

Electrochemical growth and characterization of nanostructured ZnO thin films

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ZnO is a wide band-gap (ca. 3.4 eV) semiconductor, piezoelectric, pyroelectric, biocompatible, transparent in the visible spectrum and UV light emitting material. The fabrication in 2001 of the first nanobelts of semiconductor oxide materials lead to a rapid expansion of researches concerning one dimensional nanostructures (nanotubes, nanowires, nanobelts), given their possible application in optics, optoelectronics, piezoelectricity, catalysis. Researches carried on up to date evidenced the possibility to obtain an extraordinary variety of ZnO nanostructures, in function of the experimental parameters and the used growth methods. In this work we present morphostructural results on nanostructured ZnO layers obtained by electrochemical deposition. The films have been grown on gold covered glass plates and Si wafers, in various experimental conditions such as: nature of the wetting agents, electrical polarization of the substrate (continuous, pulsed). The influence of the growth conditions on the crystalline structure and morphology of the films is revealed by scanning and transmission electron microscopy studies. The films show a variety of growth morphologies, from entangled-wires-like to honeycomb-like layers. These large-specific-surface layers will be tested as nanostructured substrates for photovoltaic cells with improved efficiency.

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1. Introduction

ZnO is a wide band gap semiconductor (cca. 3.4 eV), with piezoelectric and pyroelectric properties, biocompatible and transparent in the visible range, with UV photoemission [1]. Its intrinsic physical properties are relatively well known in the case of the bulk material. Recently, however, the interest for ZnO has risen again due to, on one hand, the successful growth in 2001 of the first nano-belts of oxide semiconductor materials and, on the other hand, the last theoretical results showing the possibility of inducing room temperature ferromagnetism in ZnO doped with transition metal ions [2, 3]. This makes that ZnO is nowadays intensely studied worldwide either as thin films or nanocrystals for applications in cutting edge fields like spintronics, nanotechnology and optoelectronics.

Last years researches on ZnO have shown the possibility of achieving an unimagined variety of nanostructures, depending on the experimental parameters of the growing techniques employed: physical or chemical vapor deposition [4, 5], molecular beam epitaxy [6], hydrothermal growth [7], metal-organic chemical vapor deposition [8], sol-gel [9]. In specific experimental conditions, ZnO nanowires, nanobelts, nanorings, nanocapsules have been grown using the above mentioned techniques. From this extraordinary morphological variety at nanometric scale, a multitude of applications can be imagined in fields like sensors, optoelectronics and photovoltaic devices. Given the achievable nanostructural diversity, using ZnO as nanostructured electrode in

organic solar cells seems a very attractive alternative with the goal of obtaining higher output solar cells.

In this work we report on growing nanostructured ZnO films by electrochemical deposition and their morphological characterization by scanning electron microscopy (SEM).

2. Experimental

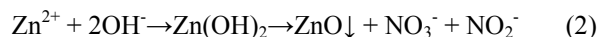
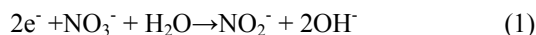
For the electrochemical deposition we have used as electrode and collecting substrate Si wafers previously coated with a 50 nm thick Au layer. The deposition bath contained a 0.1 M solution of $Zn(NO_3)_2$ as source of Zn ions. The deposition bath was maintained at 363 K and stirred during deposition. The Au coated Si wafers have been immersed in the deposition bath, so that the active area of the working electrode was around 2 cm².

The growth morphology of the ZnO coatings has been examined by SEM using a JEOL JSM 5510 electron microscope operated at 30 kV.

3. Results and discussion

We intended to study the influence of wetting agents on the films growth morphology. With this aim, we have used three kinds of deposition baths, keeping constant the concentration of Zn ions: in one case we used the pure 0.1 M $Zn(NO_3)_2$ solution, in the second case we added polyvinyl pyrrolidone (PVP) with 40 000 molecular mass,

while in the third case we added gelatin. The chemical reactions leading to the formation of ZnO are:

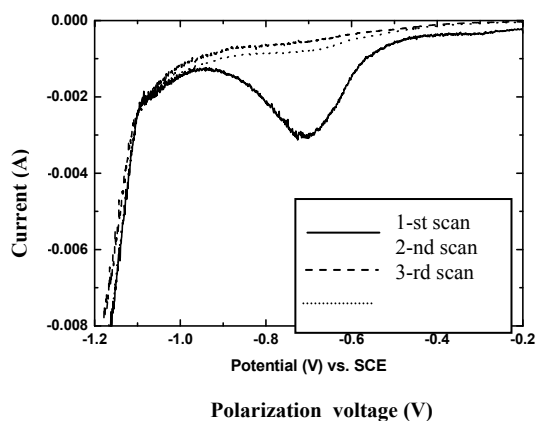


or, the global reaction:



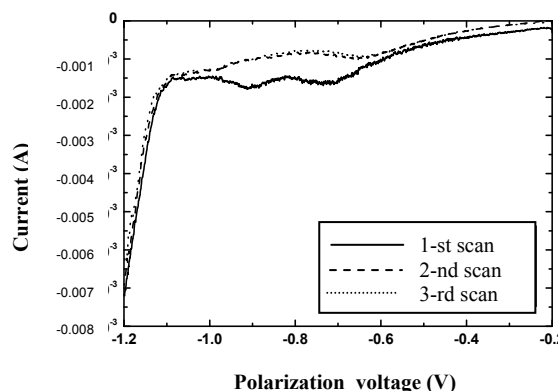
Table 1. Experimental conditions used for the samples 1-6 of nanostructured ZnO films.

| Sample No. | Layered structure | Polarization mode | Polarization voltage (mV) | Growth duration (min.) |
|------------|--------------------------|-------------------|---------------------------|------------------------|
| 1 | ZnO / Au / Si | constant | -800 | 60 |
| 2 | ZnO / Au / Si | pulsed | -800 / 0 | 80 |
| 3 | ZnO + PVP / Au / Si | constant | -1000 | 60 |
| 4 | ZnO + PVP / Au / Si | pulsed | -1000 / 0 | 90 |
| 5 | ZnO + gelatine / Au / Si | constant | -800 | 60 |
| 6 | ZnO + gelatine / Au / Si | pulsed | -800 / 0 | 90 |

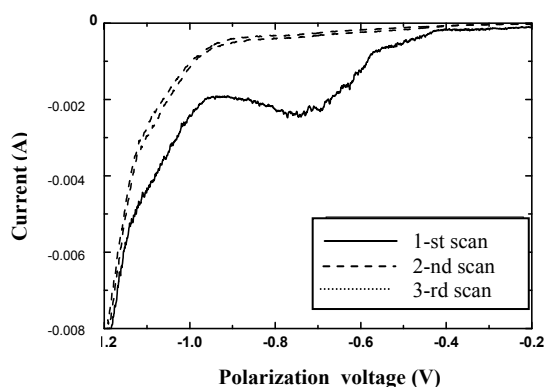


(a)

As one can see, both the bath composition and substrate nature are important.



(b)



(c)

The experimental deposition conditions are summarized in Table 1. In Figure 2 we show the polarization curves used for the pure solution and the cases where gelatine and PVP have been added.

Fig. 1. Polarization curves for the 3 deposition solutions employed: (a) no additive; (b) gelatine added; (c) PVP added.

At the first scan, when the deposition takes place directly on the Au layer, the current is higher, while it is slightly lower for the second and third scan. The fact that the current value for the second and third sweeping is lower might be explained by the presence of the already deposited semiconducting layer, with a lower electrical conductivity than the initial Au layer. The ZnO deposition occurs approximately in the $-0.5 \div -1$ V range, with slight variations depending on the bath nature. The sudden current jump at voltages higher than -1 V might be explained by the onset of the metallic Zn deposition.

The current values are in the same range for the three electrochemical baths.

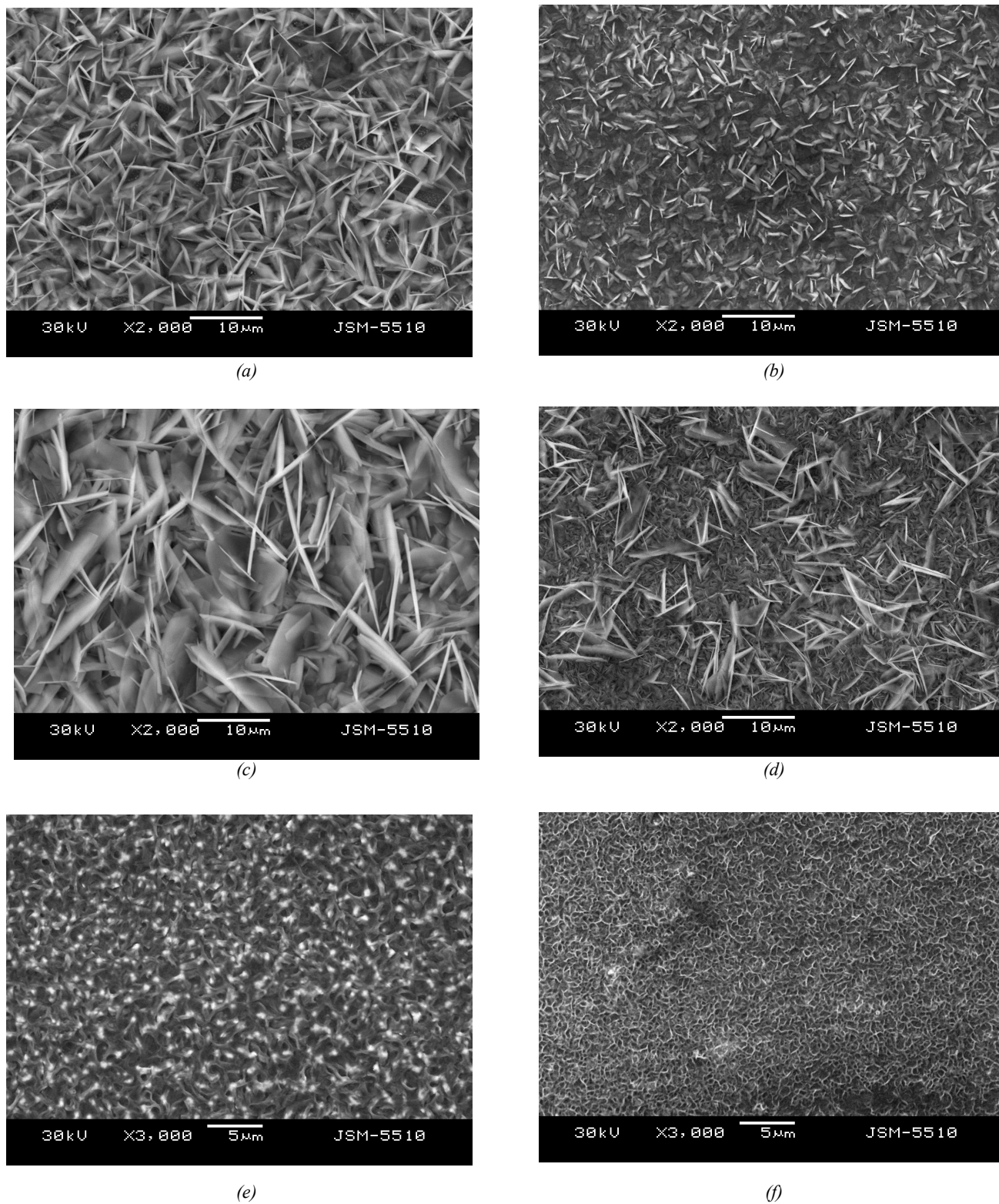


Fig. 2. SEM images of the ZnO coatings obtained in various experimental conditions: (a) pure $\text{Zn}(\text{NO}_3)_2$ solution, constant polarization voltage; (b) pure $\text{Zn}(\text{NO}_3)_2$ solution, pulsed polarization voltage; (c) PVP added solution, constant polarization voltage; (d) PVP added solution, pulsed polarization voltage; (e) gelatine added solution, constant polarization voltage; (f) gelatine added solution, pulsed polarization voltage.

The SEM images presented in Fig. 2 show a clear structured growth, with features in the micrometric and nanometric range, depending on the experimental

conditions. In four experimental situations (Fig. 2 a-d) the films grow as microplates oriented mostly perpendicular to the substrate. The microplates thickness is below 100

nm, while their lateral size varies in function of the deposition conditions.

The SEM images in Fig. 2 a and b correspond to the ZnO coatings obtained from the pure $\text{Zn}(\text{NO}_3)_2$ solution at a constant -800 mV and pulsed polarization voltage, respectively. The differences in the growth morphology between the two films come from the size and orientation of the microplates. The film grown at constant polarization potential shows platelets with a larger lateral size and a better homogeneity regarding both the size and orientation with respect to the substrate. Most of the platelets are oriented almost perpendicular to the substrate, giving the aspect of a honeycomb. For the film grown in pulsed voltage conditions, the lateral size of the platelets is around 50% smaller and only a little part of them are oriented perpendicular to the substrate. Moreover, one can distinguish two populations of platelets, by their size. The largest of them (around 3 μm lateral size) are oriented almost perpendicular to the substrate. The second population is formed of platelets smaller than 1 μm lateral size having a random orientation with respect to the substrate. In our opinion, these differences are due to a certain levelling effect of the pulsed deposition. During the deposition at constant voltage, a more or less ion depleted electrolyte layer forms in the electrode proximity. The film growth is governed by the ion diffusion through this depleted layer. In the pulsed deposition case, growth takes place only during the negative voltage pulse. Between the polarization pulses (0 V), the deposition is interrupted, while the solution regains its equilibrium regarding the ions involved in the chemical reaction occurring at the cathode.

In Fig. 2 c and d we present the SEM images of the ZnO coatings grown in the solution with PVP addition, at constant voltage and pulsed polarization, respectively. The growth morphology is similar to the one in the case of the non-added solution, the coating consisting in platelets with thicknesses below 100 nm and lateral size up to 10 μm . The platelets size is double compared to the pure solution case. The size difference might be explained by two factors: the effect of the PVP acting as wetting agent and the higher polarization voltage, raised to -1 V. Just as in the previous case, there is clear difference between the continuous and pulsed polarization situations. The platelets lateral size distribution shows a single population in the constant voltage case, with an average size around 7 μm . The size population is clearly split in two for the pulsed voltage situation, one population with an average size around 5 μm and the other, more numerous, with an average size around 2 μm .

The growth morphologies of the films deposited in the gelatine added solution are presented in Fig. 2 e and f, for the constant and pulsed voltage, respectively. The two morphologies are completely different from the situations where pure $\text{Zn}(\text{NO}_3)_2$ solution and PVP added solution have been used. The films still exhibit a structured morphology, only this time not as microplatelets. They are highly porous and show an entangled bands and entangled wires morphologies in the two cases, constant and pulsed polarization, respectively. The bright spots on the image in Fig. 2 e may correspond to metallic Zn rich areas. Like in the two previous cases, application of a pulsed polarization voltage leads to a reduction of the

morphological features specific size, from bands to wires in this particular case. The striking morphological difference in this situation indicates the effectiveness of gelatine acting as a levelling agent. Gelatine molecules get hung on points where the electrical field is more intense, namely the rapid growing features, reducing, this way, the growth rate. The presence of the levelling agents in the electrolytic solutions leads to a reduction of the grown crystal grain size. This effect has been intensely studied in the case of electrochemically deposited metallic layers. The role of the levelling agents, currently used for metallic coatings, has not yet been deeply investigated for the semiconducting layers deposition.

4. Conclusions

Micro- and nanostructured ZnO layers have been grown by electrochemical deposition at constant or pulsed polarization voltages in pure $\text{Zn}(\text{NO}_3)_2$ solution or PVP/gelatine added $\text{Zn}(\text{NO}_3)_2$ solution. Layers deposited in pure and PVP added solutions grow as microplatelets with thicknesses below 100 nm and lateral size in the 2-10 μm range, in function of the experimental conditions. The application of a pulsed polarization voltage leads to the overall reduction of the platelets lateral size and the formation of two distinct size populations regarding the constituent microplatelets. Adding gelatine to the $\text{Zn}(\text{NO}_3)_2$ solution leads to the formation of layers with different morphologies, entangled-bands and entangled-wires like morphologies, due to the strong levelling role played by the gelatine.

Acknowledgements

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