LASER ACTIVATION TO GROWTH ZnO NANOSTRUCTURES

ACTIVACIÓN LÁSER PARA EL CRECIMIENTO DE NANOESTRUCTURAS DE ZnO

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I. INTRODUCTION

ZnO is a non toxic and abundant material with electrical, optical, mechanical and chemical characteristics that make it very suitable for a diversity of applications in optoelectronic, piezoelectric, sensors and solar cells [1]. ZnO has been used in solar cells playing diverse roles like antireflecting coating, transparent conductive oxide, buffer layer, electron transport material among other, probing its tremendous functionality. In addition, it can be obtained as thin films and in a diverse family of nanostructures [2] using low cost techniques like the hydrothermal one [3], for example. The hydrothermal techniques allows, by means of creating small nucleation points called seeds in the substrate, to growth from nanorods to nanoflowers [3]. The sedimentation or also called activation process plays a key role in the growth.

In this occasion, instead of using the typical procedure, we explore the possibility of using a laser source as a local heat source. The main advantages of this approach would be the drastic decrement of time involved as well as the possibility of making micropatterns using the laser beam [4]. It might be also possible to control the seeds characteristics by changing the laser irradiation [5].

We have grown ZnO nanorods using the traditional and laser activation approach. In order to characterize and compare them we have used scan electron microscopy (SEM).

II. EXPERIMENTAL APPROACH

TCO covered glasses were used as substrates for growing the ZnO nanorods. In a solution of nitric acid and deionised water (1:2 molar ratio) the glasses were immersed after they were mechanically cleaned with detersive. After some hours the substrates were washed some times with deionised water and sonicated for 3 min. Finally they were again washed with ethanol and dried with a nitrogen gun.

For the seeds activation by the traditional method a solution of 5 mM of zinc acetate dehydrate in ethanol was prepared. The substrates were wet with a drop of this solution and a thin layer was formed using the spin-coating method for 20 s [6]. This step was repeated two times in order to achieve an entire coverage of the sample. Then the substrates were heated in a furnace with an air atmosphere at 350 degC for 20 min. The ZnO seeds film was obtaining by the thermal decomposition of zinc acetate (Figure 1) [7].

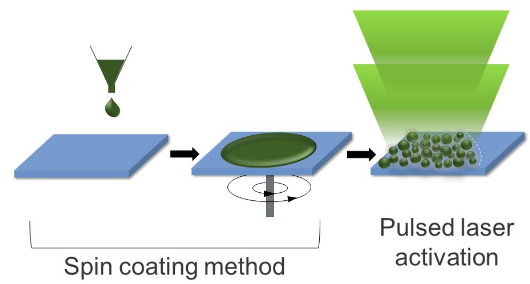

Figure 1. Diagram of the obtaining of the ZnO seeds layer using the spin-coating method and heating the sample in a furnace at 350 ^{o}C for 20 *min*.

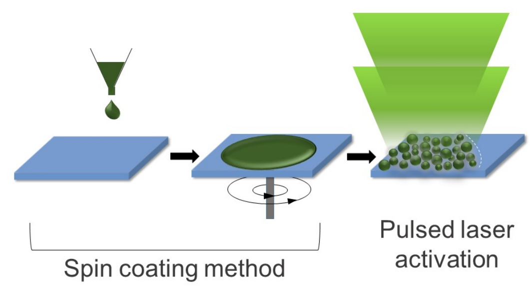

Figure 2. Diagram of the obtaining of the ZnO seeds layer using the spin-coating method and pointing a pulsed laser on the sample.

On the othe hand, for activating the seeds using a pulsed laser, the covering of the substrate with zinc acetate in ethanol by the spin-coating method was repeated ten times, in order to guarantee enough material to interact with the laser beam. A 532 nm pulsed Nd:YAG laser was then pointed on a section of the sample as a local heat source (Figure 2). The laser-sample distance was 29.4 cm. The laser fluence and frequency were 21 mJ/cm^2 and 4 Hz respectively, and the number of pulses was varied in 2 and 6 in order to study the influence that this parameter would have. The interaction time between the laser beam and the sample is in the order of seconds.

Finally, the substrates covered with the seeds layers were submerged in a solution of 50 *mM* of zinc nitrate hexahydrate and hexamethylenetetramine (HMT) with 1:1 molar ratio, for obtaining the ZnO nanorods. The solution was heated for 1.5 hr at 90 degC in a closed system. Then the samples were washed with deionised water and dried with a nitrogen gun [8].

III. RESULTS AND DISCUSSION

The seed layer was effectively activated on the site where the laser was pointed. The Figure 3 (a) shows a SEM image took at the edge of the zone where the laser beam interacted with the zinc acetate layer. Two zones can be clearly distinguished: one where the laser impacted and an homogeneous nanorods growth was obtained (Figure 3 (b)) and the other outside the laser beam spot where there was not an ordered growth (Figure 3 (c)). Image (b) was taken closer to the center of the spot showing a better coverage than in the edge of the spot.

With the laser activation the nanorods obtained were much less vertically aligned (Figure 4 c, d, e, f) than in the case of the traditional activation (Figure 4 a, b), where in addition the density is higher (about 34 rods per μm^2). For activation with 6 pulses the density is the lowest (about 8 rods per μm^2) and the vertical alignment is lost even more. With the laser activation the nanorods were obtained in the form of needles unlike the traditional method where the diameter of the rods is constant with the height.

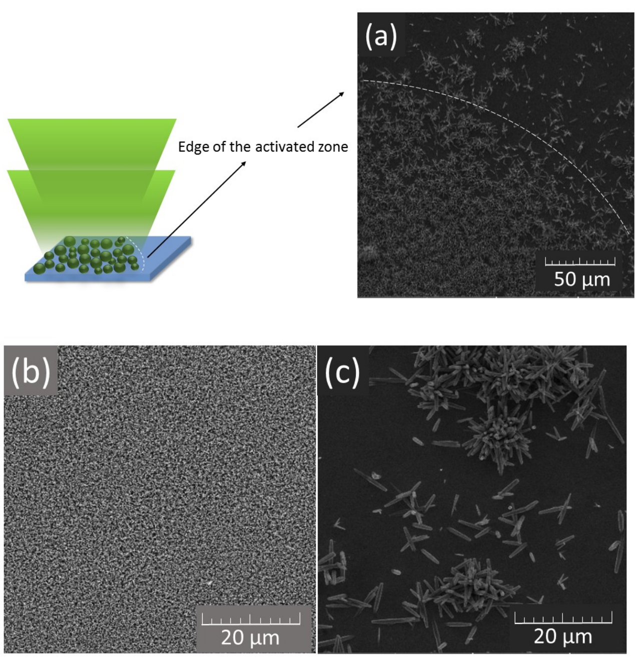

Figure 3. SEM images show: (a) edge of the laser spot (6 pulses), (b) homogeneous nanorods growth inside the laser spot (2 pulses) and (c) disordered growth outside the laser spot (2 pulses). The images scales are (a) 50 μm, (b) and (c) 20 μm.

The differences obtained in the nanorods morphology can only be explained arguing about the influence of the seeds features in this parameter since the complete set of sambles was grown in the same experiment, at the same conditions.

The seeds can have different size and distribution, and this characteristics strongly impact in the nanorods morphology and alignment [7]. The crystal orientation of the seeds is also relevant for the alignment and it is supposed that in random distributed seeds, the vertically alignment is controlled by the competition between neighbors [9].

Baruah and Dutta [10] have reported that there is an important dependence between the homogeneity in the distribution of the ZnO seeds and the temperature of the activation process. They explain that this is related with the surface tension of the solvent (ethanol) that keeps the particles together in a thin film.

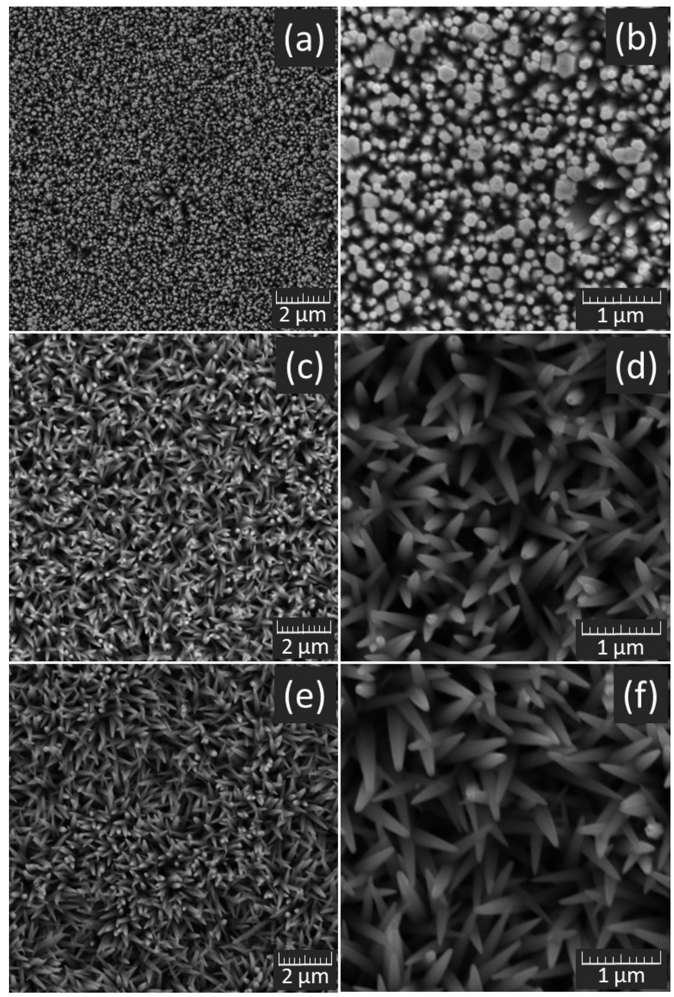

Figure 4. SEM images show the ZnO nanorods grown by traditional activation (a and b) and laser activation of the seeds: (c and d) 2 pulses and (e and f) 6 pulses. The shown scales for (a), (c) and (e) are 2μm, while for (b), (d) and (f) are 1μm.

It is our supposition that it is even more important the interaction of the nanocrystals on the surface depending of the temperature in such a way that increasing T promotes the grains diffusion and coalescence, bringing as a result a rougher surface with larger seeds.

In our case decreasing the laser fluence would be equivalent to decreasing the temperature. This would be appropriate to achieve better results in terms of controlling the density and vertical alignment of the nanorods.

IV. CONCLUSIONS

It was designed and implemented a new and simple experiment for seed layer activation using a pulsed laser. It was activated a defined zone with a homogeneous nanorods growth but less vertically aligned in comparison with the traditional method. This suggests that, due to the laser fluence used, the seeds formed were stacked, creating clusters, and the clusters formation is not favorable to grow vertically aligned nanorods. We propose to carry out a new experiment reducing the laser fluence in order to obtain a thin film of seeds homogeneously distributed over the substrate, which would contribute to a better alignment of the nanorods.

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