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Antibacterial response of titanium oxide coatings doped by nitrogen plasma immersion ion implantation

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ABSTRACT

Plasma immersion ion implantation technology has been utilized to enhance the photocatalytic activity of the anatase phase of TiO_2 thin films deposited by cathodic arc evaporation PVD. The main objective of this study is to shift the light absorbance of the titania in order to obtain antibacterial activity under visible light irradiation. TiO_2 thin films, deposited on polished stainless steel AISI 304 and silicon wafers, were implanted with nitrogen ions (N^+/N_2^+) at 20 kV energy and different temperatures between 250 and 350 °C. The antibacterial activity of nitrogen implanted titania coatings has been monitored for *Escherichia coli* under visible light irradiation. Additionally ultra violet/visible spectrophotometry tests have been carried out to measure the changes in the light absorbance of the doped films. Further characterization has been performed, including X-ray photoelectron spectroscopy, X-ray diffraction and glow discharge optical emission spectrometry. As a result of Nitrogen implantation, the light absorption peak shifted from ultra violet region (UV-A) to visible wavelength range, which led to an increase of the antibacterial efficacy under visible light irradiation.

1. Introduction

Titanium oxide is a semiconductor material that has attracted enormous attention over the past three decades in energy and environmental sciences [1,2], due to its interesting properties including a high refractive index, photocatalytic activity and chemical stability. There are three types of TiO_2 crystal structures: rutile, anatase and brookite. Anatase (band gap: ~3.2 eV) and rutile (band gap: ~3.0 eV) phases show photocatalytic activity under light irradiation at ~384 nm and ~413 nm respectively [3]. When TiO_2 is exposed to radiation exceeding its band gap, normally in the UV wavelength region (290–380 nm), electron-hole pairs are produced. These e-h pairs react with chemical species present in the environment such as O_2 and H_2O to produce free radicals which can decompose the organic compounds producing H_2O and CO_2 [4].

Asahi et al. [5] demonstrated that nitrogen doping can induce the band gap narrowing and, as a result, a shifting of photocatalytic response of TiO_2 towards the visible wavelength range. A similar effect can also be observed incorporating other elements such as metals [6–8]. Based on these principles numerous authors have reported light absorption shifts via different doping methods such as ion implantation [9–10], sol gel [11] or annealing of TiO_2 in contact with NH_3 [12]. Meanwhile, nitrogen ion implantation [13–15] in this material has proven to be a very attractive method to produce both oxygen vacancies and the introduction of nitrogen atoms in the TiO_2 lattice [16–19]. The aim of this study is to shift the light absorption of titanium oxide by plasma immersion ion implantation of nitrogen, in order to obtain antibacterial surfaces under visible light irradiation conditions.

2. Experimental

2.1. Sample preparation

Titanium oxide layers were deposited on polished stainless steel (AISI 304) and silicon wafers by a reactive cathodic arc evaporation physical vapour deposition (CAE-PVD) process. TiO_2 coatings processes were deposited in a PVD system equipped with 6 Ti planar cathodic arc sources. Ar and O_2 gases were used as precursors to tune the stoichiometry of the deposited coatings. After the PVD deposition a Monte Carlo simulation was carried out with SRIM software to select the optimal

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ion implantation conditions. Nitrogen ions (N^+/N_2^+) were implanted on the TiO_2 coatings by plasma immersion ion implantation at 20 kV energy and three different temperatures: 250 °C, 300 °C and 350 °C. Processes were performed in a high vacuum chamber at a base pressure below 1×10^{-6} mbar and a working pressure of 8×10^{-3} mbar. The fed gases were ionized using a microwave electron cyclotron resonance (ECR) plasma source at 250 W and a pulse frequency of 15 μs.

2.2. Chemical, structural and optical characterization

The chemical composition profiles of the TiO_2 and N-TiO_2 layers were analysed using glow discharge optical emission spectrometry (GD-OES) JY 10000 RF. Grazing incidence XRD measurements were performed to identify the crystal structure of the TiO_2 coating, a BRUKER D8 DISCOVER XRD equipped with a Cu source (Kα radiation) was utilized, working at an incidence angle of 1°.

X-ray photoelectron spectra were recorded with a Leybold-Heraeus LHS-10/20 spectrometer using the Mg Kα line as excitation source in the pass energy constant mode. Binding energy (BE) referencing was done with respect the C1s peak at 284.6 eV for the adventitious carbon contaminating the surface of the sample.

UV-VIS absorption was monitored with a Perkin Elmer Lambda 950 spectrophotometer equipped with a 150 mm integrating sphere, and an operating range of 185–3300 nm.

2.3. Antibacterial activity

Antibacterial activity was measured against *Escherichia coli* ATCC 8739 (CECT 516) according to JIS Z 2801:2010 standard [20,21] under visible light irradiation. An overnight culture of *E. coli* in Triptic Soy Broth at 35 °C ± 1 °C (TSB; Scharlau, Sentmenat, Spain) was diluted to obtain the desired initial concentration (~2×10^4 cells/cm^2). Inoculation was performed in sterile conditions on a Class II Microbiological Safety Cabinet (Telstar, Terrassa, Spain) on 6 samples of reference TiO_2 and 3 samples of nitrogen implanted TiO_2 surfaces. The number of viable cells/cm2 was determined immediately after inoculation on reference surfaces and after 24 h ± 1 h of exposure at 35 °C ± 1 °C, relative humidity ≥90% and visible light irradiation on both reference TiO_2 and nitrogen implanted TiO_2 surfaces. Serial dilutions on TSB were performed, and 1 ml of each dilution was dispensed by duplicate into sterile Petri plates. To each petri dish, 15 ml to 20 ml of warmed Plate Count Agar (Scharlau) were added and mixed with the inoculum. After solidifying the culture medium plates were incubated at 35 °C ± 1 °C during 24 h ± 1 h. The colony forming units (CFU) were counted and the value of antimicrobial efficacy (R) was calculated according to Eq. (1). This value R (%) represents the relative *E. coli* reduction produced at the nitrogen implanted sample in comparison with the reference titanium oxide sample.

$$R\ (\%) = \left[\left(\text{cells/cm}^2\text{on TiO}_2 - \text{cells/cm}^2\text{on N-TiO}_2\right) \times 100\right] / \left[\text{cells/cm}^2\text{on TiO}_2\right] \quad (1)$$

3. Results and discussion

SRIM simulations were carried out to determine the optimal ion implantation energy that can be controlled for each voltage applied to the substrate. As a result of the ion bombardment, the energy applied to the ions is dissipated in the implanted sample via three phenomena: ionization, phonons and atom vacancy production. The energy loss of the impinging ions is distributed differently depending on the implantation energy as presented in Table 1.

SRIM simulation results indicated the benefits of working at low implantation energies. Firstly, the percentage of energy losses caused by the generation of atom vacancies, tend to increase at low implantation energies. Moreover, the implantation profile depth depends on the energy, thus, low implantation energies permit to increase the density of vacancies close to the surface of the TiO_2 layer (Table 1).

Table 1
Energy loss distribution (%) and N implantation profile (range and peak position) as calculated by SRIM for each applied voltage.

(KeV)	Ionization (%)		Vacancies (%)		Phonons (%)		SRIM profile (nm)	
	Ions	Recoils	Ions	Recoils	Ions	Recoils	N_{Range}	N_{Peak}
70	56.55	11.51	0.29	2.27	1.27	28.12	225	118
50	50.35	12.77	0.35	2.6	1.5	32.42	180	87
30	41.19	14.42	0.46	3.1	1.94	38.9	120	54
20	35.29	15.21	0.55	3.4	2.34	43.2	90	37

Given that the maximum number of vacancies and expected nitrogen atom surface relocations is produced at 20 keV of bombardment energy, we have therefore chosen this energy 20 keV as the optimal implantation energy to achieve photocatalytic activity of the TiO_2 films in the VIS range.

Nitrogen implantation profiles on TiO_2 were analysed by GD-OES, the maximum concentration of nitrogen can be observed at around 20% and ~50 nm depth. No significant differences have been detected for different implantation temperatures, as presented in Fig. 1.

Nitrogen profiles obtained by GD-OES, show ion ranges of around 200 nm (Fig. 1), while the SRIM simulation predicted lower penetration of ions (90 nm). The SRIM simulation software utilized for the study does not consider the process temperature (250 °C, 300 °C and 350 °C), consequently, the higher penetration of nitrogen can be attributed to thermal diffusion during the implantation process.

Fig. 2 shows the XRD patterns of the reference TiO_2 and the nitrogen implanted TiO_2 layers. The peaks of the reference TiO_2 correspond to a mixture of anatase and rutile structures, with a higher anatase/rutile ratio. The XRD patterns measured after the implantation processes denote a reduction of the anatase main peaks (101) and (004), while apparently the rutile structure is not affected by the implantation. No significant differences have been observed in the XRD spectra as a function of the implantation temperature.

N(1s) XPS spectra of the different samples are reported in Fig. 3. XPS has been carried out to determine the chemical state of the implanted nitrogen atoms. Nitrogen N(1s) atoms tend to occupy mainly interstitial or substitutional positions in the TiO_2 lattice, some authors have described other possibilities for the chemical state of N implanted in TiO_2 [22]. The results of Fig. 3 reveal the existence three types of nitrogen species after nitrogen implantation. The first type presents a peak at around 402 eV, usually attributed to nitrogen species chemically bonded to oxygen (N—O). The second type of nitrogen (~395 eV) corresponds to substitutional (i.e. nitride like of the type Ti—N), while the peak observed at 399 eV can be attributed to an intermediate species of N usually ascribed to an interstitial-substitutional nitrogen (Ti—ON) that is deemed responsible for the narrowing of the TiO_2 band gap. It is shown in Fig. 3 that the ratio of the different N peaks varies with the implantation temperature. A rough quantitative evaluation of the relative percentage of nitrogen in the surface of these samples yields a value of 3–6% in the Nat%.

The UV-VIS reflectance spectra of reference TiO_2 and nitrogen implanted samples at 250 °C, 300 °C and 350 °C are shown in Fig. 4. Compared to raw TiO_2, N implanted TiO_2 surfaces show different light reflectance in the visible range (380–780 nm). At high wavelengths (red region), N doped samples tend to reflect more light and the opposite effect can be observed at low wavelength (blue region). As a result, the color of nitrogen implanted samples turn to yellow-green. Some authors have reported light absorption/reflection results for nitrogen doped TiO_2 [23].

Based on the JIS Z 2801:2010/A1 standard [21–22], the numbers of cells/cm^2 was further converted into an antimicrobial activity value (R). The corresponding R values for different tested materials are shown in Fig. 5. Clearly, under visible light irradiation the antibacterial activity exhibited by nitrogen implanted titanium oxide samples is