UDK 661.882:539.21
Original scientific article/Izvirni znanstveni članek

ISSN 1580-2949
MTAEC9, 57(6)581(2023)

INFLUENCE OF DOPING WITH CARBON AND NITROGEN ON THE PHOTOACTIVITY OF TiO_2 THIN FILMS OBTAINED WITH MePIIID

VPLIV DOPIRANJA Z OGLJIKOM IN DUŠIKOM NA FOTOAKTIVNOST TANKIH FILMOV TiO_2 IZDELANIH Z MePIIID

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Prejem rokopisa – received: 2023-04-29; sprejem za objavo – accepted for publication: 2023-09-17

doi:10.17222/mit.2023.867

Titanium dioxide is well known as a photoactive material activated under ultraviolet irradiation. It is either employed as a photocatalyst or it exhibits superhydrophilic behavior after obtaining reduced surface energy under illumination used for self-cleaning or anti-fogging surfaces. For increasing the reactivity of thin films under solar illumination, a reduced band gap is desired. Doping with transition metals or nitrogen has been reported in the literature. However, the incorporation of nitrogen into a growing film is a much more complex process that is presently not completely understood. TiO_2 thin layers were produced by metal plasma immersion ion implantation and deposition at room temperature at a pulse voltage of 0–5 kV and a duty cycle of 9 % for an apparently amorphous layer. An auxiliary rf plasma source was employed to increase the growth rate at low gas flow ratios. By adjusting the geometry between the incident ion beam, sputter target and substrate independently of the primary ion energy and species, a controlled deposition of samples was possible. Conventional ion implantation was employed to implant either carbon or nitrogen ions below the surface for bandgap engineering. The resulting thin films were subsequently investigated for optical properties, stoichiometry, structural properties, surface topography and photoactivity.

Keywords: TiO_2, MePIIID, SRIM, photoactivity

Titanov dioksid (TiO_2) je dobro znani fotoaktivni material, ki se aktivira pod vplivom sevanja ultravijolične svetlobe. Zato se lahko uporablja kot fotokatalizator. Pod vplivom osvetljevanja se obnaša kot super hidrofilni (dobro omočljiv) material, tako zmanjša površinsko energijo in je lahko zato uporaben kot samo čistilna površina in površina, ki se ne rosi. Povečanje reaktivnosti tankih filmov pod vplivom sevanja sončne svetlobe zahteva povečanja širine prepovedanega pasu za elektrone. O dopiranju TiO_2 s prehodnimi kovinami ali dušikom so poročali že številni avtorji v znanstveni literaturi. Vendar pa je vgradnja dušikovih atomov med rastjo oziroma tvorbo tankega filma zelo kompleksen proces, ki še ni popolnoma raziskan. Avtorja v pričujočem članku opisujeta izdelavo tankih filmov TiO_2 s plazemsko imerzijsko (potopno) ionsko implantacijo kovin (MePIIID; angl.: Metal Plasma Immersion Ion Implantation and Deposition) pri sobni temperaturi, napetostnih pulzih od 0 kV do 5 kV in z 9 % izkoristkom za izdelavo navidezno amorfnega filma. Uporabila sta še pomožni izvor radiofrekvenčne plazme za povečanje hitrosti rasti tankih plasti pri majhnih pretokih plina. Z namestitvijo geometrije med vpadnim kotom curka ionov, tarče za naprševanje in podlage so lahko neodvisno od primarne energije ionov in vrste kontrolirali rast vzorca tankega filma. Inženiring širine prepovedanega pasu za elektrone sta avtorja izvajala s konvencionalno ionsko implantacijo za implantacijo ogljikovih ali dušikovih ionov pod površino. Sledile so raziskave na izdelanih vzorcih tankih plasti (filmih) oziroma določitev njihovih optičnih lastnosti, stehiometrije, strukturnih lastnosti, površinske topografije in fotoaktivnosti.

Ključne besede: TiO_2, MePiiiD, SRIM, fotoaktivnost

1 INTRODUCTION

Titanium dioxide is well known as a photoactive material activated under ultraviolet (UV) irradiation,[1,2] and employed either as a photocatalyst or exhibiting superhydrophilic behavior after a reduction of the surface energy under illumination needed for self-cleaning or anti-fogging surfaces.[3] As an alternative to powders, TiO_2 can be produced as thin films using chemical sol-gel processes, operating in air, or physical vapor deposition (PVD) processes where either high temperature or increased ion energy is necessary to obtain a photoactive phase.[4] An even coating of membranes is possible using a more complex process.[5] There, temperature sensitive substrates require low temperatures, ideally near room temperature where an amorphous photoactive phase can be formed under certain conditions.[6,7]

Regardless of the phase composition, the band gap is always more than 3 eV (the exact value depends on the polymorph), thus necessitating UV-A radiation for an activation. For increasing the reactivity of thin films under solar illumination, a reduced band gap is desired. Doping with transition metals or with nitrogen has been reported in the literature.[8,9] The latter dopant is – theoretically – readily accessible during PVD processes. However, the incorporation of nitrogen into a growing film, in contrast to ion implantation into TiO_2 thin films or selective oxidation of TiN, is a much more complex process, which is presently not completely understood.[10] Alternatively, TiO_2 nanotubes with a reduced band gap, visi-

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ble-light-active TiO_2 nanorods N-doped with a hydrothermal treatment or hydrazine doping of brookite nanorods at 200 °C for 18 h have been proposed recently.[11–13] Despite a large amount of published work, even the photoactivity of pure TiO_2 thin films is still a matter of controversy.

Therefore, an experiment was set up, which provided an opportunity to reduce the bandgap of TiO_2 thin films, increasing the surface energy and leading to improved photoactive properties. TiO_2 thin films were produced with metal plasma immersion ion implantation and deposition (MePIIID). Then, we employed mixtures of energies/species, 65 keV C + 75 keV N, 30 keV C + 35 keV N and 35 keV N + 75 keV N, to increase the local dopant concentration and adjust the depth of the penetration range of the light. The purpose was to investigate whether synergy effects exist for a combination of carbon and nitrogen dopants. It was found that ion implantation at concentrations of less than 10 *x*/% can lead to an increased photoactivity under UV illumination. Reducing the bandgap with carbon and/or nitrogen implantation before changing from a semiconductor to a semimetal is challenging. This was known for direct co-deposition during PVD by vacuum arc, and now it was shown to be also true for the post-implantation after MePIIID.

2 EXPERIMENTAL PART

TiO_2 thin films are produced with MePIIID. A d.c. cathodic arc with a pure titanium (99.99 %) cathode, running at 100 A was employed to generate Ti ions. An oxygen supply of 45 sccm to 70 sccm was used to establish a working pressure between 0.03 Pa and 0.3 Pa. Converting the nominal Ti ion current from the cathode of about 10 A at an average charge state of 2.1 into a particle flux and comparing this value with the oxygen flow, a O/Ti ratio of roughly 2.5:1 to 3.5:1 was established in the gas phase (assuming a homogeneous distribution within the vacuum chamber, which is definitely not true for the Ti flux). Silicon (100) coupons were used as the substrate material, mounted at a fixed distance of 39 cm from the cathode. No additional heating system was installed, thus the temperature of the substrate always started at room temperature (RT), rising to 50 °C or less at the end of the experiment. The nominal kinetic energies of 10–50 eV for Ti ions emanating from the d.c. arc were enhanced by negative high voltage pulses between 1 and 5 kV with a length of 30 μs at a repetition rate of 1–3 kHz (a duty cycle of 3–9 %). Furthermore, a 40.68 MHz rf plasma source was selectively employed at a fixed power of 150 W to create a background oxygen plasma. Without arc, an oxygen plasma density of 6×10^9 cm^{-3} at an electron temperature of 1 eV was measured by a Langmuir probe. The utilized geometry with the substrates facing towards the arc is depicted in **Figure 1**. A total deposition time of 5 min was used for all samples.

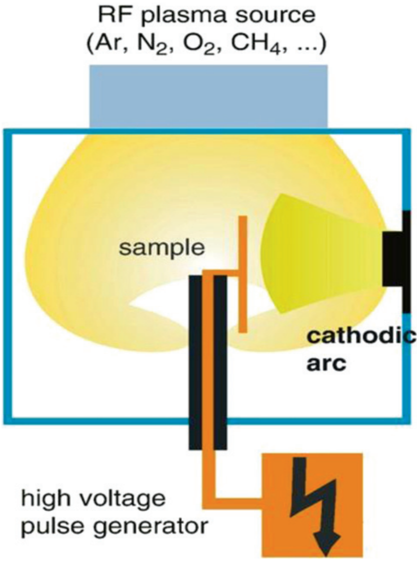

Figure 1: Schematic of the MePIIID deposition system with an auxiliary plasma source

The film morphology was investigated with scanning electron microscopy (SEM), while the surface roughness was determined by atomic force microscopy (AFM). X-ray diffraction (XRD) measurements were performed in $\theta/2\theta$-geometry. Elastic recoil detection analysis (ERDA) measurements were carried out using 200 MeV $^{197}Au^{15+}$ ions at a 19° incident angle and a detector placed at a scattering angle of 37° for a typical fluence of 3×10^{11} ions. Using the integrated count rates, O/Ti ratios with a relative accuracy of 0.25 *x*/% were derived. Raman spectra were measured using a LabRam HR Evolution Raman spectrometer with a spectral resolution of 0.7 cm^{-1} at 473 nm laser excitation (a grid with 1800 L/mm). The entrance slit of the spectrometer was 150 μm, the pin-hole of the confocal setup was 300 μm in diameter. The film thickness was derived from secondary ion mass spectrometry (SIMS) in a time-of-flight setup, stopping right at the interface and determining the sputter rate and absolute film thickness with mechanical profilometry.

The surface energy was derived from contact angle measurements (CAM) with a data analysis according to the Owens–Wendt method.[14] Contact angle measurements were performed on TiO_2 samples using the Krüss contact angle measuring system G2, and the results were obtained from the DSA II software (drop shape analysis II). In the dynamic CAM mode, two different liquids were used, i.e., deionized water and ethylene glycol, employing a manual drop position on the surface with 2–4 drops (because of high wettability of the sample surfaces after UV irradiation). From each liquid with a start volume of 3 μL and end volume of 4 μL, 10 successive snapshots were taken for each drop.

Photoactivity was examined by exposing the samples to UV-A light, generated from an actinic tube in a spec-

Table 1: Selected sample list from the photoactivity results obtained with contact angle measurements

No. of pairs	Sample ID	HV	Pulse length	Repetition rate	RF plasma	Distance from axis	Photoactivity (surface energy, mN/m)
1	9020	0 kV	30 µs	3 kHz	150 W/1 %	20 cm	42.3 (No)
	9021	5 kV	30 µs	3 kHz	150 W/1 %	20 cm	82.9 (Yes)
2	9022	3 kV	30 µs	3 kHz	150 W/1 %	20 cm	100 (Yes)
	9024	5 kV	30 µs	3 kHz	150 W/1 %	10 cm	40.6 (No)
3	9025	3 kV	30 µs	3 kHz	150 W/1 %	10 cm	95.2 (Yes)
	9027	0 kV	30 µs	3 kHz	150 W/1 %	10 cm	40.3 (No)
4	9029	3 kV	30 µs	3 kHz	150 W/1 %	0 cm	73.6 (Yes)
	9030	1 kV	30 µs	3 kHz	150 W/1 %	0 cm	47.5 (No)
Substrate holder diameter Φ = 7.8 cm (9020–9031)							

tral range of 300–460 nm and with a maximum of 365 nm, at an intensity of 1 mW/cm^2, for up to 3 h.

Then the samples were doped with carbon and nitrogen, using a conventional ion implanter, IMC-200. The aim was to reduce the band gap of the UV active TiO_2 thin films as well as to investigate the effect of implantation on non-photoactive TiO_2 thin films. The following implantation parameters were used: energies for C^+ ions – 30 keV and 65 keV, energies for N^+ ions – 35 keV and 75 keV, the average implantation time – 35 min, and the total fluency – 2×10^{16} cm^{-2}.

3 RESULTS AND DISCUSSIONS

The films produced with this method were slightly substoichiometric titania films with an O/Ti ratio of 1.90–1.95, as determined by the ERDA. The film thickness was always close to 300 nm, indicating a growth rate of about 1 nm/s and no strong influence of the varying ion bombardment on the growth rate. No crystalline anatase or rutile phases could be detected at RT for the pulse voltage range from 0 kV to 5 kV, being independent of the gas flow or plasma activation, and indicating either an amorphous structure or nanocrystallites with a size of less than 5 nm. Similar results were obtained for the film morphology when investigating thin-film cross-sections with SEM. No contrast was visible for a film deposited at room temperature with a 5 kV pulse voltage. AFM results confirmed SEM results with regard to the morphology; the measurements showed that the surface was very smooth, i.e., the root mean square (rms) roughness was $\sigma \leq 0.22$ nm. Detailed results for the structural properties, surface topography and influence of the deposition conditions on the growth rate of the TiO_2 thin films produced with this method are given in previous works.[10,15,16]

From the samples produced, we selected four pairs, within which one sample was promising to be photoactive, while the other was not. The sample parameters and photoactivity characteristics are depicted in **Table 1**.

Then, the above listed amorphous samples were doped with carbon and nitrogen, using the IMC-200 ion implanter. The aim was to reduce the band gap of the UV active TiO_2 thin films as well as to investigate the effect of implantation on non-photoactive TiO_2 thin films.

The concentration profiles of carbon and nitrogen, calculated with the stopping and range of ions in matter (SRIM) analysis, are shown in **Figure 2**.

After implantation the samples were illuminated with UV light for three hours and the surface energy was derived from contact angle measurements. The results of contact angle measurements are presented in the **Figure 3**. We observe an increase in the surface energy of

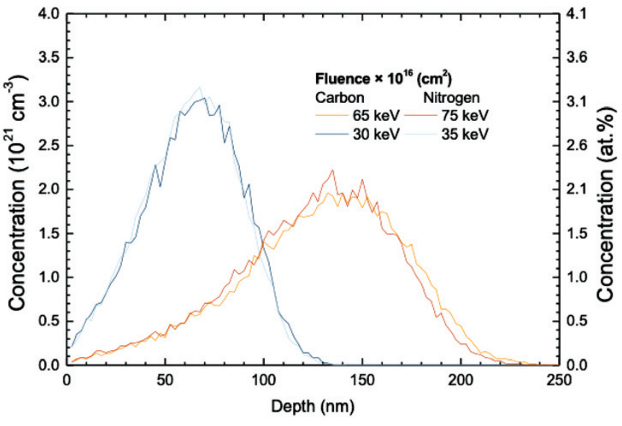

Figure 2: Concentration profiles of carbon and nitrogen

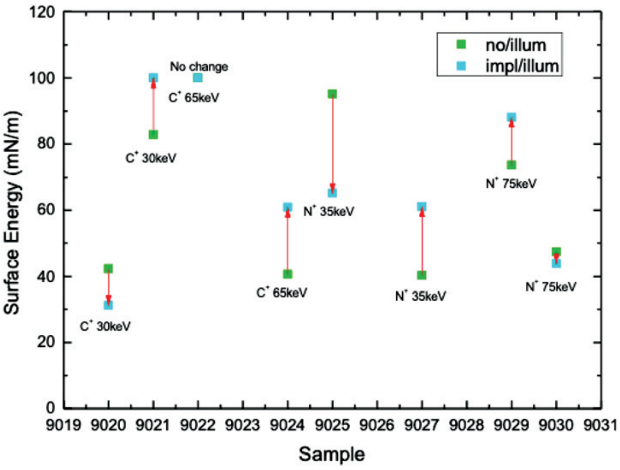

Figure 3: Surface energy of selected samples before and after implantation with/without UV-illumination

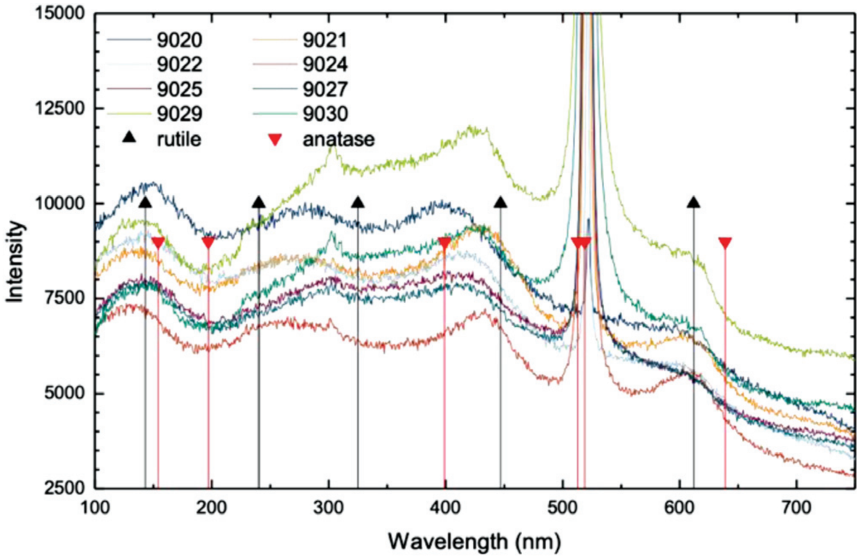

Figure 4: Raman spectra of selected samples after implantation, together with the reference spectra of a rutile thin film and anatase powder (APS 32 nm, Alfa-Aesar).[17] The prominent peak at 520 cm^{-1} arises from the Si substrate.

some samples after implantation, but for other samples no change or decrease in the surface energy can be seen on this graph.

For clarifying these findings, Raman measurements were performed with a 473 nm laser excitation. Two spectra, one with a laser intensity of 2 mW on a sample and one with a laser intensity of 8 mW on a sample were measured at different positions. The acquisition time was 20 s for each measurement. In order to filter out random spikes, each measurement was done twice.

As seen in **Figure 4**, the spectra obtained here for the films after implantation prepared with MePIIID are very similar to that of the nanocrystalline rutile layer on Ti, shown as a reference. The low intensity of the signal must be a combination of a small grain size and low crystalline quality.[18]

The next experiment consisted of doping samples with carbon and nitrogen using ion implanter IMC-200. We employed mixtures of energies/species, 65 keV C + 75 keV N, 30 keV C + 35 keV N, and 35 keV N + 75 keV N, to increase the local dopant concentration and adjust the depth of penetration range of the light. The purpose was to investigate whether synergy effects exist for a combination of carbon and nitrogen dopants. We had combinations of fluencies up to 7×10^{16} cm^{-2}, corresponding to local concentrations of up to 10 at.%. **Figure 5** presents calculated depth profiles for selected samples.

The effect of the ion implantation fluency on the photoactivity is depicted in **Figure 6** below. No systematic differences were found before illumination. From the data obtained for the surface energies after illumination, a strong, positive influence of the ion fluency on the photoactivity is observed. The time between the end of the illumination and the contact angle measurements was always less than 1 h; no influence of the small changes in this delay time on the results was observed. For the samples implanted with combinations of fluencies up to 7×10^{16} cm^{-2}, the surface energies of around 100 mN/m, indicating photoactivity, were obtained.

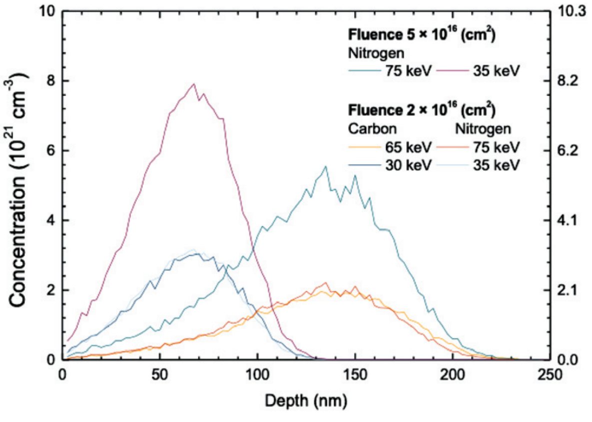

Figure 5: Concentration profiles of carbon and nitrogen obtained with SRIM

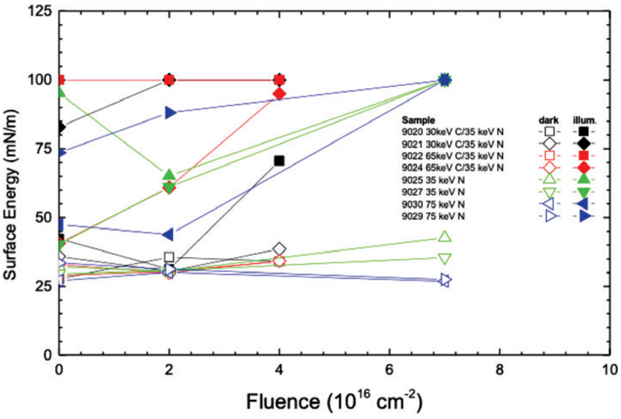

Figure 6: Variation of surface energy with ion fluency before and after illumination

4 CONCLUSIONS

Using the PVD processes – metal plasma immersion ion implantation and deposition and conventional ion implantation – the formation of photoactive TiO_2 thin films is reported.

It can be stated that ion implantation at concentrations lower than 10 at.% can lead to an increased photoactivity under UV illumination. Reducing a band gap with carbon and/or nitrogen implantation before changing a semiconductor into a semimetal is challenging. This was known about direct co-deposition during PVD by a vacuum arc, and now it is shown to be also true for post-implantation after metal plasma immersion ion implantation and deposition. Furthermore, the doping process increases the surface energy, which leads to improved photoactive properties. The doping influence on the surface energy is interesting, promising and not often reported in the literature. However, further work is necessary to elucidate its mechanisms and establish whether this is a doping or a damage effect.

Acknowledgment

This study was supported by the DAAD Grant, Research Stays for University Academics and Scientists, (57378441), personal ref. no. 91656534. We would like to thank S. Mandl, the supervisor, who also assisted us with Raman and IMC-200 Implanter measurements, and Darina Manova for valuable discussions during the evaluation of the results.

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