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Titanium dioxide (TiO2) represents a perfect example of a multifunctional metal-oxide semiconductor with applications ranging from microelectronics to photo catalysis or medical device materials [1]. Atomic layer deposition (ALD) is widely regarded as one of the most promising techniques for the growth of thin TiO2 films due to its simplicity, reproducibility, the high conformity of the obtained films and an excellent control of the layer thickness at the angstrom level [2].

One of the factors that often dictates the properties of ALD films, and therefore their possible applications, is the crystallinity of the final film. While amorphous films of TiO2 are preferable if diffusion barriers are required for a particular application, crystalline films with a specific phase are often desired for their specific chemical or electrical properties. In addition, the formation of crystallites in TiO2 films is of great technological interest. For example, TiO2 has been regarded as one of the most promising photo-catalytic materials for environment-protective coatings due to its high photo-catalytic activity, high chemical stability and low toxicity [3].

In the present work, the photocatalytic activities of TiO2 thin films, grown by ALD, were investigated as a function of the grain size and crystal structure. The samples were characterized by scanning electron microscopy, grazing incidence X-ray diffraction, secondary ion mass spectrometry, X-ray photoelectron spectroscopy, atomic force microscopy, and near-edge X-ray absorption fine structure spectroscopy. We show that the crystallinity and the size of crystallites can be controlled over a large range of diameters, from around 70 nm up to 1 μm with five parameters: the type of substrate, the type of Ti precursor, the deposition temperature, the number of ALD cycles (i.e. the film thickness) and the nanometric Al2O3 buffer layers deposited on substrates in the same ALD sequences prior to TiO2 films. The most dramatic increase in size of the plate-like anatase grains, to more than 1 μm in diameter, was obtained on films grown at 250 oC on Si substrate covered with a 10 nm Al2O3 layer.

The photocatalytic activity, determined for each TiO2 film from the degradation of methylene blue under UV irradiation, is more efficient for the anatase phase of TiO2 than for the rutile phase, and increases with the grain size of crystallites. The high photocatalytic activity, combined with the low processing temperatures used in the present study, open a wide range of applications for different substrates coated with ALD TiO2 films, such as polymers or cellulose-based substrates, ranging from packaging materials for food to water or air purification systems.

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