ELECTRODEPOSITION OF NANOSTRUCTURED, TERNARY AND HYBRID FILMS BASED ON ZINC OXIDE

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Abstract

A prospect for synthesizing nanostructured, ternary and hybrid ZnO-related compounds by electrodeposition as well as their respective physico-chemical properties are depicted in this paper. The influence of the solvent on the morphology of the electrodeposited films and its impact on the final application will be illustrated.

Introduction

Control of morphology, orientation and assembly properties of nanostructured materials is the key parameter for their implementation onto technological devices. Electrochemical procedures are well suited for this purpose since they allow the growth of different morphologies depending on the type of solvent, electrolyte and substrate used.

The huge variety of parameters controlling the electrodeposition process allows the synthesis of materials with very different properties. For the same material a considerable diversity of morphologies, crystal structures and compositions are available. For instance, in the case of ZnO the choice of the solvent is the main factor that influences on the morphology while the crystal structure (wurtzite or spinel) depends on the supporting electrolyte.

For zinc oxide related compounds, electrodeposition in aqueous media produces discontinuous structures under the form of nanocolumns while when using a non-aqueous solvent, like dimethylsulfoxide (DMSO), extremely smooth and continuous films are mainly obtained [1]. These morphologies exhibit different properties. Continuous films are highly transparent due to the flatness of the surface which results in low diffusivities. In contrast, nanocolumnar ZnO structures obtained from aqueous solutions exhibit high diffusivity and intense photoluminescence.

The synthesis of ternary ZnMO semiconductor compounds (certainly difficult with water) can be easily prepared when an organic solvent is used. Several ternary compounds like ZnMO (M=Cd, Co, Mn, Fe) compounds can be electrodeposited using a bath containing dissolved Zn and M anions from suitable precursors [2].

ZnO can also be used for producing hybrid materials for photovoltaic applications [3]. This application requires a nanostructured inorganic structure able to absorb organic dye molecules. Again hybrid ZnO/Eosin-Y films can be produced by one step electrodeposition procedure from aqueous solutions [4]. Hybrid ZnO films are not reachable with DMSO because the addition of organic molecules between the layers drops the resistivity and impedes the film growth.

Experimental

Ternary and hybrid ZnO-based films were grown by electrodeposition onto ITO-coated glass substrates. The electrodeposition procedure consists of a classical three electrode electrochemical cell and a solution containing the suitable precursors in different concentrations, a supporting electrolyte and dissolved oxygen in water or DMSO solution.

Ternary compounds were always synthesized using DMSO while hybrid ZnO/Eosin-Y films can only be effectively produced using aqueous electrolytes. A potentio/galvanostat was used to keep a constant potential. The amount of deposited substance was controlled through the amount of deposited electrical charge and/or using an electrochemical quartz microbalance (ECQM).

Results and discussion

Controlling morphologies

Fig. 1 illustrates the effect of both substrate and solvent on the morphology of electrodeposited ZnO. Electrodeposition using water as solvent and polycrystalline ITO as substrate produces a coalescent and discontinuous structure under the form of nanocolumns (Fig.1 a). Moreover, if an appropriate substrate is used (GaN in this case) discrete and hexagonal columns grow orderedly and perpendicularly to the substrate following the 002 direction (Fig 1 b).

On the contrary, using organic solvents as dimethylsulfoxide (DMSO), ZnO films grow with a morphology composed by extremely smooth and continuous layers (Fig. 1 c).

Obviously, both morphologies exhibit different properties. Continuous films are highly transparent due to the flatness of the surface which results in low diffusivities. In contrast nanocolumnar ZnO structures obtained from aqueous solutions exhibit high diffusivity and intense photoluminescence [1]. The results point out the advantage of using dimethylsulfoxide when uniform, oriented and highly transparent films are required while using aqueous bathes produce perfectly defined hexagonal ZnO columns which can be fully oriented by chosen a

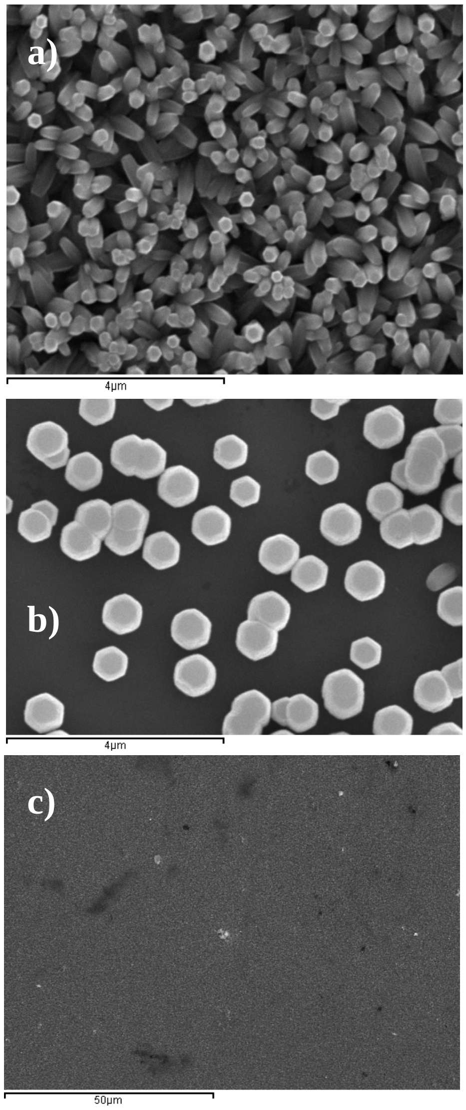

Fig. 1 Morphologies of ZnO using different solvents and substrates, a) water and ITO, b) water and GaN, c) DMSO and ITO.

suitable substrate.

Crystal structures are in agreement with morphologies evidenced by SEM micrographs. Columnar structures obtained onto polycrystalline ITO substrates in water (Fig.1a) exhibit a preferred orientation following the 002 direction of the hexagonal wurtzite ZnO structure but the rest of crystal orientations are also present (Fig 2 a). On contrary films grown on hexagonal GaN in water or on ITO in DMSO (Fig.1 b, c) only show the 002 direction (Fig. 2 b).

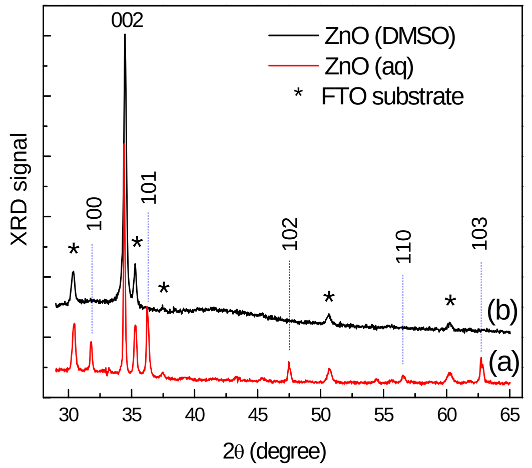

Fig. 2 XRD diagram of two ZnO layers deposited on FTO covered glass from aqueous (a) and DMSO (b) solvents.

Synthesis of ternary compounds

The synthesis of ternary ZnMO semiconductor compounds (certainly difficult using water) can be easily prepared when an organic solvent is used. In our case, several ternary compounds ZnMO (M= Cd, Co and Mn) have been successfully synthesized using DMSO as solvent [2]. Ternary ZnMO compounds are electrodeposited from baths containing dissolved Zn and M anions from suitable precursors.

Independent of the third element used (Cd, Co or Mn) very flat films are obtained as long as the wurtzite structure corresponding to ZnO is preserved. The M/Zn ratio in the final film is achieved by choosing the suitable M/Zn ion concentration ratio in the starting solution. In some cases the final concentration of the third element tends to saturate when attaining the solubility limit of the M element in the ZnO lattice.

In other cases, such as $Zn_{1-x}Mn_xO$, the composition of the films covers the overall x range between 0 and 1. Final composition for $Zn_{1-x}Mn_xO$ films obtained from Energy Dispersive Spectroscopy (EDS) versus the initial molar fraction appears in Fig. 3. $Zn_{1-x}Mn_xO$ films with low Mn concentration exhibit hexagonal wurtzite. Increasing the Mn amount results in a continuous deformation of the crystal structure and the film become amorphous. Further increase of Mn in the starting blend produces films with the structure of manganese oxide.

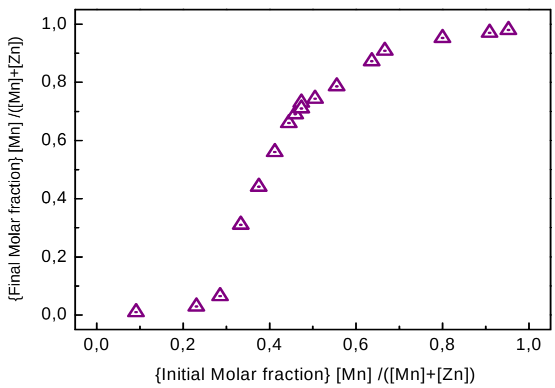

Fig. 3 Mn molar fraction present in the $Zn_{1-x}Mn_xO$ film as a function of the Mn molar fraction in the starting solution.

Similar effects are observed for $Zn_{1-x}Co_xO$ films. The wurtzite crystal structure is preserved for Co amounts lower than 15%. For higher amounts of Zn the films are amorphous. The difference between Co and Mn compounds attains their magnetic properties. For x close to to 1, the ZnCoO films are paramagnetic while ZnMnO films exhibit antiferromagnetic behaviour.

Synthesis of hybrid materials

Electrodeposition allows the synthesis of hybrid materials (ZnO-organic) in one step procedure by only adding a suitable amount of Eosin-Y into the usual electrolyte prepared for sinthezising ZnO. In this case only discontinuous morphologies with high surface/volume ratios are capable to adsorb efficiently the dye molecules. Fig.4 shows the absorbance of ZnO film compared with the absorbance of a ZnO/Eosin-Y hybrid film. The presence of the dya produces a high absorbance centred at about 540nm.

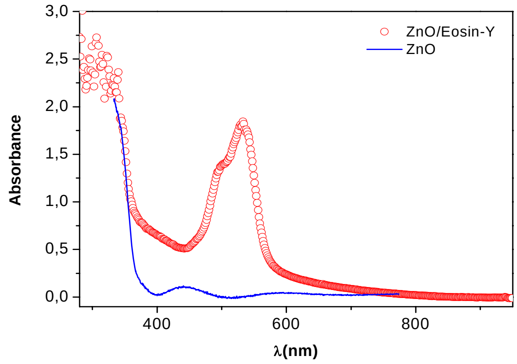

Fig. 4 Absorbance of a ZnO film with and without Eosin-Y. Note the high absorption of Eosin-Y centred at 540nm.

Fig. 5 shows the deposited mass obtained from the ECQM as a function of the deposited charge for two different electrolytes, one containing Eosin-Y and the other without it.The mass/charge ratio is higher for samples containing Eosin-Y revealing that a percentage of the deposited mass comes from the dye. Taking into account the slopes obtained for each material and the molecular mass of ZnO and ZnO/Eosin-Y a molar fraction (Eosin-Y/ZnO) of 2.1% is obtained.

Summarising, electrodeposition procedure is a simple and convenient method for producing both ternary and hybrid ZnO-related films. Ternary compounds involve the use of an organic solvent like DMSO while ZnO/Eosin-Y hybrid films require nanostructured morphology and consequently aqueous electrolytes are mandatory.

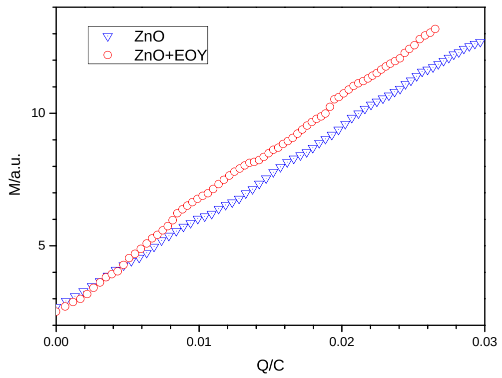

Fig. 5 Electrodeposited mass with and without eosin-Y as a function of the deposited charge.

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