2025

Title Laser-induced Formation of TiO_2 with Controllable Phase on the Surface of Titanium

［1］Organization（10.5 points）
Project Leader：Prof.　Arturs Medvids
(Riga Technical University)
Representative at RIE：Prof. Hidenori Mimura
(Research Institute of Electronics, Shizuoka University, Japan)
Participants：Dr. Edvins Dauksta
(Riga Technical University)

［2］Research Progress（10.5 points）

Titanium dioxide (TiO2) is a wide band gap metal oxide semiconductor with numerous applications in science and technology [1]. The main fields are photovoltaic and photo catalytic for water purification. TiO2 is known to form many polymorph phases, but the most studied TiO2 polymorph phases are anatase, rutile and brookite. It is known that the anatase is more favorable for photo catalytic applications, while the rutile exhibits better optical and electrical performance [2]. In recent years, researchers started to focus on anatase/rutile heterostructures, which showed improved photo catalytic efficiency. In this study, the effects of laser radiation on TiO2 crystal were investigated with aim to show the possibility of phase transition from rutile to anatase.

Nb:0.05wt% doped TiO_2 crystal was used in experiments. The crystal was irradiated by fourth harmonic of Nd:YAG laser with following parameters: λ=266 nm, τ=3 ns, intensity I=56.0 MW/cm^2. The sample was irradiated in one spot from 1 till 10000 laser pulses. From Raman scattering spectra, it can be seen that the crystal consists of rutile phase before the irradiation (Fig.1). After irradiation the crystal is transformed in to the anatase phase, as can be seen in Raman scattering spectra [3].

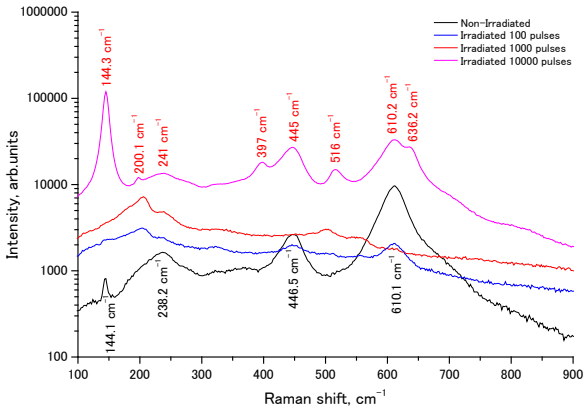


Fig.1. Raman spectra of TiO_2 thin films before and after irradiation by the fourth harmonic of Nd:YAG laser at I=56.0 MW/cm^2.

References
[1] M. Grätzel, Nature **414,** 338 (2001).
[2] H. Cheng and A. Selloni, Phys. Rev. **B 79**, 092101 (2009).
[3] H.L.Ma, J.Y.Yang et al. Appl.Surf. Sc. **253**, 7497(2007)

［3］Results（10.5 points）
（3－1）Research results

We were planning elaborate laser technology of TiO_2 thin film formation with controllable phase on the surface of titanium plate. Depend on laser parameters: intensity, wavelength and pulse duration, TiO_2 thin film will be in different phases. For characterization of the obtained thin films the following equipment will be used: Nd:YAG laser, SEM, AFM, FTIR, Raman and optical spectrometers.

This work is connected with medicine, biology and physics.

Preparation of the samples

Cleaned Ti substrate was secured on sample table. Laser (Q-switched nanosecond Nd:YAG laser Ekspla Nl301G, λ = 1064 nm) with top hat beam profile was used to irradiate samples. Focused laser pulse mode (τ = 6 ns) with pulse energy of 33 mJ was used. The sample was irradiated with 53 MW/cm^2 in ambient air atmosphere (Fig.2.). Sample irradiation was performed by scanning the sample with laser spot size of 0.44 mm^2 and scanning speed of 220 μm/s. Under rapid heat of laser radiation natural TiO_2 is evaporated opening clean Ti surface, where by adsorbing atmosphere oxygen TiO_2 is formed.

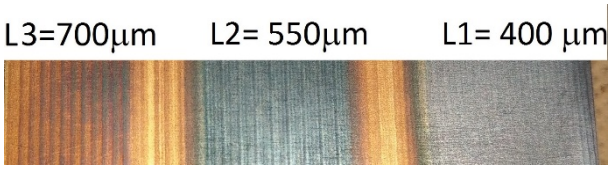


Fig.2 TiO_2 thin film formed by Nd:YAG laser radiation with different dose.

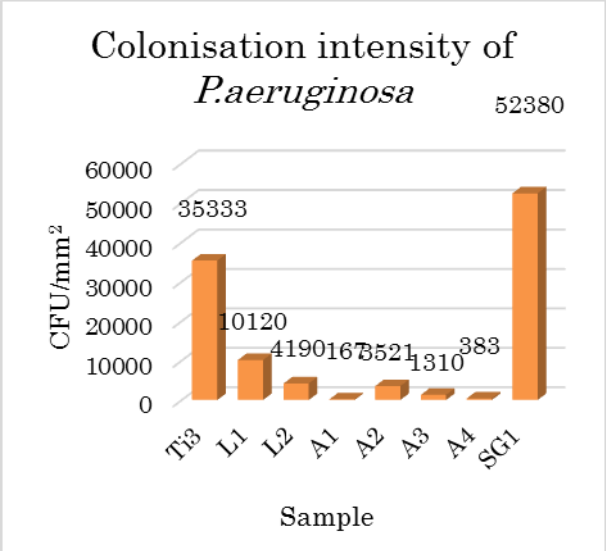
Microbiological activity

Bacterial colonisation intensity was tested using *Staphylococcus epidermidis* (*S.epidermidis*) (ATCC 12228) and *Pseudomonas aeruginosa* (*P.aeruginosa*) (ATCC 27853) bacteria reference cultures.

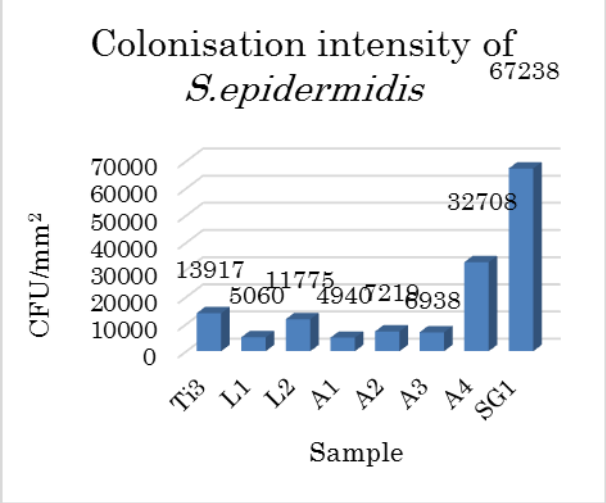
Determining microorganism colonisation in vitro

We prepared 1 ml TSB (Triptycase soy broth) (Oxoid, UK) bacterial suspensions from bacterial pure cultures in concentration of 10^2 CFU/ml. In order to determine colonisation intensity, samples were cultivated at 37°C for 24 h. Unattached microorganisms after incubation were rinsed off. Samples were processed in ultrasound bath (Cole-Palmer, USA) for 1 minute (at 45 kHz frequency) at maximum velocity in Vortex centrifuge (Biosan, Latvia), in order to separate attached bacteria from the surface of the sample. Three cultures were produced on TSA (Triptycase soy agar) (Oxoid, UK) from each sample, and they were cultured for 24 hours in 37°C, in order to determine the total amount of microorganisms per sample area.

We found out in the study that the colonization intensity of *S. epidermidis* and *P.aeruginosa* is increased or decreased depends on the samples used in the study.



(a)



(b)

Fig.3. The colonization intensity of *S. epidermidis (a)* and *P.aeruginosa (b).*

Photocatalytic activity studies.

For the determination of photocatalytic activity, the samples where immersed in 30 mL of a solution of methyl-orange (MO) with a concentration of 0.034 mM. The samples where then irradiated for 10 hours using a 100W High-pressure mercury lamp with a peak wavelength of 365 nm and an irradiance of 20 mW/cm2. The samples were cooled using an array of 120 mm fans and heatsinks in order to maintain a constant temperature. After each hour a sample of 1 mL was taken from the reaction vessel. Changes in concentration of MO where determined using a UV-Vis spectrophotometer (Gensys 10S) by measuring the absorbance at 465 nm. A darkness test was also conducted to

evaluate the adsorption of MO on the sample surface.

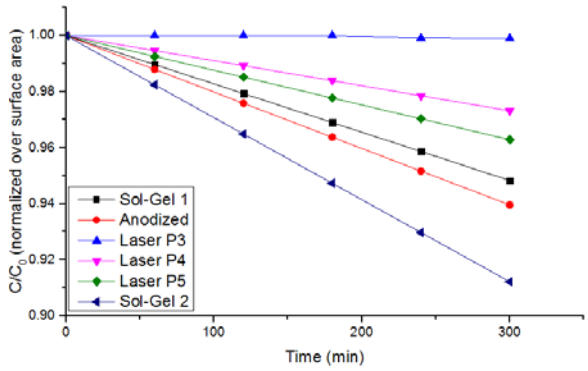


Fig.4. Methyl orange degradation dependence on method of TiO_2 layer formation onTi substrate.

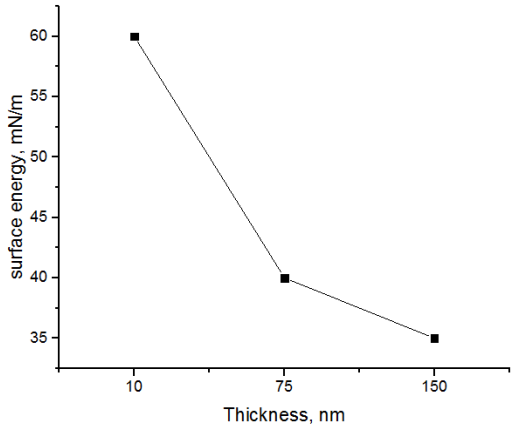


Fig.5. Surface energy of the TiO_2/Ti structure formed by the laser radiation dependence on TiO_2 thickness.

Conclusion

We have found that irradiation of TiO_2 single crystal by nanosecond laser with λ=266 nm, I=46.0 MW/cm^2 and 10000 pulses leads to the partial conversion of rutile to anatase.

We found out in the study that the colonization intensity of *S. epidermidis* and *P.aeruginosa* is increased or decreased depends on the samples used in the study.

(3－2) Ripple effects and further developments

Exchange of scientific expertise between the participants was very helpful for coordination of experimental work towards the goal of this project. Also, it has contributed to strengthening of domestic and international collaboration at Research Institute of Electronics. Joint work and discussions between the participants of this project have broadened the scope of existing domestic and international research collaborations at RIE, as well as opened new venues for collaboration in the future.

［4］Achievements (List of Publications) (10.5 points)

（1）A.Medvid', P. Onufrijevs, E. Dauksta, H. Mimura "Phase Transitions in Metal Oxide Semiconductors Induced by Laser Radiatin", Materials of Scientific and Technical Conference.Laser Technologies.Lasers and Their Application., June 7-9, Truskavets, Ukraine, pp. 96-98, 2017.

（2）T. Potlog, E. Dauksta, A. Medvids, L. Ghimpu, C. Moise, K. Murakami, H. Mimura, EFFECT OF LASER IRRADIATION ON THE REFRACTIVE INDEX OF THE TiO2 THIN FILMS, Submitted to Optics and Laser Technology Journal.

Travelling Report (Mention each travel by CRP budget.)

Name : Prof. Arturs Medvids
Affiliation : Riga Technical University
Period of time : 15.10.2017-04.11.2017.
Destination : Shizuoka University, Japan
Purpose : To carry out a joint research, plan the future collaboration, participate at the workshop and report previously obtained results.
Name of receiver : Prof. Hidenori Mimura