

Orientation, morphology and photocatalytic properties of ZnO thin films grown by PLD with or without oxygen on various substrates

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Abstract – ZnO thin films were grown by Pulsed Laser Deposition on amorphous glass, R-sapphire and CeO₂ coated R-sapphire, with or without oxygen, in order to evaluate the effect of growing conditions on film orientation, morphology and photocatalytic activity. It was observed that substrate induces particular orientation while atmosphere plays an important role on morphology of thin films. Concerning dye color removal, all samples show high efficiency and keep their efficiency even after 4 uses, but no correlation can be found up to now between orientation and morphology and catalytic activity.

Advanced oxidation processes (AOP) have attracted lot of attention because it constitutes an interesting alternative for waste water treatment. Heterogeneous AOP is a variant which employs semiconducting oxides as photocatalysts [1]. Several oxides have been studied for this purpose and among them zinc oxide, which is a low cost alternative to TiO₂. Among various factors, particle size, morphology and/or preferential growth are expected to change the catalytic properties [2]. Moreover, in order to reuse more easily the catalyst, the use of fixed material, such as thin films, seems to be a great asset.

In this work, we investigate the influence of substrate (amorphous glass, R-sapphire and CeO₂ coated R-sapphire) and atmosphere (oxygen flow or vacuum) on ZnO thin films growth and on photocatalytic properties. Thin films were grown by pulsed laser deposition and their structure and microstructure were characterized by θ -2 θ X-ray diffraction and scanning electron microscopy. CeO₂ thin films (about 150Å) have been previously grown under oxygen flow or in vacuum. Different ZnO orientations as function of substrates were evidenced by XRD. (110) oriented films were obtained on R-sapphire with a mosaicity of 0,6-1,5° attesting a good crystalline quality; in plane ordering was probed by XRD phi-scans, evidencing an epitaxial growth which was confirmed by Electron Channeling Patterns (Fig.1). Growth of ZnO on glass resulted in a texture with a (002) orientation and a mosaicity of several degrees. On CeO₂ coated R-sapphire a texture is also observed. Oxygen atmosphere seems to affect only the growing process of CeO₂ films; (200) epitaxial CeO₂ films were obtained under oxygen flow while (111) textured ones have grown in vacuum. The orientation of ZnO films is the same with and without oxygen. Nevertheless, atmosphere plays an important role concerning morphology. In general, films grown in oxygen atmosphere are granular and rough (Fig. 2) whereas those grown in vacuum are denser and quite smooth (Fig. 3). Moreover, thin films realized under vacuum are thinner than those prepared under oxygen flow.

Photocatalytic activity was performed studying the degree of color removal of an aqueous solution containing 10 mgL⁻¹ of the textile azo dye remazol red FB 133%. Photocatalytic tests were carried out in a batch reactor equipped with UV-C lamps for 1 hour, without stirring or pH correction (pH = 6). Dye concentration was determined by UV-Vis spectrometry, monitoring absorption peaks at 510 nm (related to chromophore group) and 200 nm (related to aromatic rings). Films were reused 4 times in order to evaluate eventual loss of activity. All samples showed a high degree of color removal, thus it was not possible to establish a clear correlation between morphology and catalytic activity.

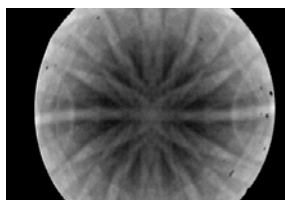


Figure 1 - Electron channeling pattern of ZnO films deposited in oxygen flow on R-sapphire

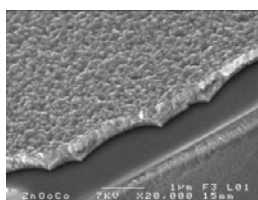


Figure 2 - SEM image of ZnO film deposited under vacuum on R-sapphire

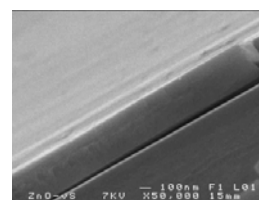


Figure 3 - SEM image of ZnO/CeO₂/R-sapphire thin film (ZnO and CeO₂ were deposited in oxygen flow)

[1] K. Rajeshwar *et al*, Photochem. photobiol. C : Photochem. rev. 9 (2008) 171-192

[2] R.K. Wahi *et al*, J. Mol.Catal. A Chem. 242 (2005) 48- 56