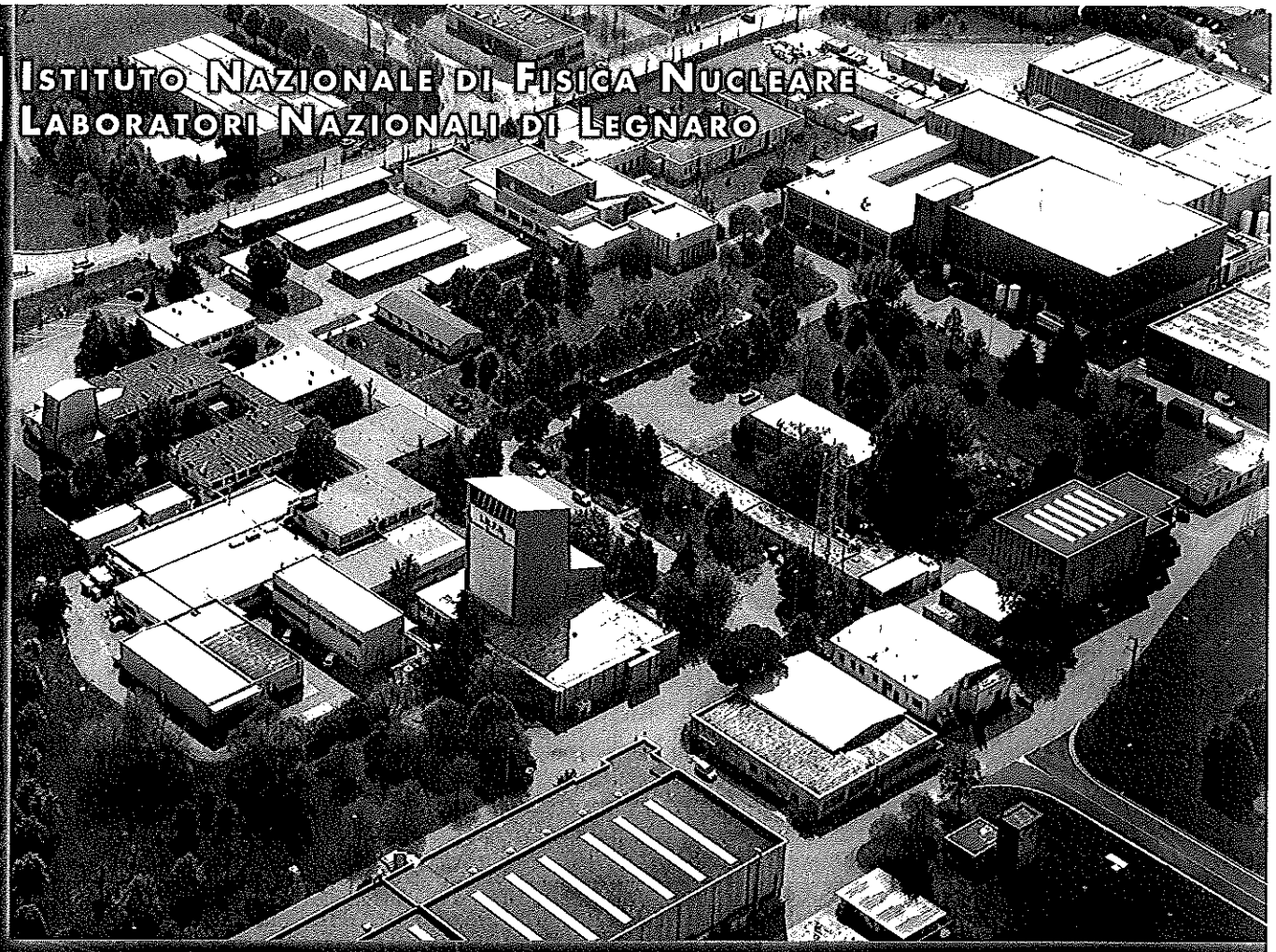

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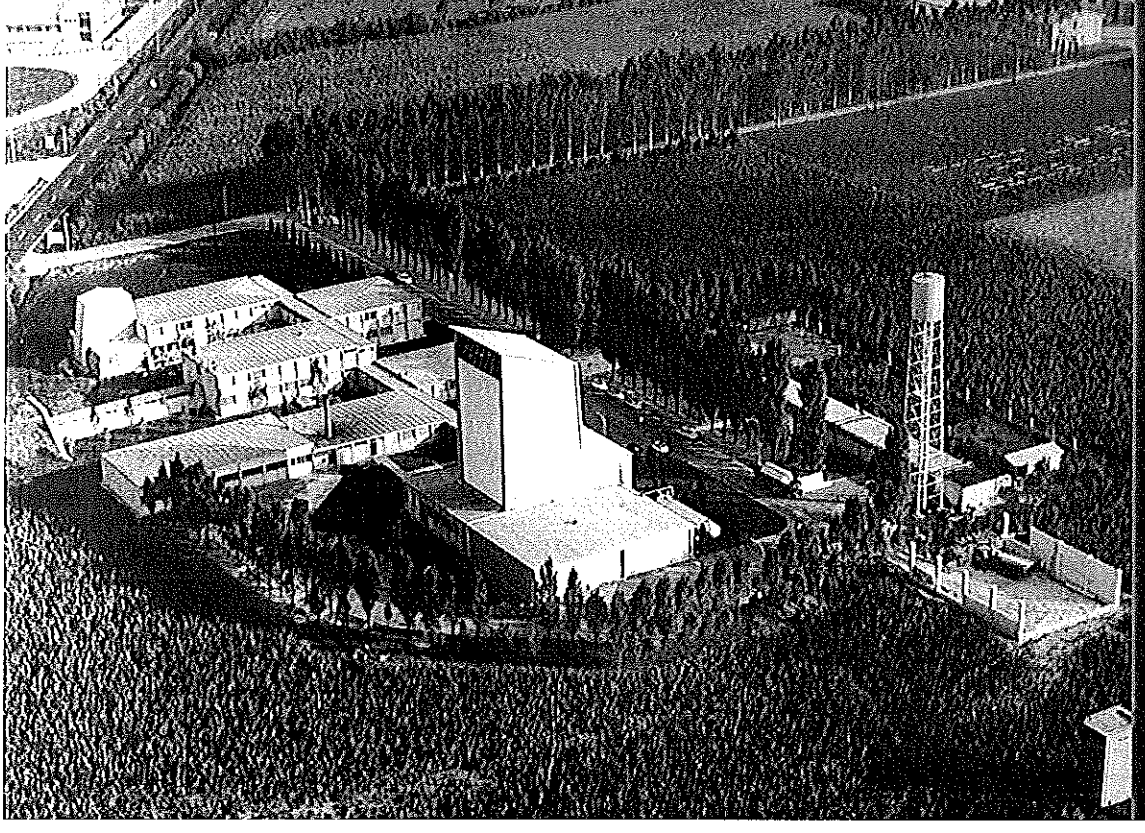

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MOCVD Deposition and Characterization of Photocatalytic Anatase TiO_2 Thin Films

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INTRODUCTION

In the last decades following the pioneering works of Fujishima [1] and Graetzel [2], a tremendous amount of research has been devoted to titanium oxide materials, which has led to many promising applications in areas ranging from photocatalysis and photovoltaics to photo-electrochromics and sensors. TiO_2 materials are expected to play an important role in helping to solve not only many environmental and pollution challenges but also energy problems through the effective utilization of solar energy based on photovoltaic and water-splitting devices. In particular, TiO_2-supported materials can solve the practical problem of catalyst recovery in the photocatalytic treatment of water by avoiding the use of suspended catalysts. A variety of reviews has been recently published which testify the great interest and expectations on titanium oxide materials, either pure or modified ad hoc to improve their performances [3-7]. Notwithstanding this tremendous work, there is still a great need to understand the link between TiO_2 thin film deposition parameters, their structural, chemical and morphological properties and their photocatalytic activity. Here we are concerned with clarifying some of these aspects for TiO_2 anatase films realized by metal-organic chemical vapor deposition (MOCVD).

EXPERIMENTAL

MOCVD deposition of TiO_2 thin films was performed on glass and silicon substrates and on glass fiber wool using a horizontal hot-wall reactor. Tetra-isopropoxide titanium is used as the metal-organic precursor and nitrogen as carrier gas. Depositions were carried out at a reactor pressure of 120 Pa and a temperature of 400°C. Film thickness on glass and silicon substrates was determined by using a KLA Tencor Alpha-Step IQ surface profilometer, measuring the film step height on partially masked samples. Surface morphology was analysed by atomic force microscopy (AFM) using a DME DualscopeTM instrument equipped with silicon cantilever tips having nominal tip radius of 10 nm and operating in non-contact mode. X-ray diffraction (XRD) patterns were recorded with a Philips PW 1830 powder diffractometer in Bragg-Brentano geometry, using Cu Kα radiation.

Composition measurements were done by Rutherford Backscattering Spectrometry (RBS) using 2 MeV $^4He^+$ beams at AN2000 and CN accelerators at INFN-LNL laboratories, Legnaro. The photocatalytic activity of the TiO_2 films was estimated by measuring the degradation of nalidixic acid dissolved in water. The TiO_2 coated glass fibre wool is inserted into a cylindrical 0,5 l glass reactor filled with water together with a rod shaped 17 watt UV mercury vapour lamp (λ=254 nm, radiant flux 0,098 W/cm², radial optic path length 1,8 cm). Photodegradation efficiency is estimated by determining the time evolution of the residual concentration of the nalidixic acid solution as a function of UV exposure duration.

RESULTS AND DISCUSSION

Film thickness was found to increase linearly with deposition time, corresponding to a growth rate of about 15 nm/min, while film surface root-mean-square roughness values - determined by AFM - showed an initial increase up to a film thickness of 800 nm and then saturated at 40 nm. XRD spectra of films with different thickness are shown in figure 1. From the spectra we deduced that films grow in the anatase TiO_2 crystalline phase (ICCD-021-1272). Moreover the texture of the films displays a preferential orientation of the (200) plane parallel to the film surface. This can be seen more clearly by evaluating the intensity ratio I2/I1 where I1 and I2 are the intensities respectively of the (101) and (200) Bragg peaks. The experimental values of the ratio were always higher than the theoretical value I2/I1=35/100 for a randomly oriented polycrystalline anatase powder. As shown in figure 2 the ratio I2/I1 increases with increasing film thickness, indicating that the (200) preferential orientation becomes more pronounced with increasing film thickness. The crystallite sizes estimated from the XRD spectra, using the Scherrer formula, was ≈75 nm. The stoichiometry of the TiO_{2-x} anatase phase was determined by RBS composition measurements. A typical RBS spectrum of our films on silicon substrates is shown in figure 3. The spectrum shows clearly the Ti and O edges besides the edge of the Si substrate. No other elements could be identified, indicating good compositional purity. The O:Ti ratio was determined from the ratio of the integrals of O and Ti signals and the respective Rutherford backscattering cross-sections. The results for films of different thickness are as follows: O:Ti = 1,64 (300 nm), O:Ti = 1,61 (600 nm) and O:Ti=1,71 (900 nm).

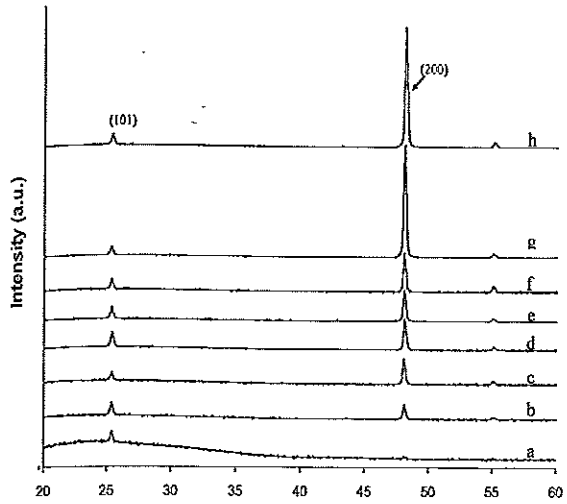

FIG. 1. *XRD spectra of TiO_2 films on glass substrates (film thicknesses are a) 60 nm, b) 455 nm, c) 615 nm, d) 825 nm, e) 990 nm, f) 1250 nm, g) 1650 nm, h) 1735 nm).*

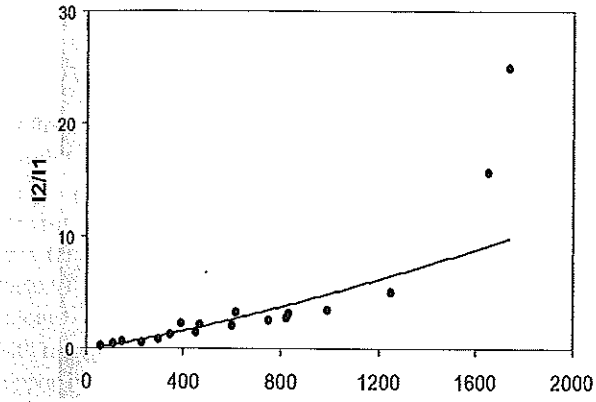

FIG. 2. *Peak intensity ratio I2/I1 versus film thickness. I1=intensity of (101) peak, I2=intensity of (200) peak.*

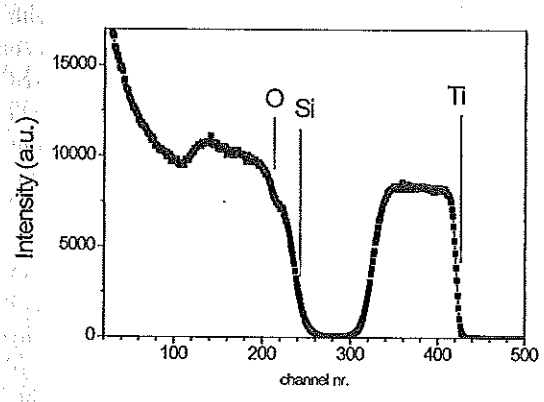

FIG. 3. *Typical RBS spectrum of a TiO_2 film (600 nm thick) deposited on a Si(100) substrate.*

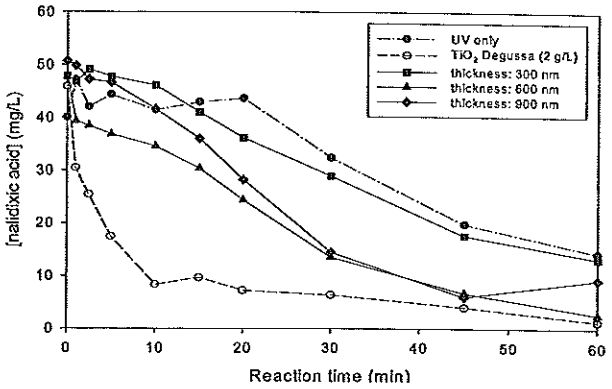

FIG. 4. *Degradation of nalidixic acid in water during UV exposure without catalyst, with the conventional suspended Degussa TiO_2 and with three TiO_2 coated glass-fibre wools of different film thickness.*

Glass fibre wools coated with TiO_2 films of different thickness were tested for their photocatalytic efficiency by monitoring the degradation of nalidixic acid in water (figure 4) and compared to those of a conventional nanocrystalline TiO_2 powder (Degussa) and to the photolysis. Results showed that TiO_2 coated glass-fibre wools allowed degradation performance comparable to that obtained with the Degussa catalyst.

CONCLUSIONS

The preliminary results obtained indicate the possibility of using the TiO_2 anatase on fibres for the degradation of organic contaminants in water. The use of fibres instead of powders has a practical environmental implication because the drawback of separating the catalyst at the end of the water treatment is no longer present. The study of the growth parameters indicates that the structural orientation is a factor to bear in mind for its influence on the photocatalytic activity, while the role of substoichiometry is still not well understood, and further studies are in process.

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