

PLD fabrication of ZnO nanostructures on metal-coated substrates

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Abstract. In this work, ZnO nanostructures were fabricated on metal (a metal alloy containing Fe, Cr, Mn and Ni) coated silicon substrates by applying pulsed laser deposition. The samples were prepared at substrate temperatures in the range of 550 – 650 °C, oxygen pressure of 5 Pa, and laser fluence $\leq 1 \text{ J cm}^{-2}$, i.e., process parameters usually used for thin-film deposition. We found that the metal layer's role is substantial in the preparation of nanostructures, the morphology of the catalyst layer determines the growth of the ZnO nanowalls and the increase of the process temperature leads to nanorods formation on the nanowalls.

1. Introduction

The synthesis of semiconducting nanostructures has attracted considerable interest due to their potential importance in the fabrication of nanodevices. ZnO is one of the semiconducting materials of great current interest because of its wide direct band gap (3.37 eV) and large exciton binding energy (60 meV). The potential uses of such materials include gas sensors, UV emitting diodes and UV sensitive photocells, whose efficiency benefits from a large surface area [1,2].

A variety of fabrication techniques have been employed to synthesize nanostructures; these include thermal evaporation, laser-assisted ablation, template-based methods, solution-phase syntheses, etc. [3,4]. Pulsed laser deposition (PLD) has also proved to be a suitable method for the synthesis of nano-scale materials [5-7]. The method involves direct laser ablation of the target material into a gas phase, which is then transferred to a substrate held at a specific temperature. Because of the high deposition rate as a result of the energetic plasma and the high absorption rate of the target materials, especially suitable for those with high melting point, the PLD method has been extensively applied for deposition of oxide materials. By modifying the deposition conditions (including the process gas and its pressure, the substrate temperature, the target-to-substrate distance, the laser wavelength and fluence, the pulse repetition rate, etc.), it is possible to produce a variety of nanostructures, such as nanorods, nanowires, nanoparticles, etc. [8,9,6,10].

Basically, nanostructures can be formed with or without catalysts. A catalyst-free approach allows the fabrication of nanostructures directly or by a seed layer on the substrate [11,6,12]. A catalyst

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approach requires a metal catalyst, namely, a stable and effective nucleation agent deposited on the substrate [13,9,14,15]. The Au catalyst has been widely used for growing 1-D ZnO [13,14,10,9]. Investigating the growth of different nanostructures using catalysts other than gold is important from the viewpoint of both fundamental research and applications. Other catalysts that have been used include Ag, Cu, Ni, and Fe [15-17]. Zhu et al. made a comparative study of the growth of ZnO nanowires with Au, Ag, Fe, and Ni as catalysts [18]. Iron has been extensively used in the catalytic growth of carbon nanotubes, but its application to the fabrication of other nanostructured materials has rarely been studied. Randomly oriented Fe-related ZnO nanowires were successfully grown on Si and sapphire substrates [18]. Kuo et al. demonstrated the growth of uniform and vertically aligned ZnO nanorods with a diameter of 80 – 100 nm on a sapphire substrate covered by a Fe/ZnO bilayer [17]. The authors discussed also the mechanism of ZnO nanorods and nanowalls growth in the presence of a Fe-based catalyst. However, to the best of our knowledge, pure metals have only been used for the deposition of a catalyst. This is why we focused our investigations on the formation of nanostructures by means of deposition of a metal-alloy catalyst.

The aim of this work was to fabricate ZnO nanostructures by PLD using a Fe-based catalyst layer deposited on the substrate before the nanostructure growth. The morphology of the ZnO nanostructures depends on the substrate temperature and on the morphology of the pre-deposited catalyst layer.

2. Experimental

The experiments were performed in a standard on-axis PLD configuration. The third harmonic of a Nd:YAG laser ($\lambda = 355$ nm, $\tau = 18$ ns full-width at half-maximum (FWHM), and a repetition rate of 10 Hz) was used for ablating a ZnO ceramic target. The laser fluence applied was 0.5 J cm^{-2} . (100)-oriented silicon (Si) covered by a metal-alloy layer was used as a substrate. Catalyst layers with an average thickness of 40 nm were produced by thermal evaporation of a metal target while the substrate was kept at room temperature. The distance between the target and the substrate was maintained constant at 60 mm. Two different substrate temperatures were applied in the experiments, namely, 550 °C and 650 °C. All experiments were performed in an oxygen atmosphere at a pressure of 5 Pa for and deposition time of 90 min.

The surface morphology of the nanostructured ZnO samples was analyzed using scanning electron microscopy (SEM). The elemental composition and chemical state of the sample surfaces were studied using X-ray photoelectron spectroscopy (XPS). Electron dispersive X-ray spectroscopy (EDX) was employed in order to determine the elemental content of the metal-alloy target.

3. Results and discussions

As a first step in the nanostructure growth, all silicon substrates were covered by thermal evaporation of the metal-alloy target. The elemental analysis of the metal target material is presented in figure 1. As it is seen, the metal target is a Fe-Cr alloy with small additions of Mn and Ni. After deposition of a thin metal film with a thickness of about 40 nm, XPS analysis on the surface was performed in order to determine the elemental content of the as-prepared catalyst layer. The results obtained show that the metal film has a native surface-oxide layer. Furthermore, the thickness of this layer undoubtedly increases in the process chamber while the substrate is heated in the oxygen atmosphere.

The surface morphology of the covering layer after heating the substrate for 10 min up to 650 °C is presented in figure 2. The nanostructure growth temperature used in this work (550 or 650 °C) is much lower than the melting point of Fe or Fe-oxide (1538 °C or 1377 °C). This makes it unlikely that melting of the thin film or formation of metallic nanocluster occurred during the heating procedure before the growth of ZnO nanostructures. As it is seen in the figure, no nanoparticles or nanoclusters exist. However, one can observe the initial stage of the formation of holes in the film. The holes formation is probably due to the poor wetting of the Si surface. It should be mentioned that no Si compounds were detected by the XPS analyses performed after heating the Fe-Cr alloy film.

In summary, the increase of the substrate temperature during the heating (before ZnO deposition) changes the morphology but preserves the elements' content in the metal layer (no Si-compounds).

The second step of the nanostructure growth was PLD of ZnO material on the metal-covered substrate. The surface morphology of the ZnO nanostructures fabricated at different substrate temperatures is presented in figure 3. The growth of ZnO follows the nanowalls formation. The top view of the structures for both temperatures used resembles a net (figure 3a and 3b). The higher substrate temperature applied during the experiments forms nanorods on top of the nanowalls (figure 3b). The diameter of the nanorods is approximately 50 nm, their length being defined by the deposition time.

When the ZnO target ablation starts, the laser-generated plume ensures the presence of charged (Zn^{2+} , Zn^+ , O^+ ions) and neutral (Zn and O atoms) species, which react with the metal layer. The use of a metal layer and high process temperatures suggests a vapor-liquid-solid (VLS) mechanism for the nanostructures growth. Typical for the VLS mechanism is the presence of metal particles on the tips of the nanostructures. In our case, no elements originating from

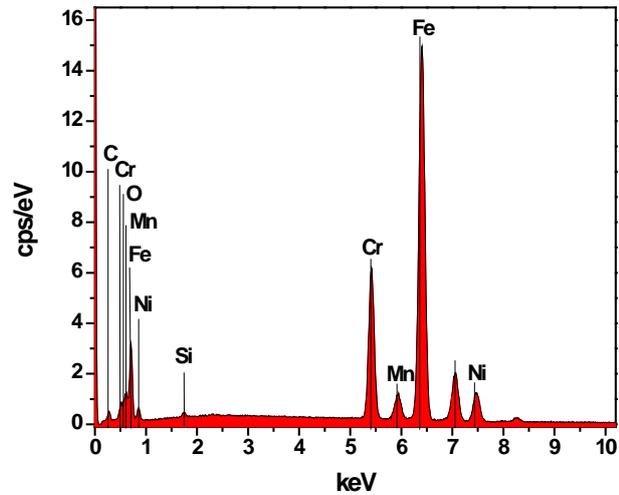


Figure 1. EDX analysis of the metal target material.

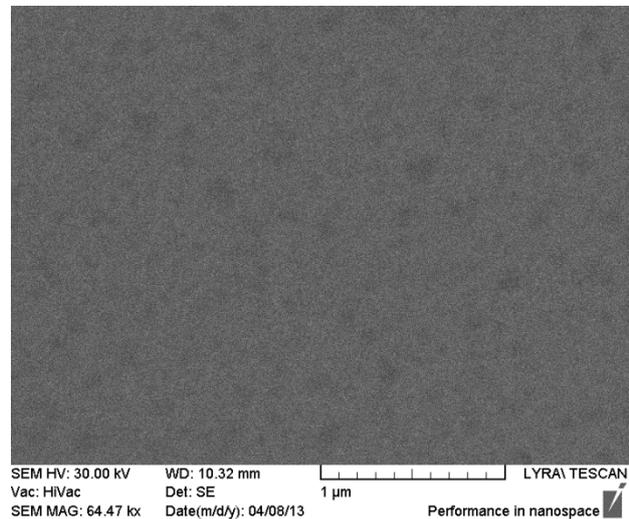
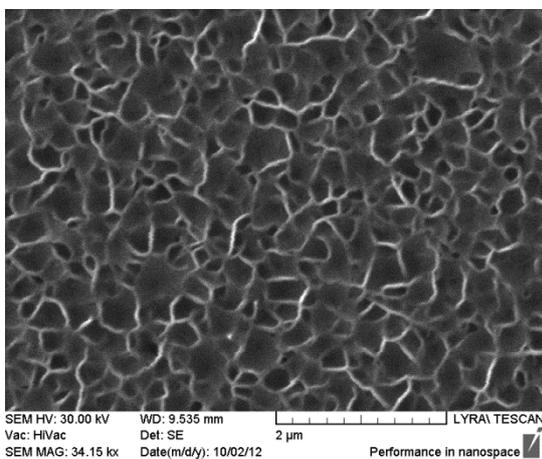
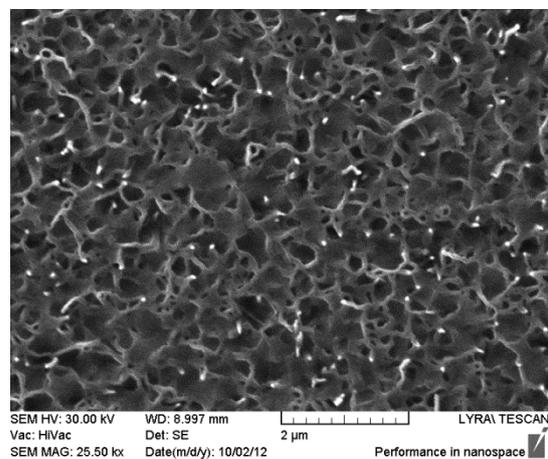


Figure 2. SEM image of the metal-alloy layer after heating up to 650 °C.



(a)



(b)

Figure 3. Top view of the ZnO nanostructure prepared at substrate temperature (a) 550 °C and (b) 650 °C.

the metal-alloy layer were detected by the XPS analyses performed on the samples' surfaces. These results give us a reason to suggest that the growth of the ZnO nanostructures follows a vapor-solid (VS) growth mechanism.

The metal layer's role is substantial for the preparation of nanostructures. A thin ZnO film was produced on a pure Si substrate (without a metal-covered layer) under the same experimental conditions. The morphology of the covering layer defines the nanostructure's growth and development. The use of different metals or alloys with differing physical and thermodynamic properties for forming a cover layer allows one to produce a variety of surface morphologies of the covering layer and, subsequently, of the nanostructures.

4. Conclusions

ZnO nanostructures were grown with a Fe-based catalyst deposited on silicon by PLD. The morphology of the catalyst layer defines the further evolution of the nanostructure. Heating the Fe-alloy layer leads to the formation of holes in the surface. Subsequently, the growth of ZnO on the catalyst layer follows the nanowalls formation. A higher substrate temperature applied results in the formation of nanorods on top of the nanowalls. The ZnO nanowalls growth follows a vapor-solid growth mechanism.

Acknowledgements

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