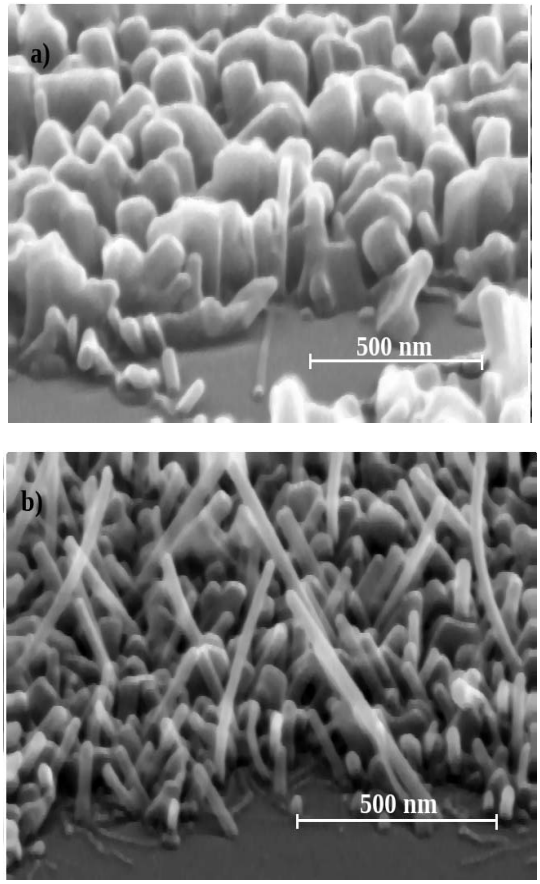

Fig. 6 SEM-morphology with a helical mask of wire diameter of: a) 1mm and b) 2 mm.

A further step for plume control was the changing of the mask type from plain to helical. A generic setup scheme is given in Fig. 5 and more constructive and

experimental details were published elsewhere [21]. We should briefly mention as a main difference between this mask and the plain one the fact that the plume, while interacting with the obstacle, is no longer going around the mask but through the mask. This makes a big difference in plume uniformity after interaction with the mask. Thus, such a helical mask presents the big advantage of an uniform plume distribution on the shadowed area for an optimized mask geometry.

Using such a helical shadow mask system and setting the laser power to the most stable energy (around 50 mJ) we have decided to control the plume by tuning the mask penetration. The easiest way for this is the adjustment of the spire diameter [21]. In Fig. 6 there are presented two samples grown in the same experimental conditions excepting mask wire diameter, respectively using 1 mm and 2 mm wire. For the case of the 1 mm mask wire diameter the ZnO morphology is still considerably affected, respectively nanostructure's diameter is still larger than the original catalyst diameter estimated at about 20 nm, suggesting a thin film growing over the VLS grown structures. For the case of the 2 mm wire mask the nanowires morphology is a good one. Nanowires are about the same diameter as the estimated catalyst diameter and, unlike the case of the plane mask, the entire surface of the substrate is uniformly grown. The drawback of the mask wire diameter increase is a decrease of about half of the nanostructures growing rate, by decreasing mask penetration. By further increasing mask wire diameter to 3 mm the plume penetration is dramatically decreased together with the deposition rate and the wire is no longer growing by using these ambient conditions and laser power.

For interpretation of these results we consider the competition between the thin film growing and the VLS growing. Thus if the VLS has the optimum conditions, most of the particles are going to be absorbed by the liquid catalyst and the grown deposited morphology is going to be nanowire of a diameter given by catalyst size and the length determined by the deposition time. When the growing conditions start deviating from the VLS optimal ones, the thin film formation start being significant (Fig 6 b) and furthermore dominant (Fig. 4 b). In our case the only change in growing conditions is the ablated particles plume, and we consider the particle's incident flux variation as 'critical' for the VLS growing process. Thus, if the incident flux is to small, the critical concentration inside the catalyst droplet, needed for VLS growing, could not be reached as also observed for the MgO [24] and while the flux is too strong, the VLS growing rate does not seem able to rise over a certain value, and the thin film growing process starts again becoming significant or even dominant over the VLS process.

4. Conclusions

In conclusion, ZnO nanowires have been grown using PLD/VLS technique. ZnO nanowire growing process has been proved to be very sensitive to plume variation. In similar ambient conditions we were able to change the growing morphology from films to nanowires only by controlling the ablation plume. Thus, flux optimization proved to be an important factor for nanowire morphology control. Furthermore, if we control plume by geometrical techniques, plume spatial uniformity over the substrate is an important issue. Using a helical mask with an optimized penetration rate we were able to obtain a uniform ZnO nanowire growth on the 1 × 1 cm deposition area.

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