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PHOTOINDUCED BACTERICIDAL ACTIVITY OF TiO_2 THIN FILMS OBTAINED BY RADIOFREQUENCY MAGNETRON SPUTTERING DEPOSITION

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This paper reports results of an atomic force microscopy (AFM) investigation of cell damage and death of bacteria deposited on titanium dioxide (TiO_2) thin films irradiated by the UV light. The bactericidal activity against *Diplococcus pneumoniae*, *Staphylococcus aureus* and Escheridria *Coli* was investigated for the TiO_2 films deposited on silicon Si (100) wafers by radio frequency magnetron sputtering of a pure ceramic TiO_2 target in Ar-O_2 mixture gas at 10 mTorr. These films were reported to be amorphous with a short range anatase like atom ordering and to have a good photocatalytic activity (good UV light induced hydrophilicity). The AFM measurements revealed that one hour after UV irradiation most of the bacteria on the UV irradiated surface of TiO_2 thin films presented membrane destruction, which led to death of the cells. AFM measurements made 6 hours after the UV irradiation showed that all the cells on the TiO_2 surface were killed.

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1. Introduction

Because its good photocatalytic property, titanium dioxide (TiO_2) has a good capacity of degrading organic contaminants. This makes TiO_2 an important environmental material with applications in air and water purification and fabrication of self-cleaning and antibacterial surfaces [1]. It is believed that the good capacity of degrading organic macromolecules of the UV irradiated TiO_2 is due to the great oxidation potential of the chemisorbed radicals [2] and this leads to the bactericidal property of this material, *i. e.* light-activated TiO_2 surface can kill bacteria or other dangerous pathogens. The TiO_2 photocatalytic activity is related by a more recent discovered property, the UV light induced hydrophilicity [1]. The UV light irradiated TiO_2 surface becomes super hydrophilic because of the photocatalytic decomposition of either water or hydrophobic adsorbate molecules. The effect is reversible, the surface turning hydrophobic during storage in dark or visible light [3] or by wet rubbing [4]. Good bactericidal activity of UV light irradiated TiO_2 was reported in air [5] and aqueous solutions [6]. This property makes TiO_2 coatings important for microbiologically sensitive environments, as medical and sanitary facilities that have to be keep clean of biologic contamination. A variety of coating techniques has been developed to produce photocatalytic TiO_2 surfaces [7-9]. Among these techniques the sputtering deposition is known to produce films with high adhesion and hardness, but with relatively low photocatalytic activity [8]. It has been found that the low photocatalytic activity of these films corresponds to their heterogeneous crystalline and amorphous mesostructure [10, 11]. However, a good choice of the sputtering deposition parameters may yield high quality films. In a previous work [10] we reported that the radio frequency magnetron sputtering deposition of a pure TiO_2 target in Ar(90%)-O_2(10%) mixture gas at pressure of 10 mTorr produces amorphous TiO_2 films with microscopically homogeneous surfaces and good UV-light-induced hydrophilicity.

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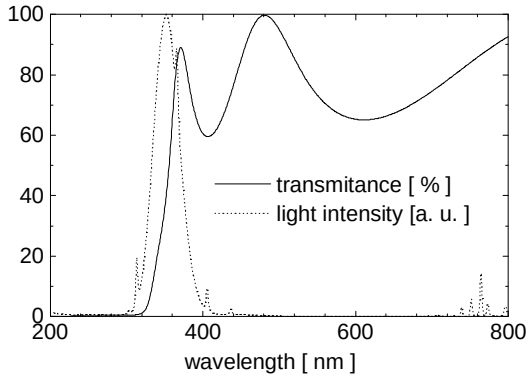

Fig. 1. TiO2 thin film transmitance and light intensity spectrum of the lamp used for the UV light irradiation of the film.

The aim of the present study is to investigate directly through atomic force microscopy (AFM) techniques the cell damage and death of bacteria on the film TiO_2 thin film deposited at 10 mTorr pressure of the Ar-O_2 gas mixture. The TiO_2 film bactericidal activity against *Diplococcus pneumoniae, Staphylococcus aureus* and *Escherichia Coli* was investigated. The bacteria contaminated films were irradiated by UV light at low power density and subsequent modifications in topography and cantilever phase lag images taken by dynamic force microscopy (DFM) in tapping mode in air were observed.

2. Experiment

The TiO_2 thin film deposition has been performed by sputtering a cathode target (a sintered TiO_2 disk with the diameter of 10 cm) in a 200 W power radio frequency discharge in an Ar (6 sccm) and O_2 (0.6 sccm) gas mixture at 10 mTorr pressure. The deposition chamber of the magnetron was connected to the vacuum pumps and a gas supply system with mass flow controllers (MFC) for Ar and O_2 gases. The substrate holder including a heating system was installed at 10 cm in front of the cathode. The films were deposited during 2 hours on p-Si (100) wafers heated to 300^{o}C. The film structure and composition were investigated by the X-ray diffraction (XRD) and Fourier transform infrared spectrometry (FTIR). The XRD spectrum of the film (not shown here) had no diffraction peak. The FTIR spectrum (not shown here) had a relatively sharp peak at 447 cm^{-1} that could be attributed to Ti-O-Ti vibrations in an amorphous with a short range anatase-like structure. The film thickness and refractive index were measured independently by stylus profilometry and ellipsometry (632.8 nm wavelength), and found to be 120 nm and 2.3, respectively. The relative high value of the refractive index of the film is explained by the occurrence of short-range anatase type atom ordering in the film. The films were irradiated by a UV light lamp (Hitachi FL8BL-B) at a power density of 1 mW/cm^2. Fig. 1 shows the optical transmitance of the film and the light intensity spectrum of the UV light lamp. While the film is transparent in visible light (the minima and maxima observed on the visible part of the transmitance spectrum are due to constructive and destructive light interference, respectively), it adsorbed the optical radiation with wavelength smaller than 360 nm. The spectrum of the light emitted by the UV lump shows a broad peak at 350 nm.

The bactericidal effect of UV irradiated TiO_2 thin films on different bacteria was studied through direct AFM observation of cell damages and cell death. *Diplococcus pneumoniae*, *Staphylococcus aureus* and *Escherichia Coli* bacteria were grown without thermal control in nutrient broth at room temperature of 25 °C during 72 hours. The TiO_2 films were covered partially by bacteria and irradiated in air during 30 minutes by the UV lamp at a power density of 1mW/cm^2. The destruction of bacteria was observed by AFM measurements at different time moments after UV irradiation.

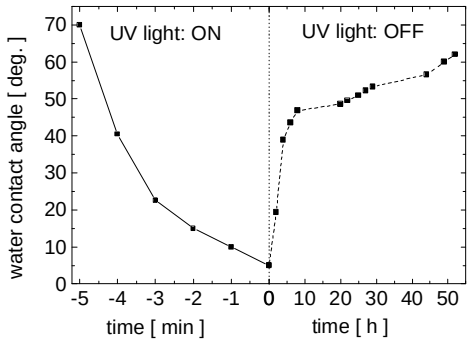

Fig. 2. Time variation of water contact angle during UV light irradiation (1 mW/ cm2) and storage in dark.

3. Results and discussion

The film photocatalytic activity was measured indirectly by the water contact angle measurements. Fig. 2 shows the water contact angle variation during an on-off cycle of the UV light irradiation. While the film surface becomes hydrophilic in about 5 minutes of UV light irradiation, it looses the hydrophilicity in about 12 hours of storage in dark. This shows that, even at low power density of the UV light intensity, the film is quickly activated. Then, the film becomes inactivated in about 12 hours.

The topography and chemical homogeneity of the film surface was investigated by taping mode dynamic force microscopy (DFM). Fig. 3 presents images of film surface topography and cantilever oscillation phase lag. The topography image shows a surface with root mean square (rms) roughness of 1.7 nm with small grains (typical diameter and height of 50 nm and 5 nm, respectively). The phase image shows a structurally homogeneous surface, the small phase lag variations being attributed to the surface topography effects.

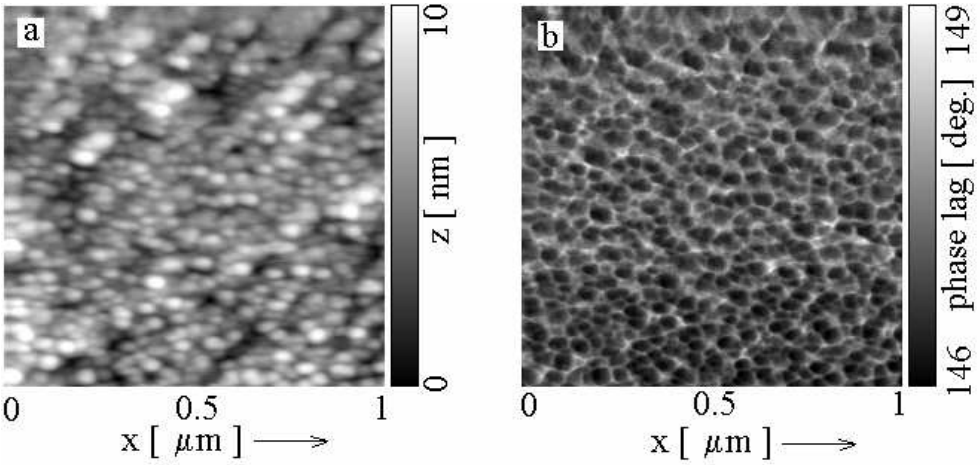

Fig. 3. Topography (part a) and phase lag (part b) images of the TiO_2 thin film surface. The scanned area is $1\mu m \times 1\mu m$.

The TiO_2 films were covered partially by bacteria and irradiated in air during 30 minutes by a UV lamp at a power density of 1 mW/cm^2. The evolution of the bacteria destruction on the irradiated substrate was observed by tapping-mode DFM measurements. Fig. 4 shows the topography images of *Diplococcus pneumoniae* bacteria on the TiO_2 film before UV light irradiation (part **a**) and 1 hour (part **b**), 6 hours (part **c**) and 16 hours (part **d**) after UV light irradiation, respectively. The topography image taken one hour after UV light irradiation shows an onset of

bacteria membrane destruction. The image taken 6 hours after UV light irradiation shows that the bacteria were completely destroyed. The topography image taken after 16 hours after UV light irradiation shows that the decomposition of the organic material resulted from the dead bacteria continued. To prove that the death of the bacteria resulted from the photocatalytic activity of the TiO_2 thin film, a control probe consisting of bacteria on a glass slide was prepared. The control probe was irradiated by UV under the same conditions as the TiO_2 probe. Topography images (not shown here) of the control probe surface showed no noticeable bacteria destruction 6 hours after UV irradiation. The bactericide activity of the TiO_2 film against *Staphylococcus aureus* and *Escherichia Coli* bacteria were also investigated and results similar to those obtained for *Diplococcus pneumoniae* bacteria were found. The bactericide activity of the UV light irradiated surface can be quantitatively characterised by the quantum yield (*QY*), which is defined by the ratio between the destroyed bacteria number (N_b) and incident UV photon number (N_{ph}) [6]:

$$QY = \frac{N_b}{N_{ph}}. \tag{1}$$

The UV irradiation dose expressed by N_{ph} is computed by:

$$N_{ph} = \frac{I \cdot S \cdot t}{h\nu}, \tag{2}$$

where I is the UV light density of power, S irradiated surface area, t, irradiation time, ν, the UV frequency and h is the Plank's constant. For the case presented here, the QY of TiO_2 thin film was estimated to be above 6×10^{-11} by taking a mean value of the UV light wavelength of 350 nm (which corresponds to the peak intensity in the UV light spectrum), an irradiation time of 30 minutes and a surface area of 25 μm^2 with a number of about 50 killed bacteria.

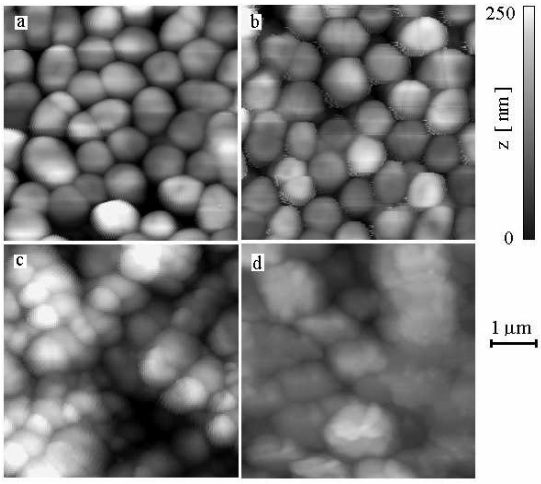

Fig. 4. Topography images of *Diplococcus Pneumoniae* on TiO_2 before UV light irradiation (part a) and 1 hour (part b), 6 hours (part c) and 16 hours (part d) after UV light irradiation, respectively.

4. Conclusion

The bactericidal activity of UV light irradiated TiO_2 thin films obtained by radio frequency sputtering deposition was investigated through atomic force microscopy imaging of cell damage and bacteria death. The TiO_2 films were deposited on silicon Si (100) wafers by radio frequency magnetron sputtering of a pure ceramic TiO_2 target in Ar-O_2 mixture gas at 10 mTorr. In a previous

work we reported a good photocatalytic activity of the films deposited at this gas pressure value [11]. The bactericidal activity against *Diplococcus pneumoniae*, *Staphylococcus aureus* and *Eschirichia coli* was investigated. These bacteria were grown in nutrient broth at room temperature of 25 °C during 72 hours. The bacteria were transferred to the film surface and the obtained bacterial probes were irradiated by UV light at low power density. The AFM measurements revealed that one hour after UV light irradiation most of the bacteria on the UV irradiated surface of TiO_2 thin films presented membrane destructions, which led to death of the cells. The AFM measurements made 6 hours after the UV light irradiation showed that all the cells on the TiO_2 surface were killed. The quantum yield of the TiO_2 film against *Diplococcus pneumoniae* was evaluated to be above 6×10^{-11}.

It must be pointed out that the simultaneous action of TiO_2 surface and UV irradiation has a synergie character, the bactericidal effect being thus strongly amplified.

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