Change in Water Contact Angle of Carbon Contaminated TiO₂ Surfaces by High-energy Electron Beam

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We studied change in water contact angle on TiO₂ surfaces upon high-energy electron-beam treatment. Depending on conditions of e-beam exposures, surface OH-content could be increased or decreased. In contrast, water contact angle continuously decreased with increasing e-beam exposure and energy, *i.e.* change in the water contact angle cannot be rationalized in terms of the overall change in the surfacestructure of carbon-contaminated TiO₂. In the C 1s spectra, we found that the C-O and C=O contents gradually increased with increasing e-beam energy, suggesting that the change in the surface structure of carbon layers can be important for understanding of the wettability change. Our results imply that the degree of oxidation of carbon impurity layers on oxide surfaces should be considered, in order to fully understand the change in the oxide surface wettability.

Key Words: Electron beam, TiO₂, Water contact angle

Introduction

Change in the wettability of oxide surfaces such as TiO₂, WO₃, and ZnO by external stimulation is an important issue in many aspects. Reversible transition from hydrophobic to hydrophilic surfaces can have industrial implications as switch in smart devices.[1] Preparation of super-hydrophilic or super-hydrophobic surfaces can be important for creating antifogging, self-cleaning, and antibacterial agents.[2]

Previously, change in the wettability of oxide surfaces was observed, when TiO₂ surfaces were exposed UV-light.[3] Ozone and immersion in aqua media can also induce superhydrophilicity of TiO₂ surfaces.[4] Under dark conditions, the hydrophilic surface became hydrophobic, *i.e.* transition from the hydrophobic to hydrophilic surface is reversible.[2-6] Similar behavior could also be found for other oxides such as WO₃, and ZnO.[1,6-8] Various factors influencing hydrophilicity of oxide surface were suggested in previous studies, which will briefly be summarized in the following.

i) Many studies proposed that removal of hydrophobic organic stains by photocatalytic oxidation on TiO₂ should be responsible for the creation of hydrophilic TiO₂ surfaces.[4,9] TiO₂ has a band gap of 3.2 eV, and UV light with a higher energy than the TiO₂ band gap can create electron-hole pairs, which initiate photocatalytic degradation of hydrophobic organic molecules. ii) According to Wenzel's equation, increase in the surface roughness makes hydrophilic and hydrophobic surfaces more hydrophilic or hydrophobic, respectively.[10] iii) When OH-groups are formed on TiO₂ by dissociative chemisorptions of water on defect sites, hydrophilicity can be increased.[2,3]

Recently, superhydrophilic TiO₂ surfaces could be prepared without external stimulation such as UV-light using polyethylene glycol, which was used for controlling the surface porosity.[11] High surface roughness and content of OH groups were suggested to be responsible for the superhydrophilicity

of this TiO₂ structure.

In the present work, we studied contact angle of water of TiO₂ surfaces treated by high-energy electron-beams with different exposure conditions. High energy e-beam has been used in various areas including sterilization of foods and medical instruments. E-beam treatment under atmospheric conditions can result in various changes on oxide surfaces: i) collision of electrons on the surface can result in structural modification of TiO₂ such as formation of oxygen vacancies. ii) C or other impurities such as N and S can be incorporated into oxide structure, which can result in geometric and electronic modification of the oxide. iii) e-beam can activate molecules existing in the air, thereby forming reactive species such as O and OH radicals and ozone, which can change oxide surface structures. iv) surface impurity can be removed by e-beam, thereby changing chemical and electronic properties of oxide surfaces. It was previously suggested that the OH-concentration is closely related to the hydrophilicity of TiO₂ surfaces. In the present work, variation in the OH-group concentration could not be directly correlated with the contact angle change. Photoemission spectroscopy data suggest that the increase in C-O and C=O bonds on TiO₂ upon e-beam treatment should be closely related to the change in the wettability. Our results imply that by controlling C-O and C=O contents on the surface, surface wettability can be adjusted.

Experimental

The Ti foils covered by native oxide layers (TiO₂) were exposed to e-beam of 0.3 and 1.0 MeV in energy with exposures of 30, 60 and 90 kGy (kJ/Kg), respectively from a linear electron accelerator under ambient conditions in Korea Atomic Energy Research Institute, Daejeon, Korea. After e-beam exposures, water contact angle of each sample was measured using a S.E.O. 300 A model of Surface and electro-

optics comprising a CCTV camera connected to a computer (software imagePro 300). 3 µL of water droplet was deposited for each measurement. For each sample, the contact angle was measured twice and the average value was recorded.

The photoemission spectroscopy (valence and core level spectra) experiments were performed at the 7B1 beamline in the Pohang Accelerator Laboratory. All experiments here wereperformed in an ultrahigh vacuum (UHV) system with a base pressure in the middle 10^{-10} torr range. For the valence band spectra, photon energy of 55 eV was used. For C 1s and O 1s level spectra, photon energy of 630 eV was used.

Results and Discussion

Fig. 1 shows results of the water contact angle measurements of native TiO_2 films on Ti foils before and after high-energy e-beam treatments with various exposure conditions. Based on X-ray Photoelectron Spectroscopy (XPS) results, the oxide film thickness was suggested to be at least 3-4 nm, since only Ti(IV) could be identified in the Ti 2p spectra without Ti(O) peaks.[12] No impurities other than C could be identified using XPS. Amount of C was suggested to be comparable to that of TiO_2 in our qualitative analysis of the XPS spectra, *i.e.* significantly large area of TiO_2 surface should be covered by carbon layers. The native sample showed the water contact angle of 84°. With increasing e-beam exposure, decrease in the water contact angle could be observed. For both e-beam energies used in the present work, similar results could be found, *i.e.* decrease in water contact angle resulted from e-beam exposures, independent of the electron energy. Upon e-beam exposure of 1.0 MeV / 90 kGy (Gy = J/Kg), contact angle became 50°, which is lower than the value of non-treated sample by 84°.

In general, TiO_2 surfaces exposed to UV-light experience a hydrophobic-to-hydrophilic transition, and the hydrophilic surfaces produced in this way can be transformed within several days to the hydrophobic state under dark conditions.[5] The TiO_2 film exposed to 1.0 MeV / 90 kGy e-beam showed still a lower contact angle of water comparing to that of the non-treated TiO_2 three weeks after the e-beam exposure, *i.e.* the lowered contact angle of water upon high-energy e-beam treatment could be sustained for several weeks (Fig. 2).

In order to shed light on the change in surface structure of TiO_2 upon e-beam treatment, synchrotron radiation based photoemission spectroscopy (SRPES) was used. Fig. 3 shows the valence band spectra of TiO_2 before and after e-beam treatment. When 0.3 MeV of e-beam was used, appearance of an additional state could be identified at 1-2 eV below the Fermi level (Fig. 3). The origin of the appearance of the band gap state is unclear. Either formation of oxygen vacancy or structural modification by other impurities such as carbon can be responsible for the band gap state.[13-15] By e-beam treatment, carbon impurity on TiO_2 can be incorporated into deeper TiO_2 layers, and consequently TiO_2 structure can be modified, resulting in appearance of the band gap state.[15] When 1.0 MeV was used for the TiO_2-treatment the band gapstate disappeared. Our result shows that e-beam energies of 0.3 and 1.0 MeV resulted in different changes in the surface structure.
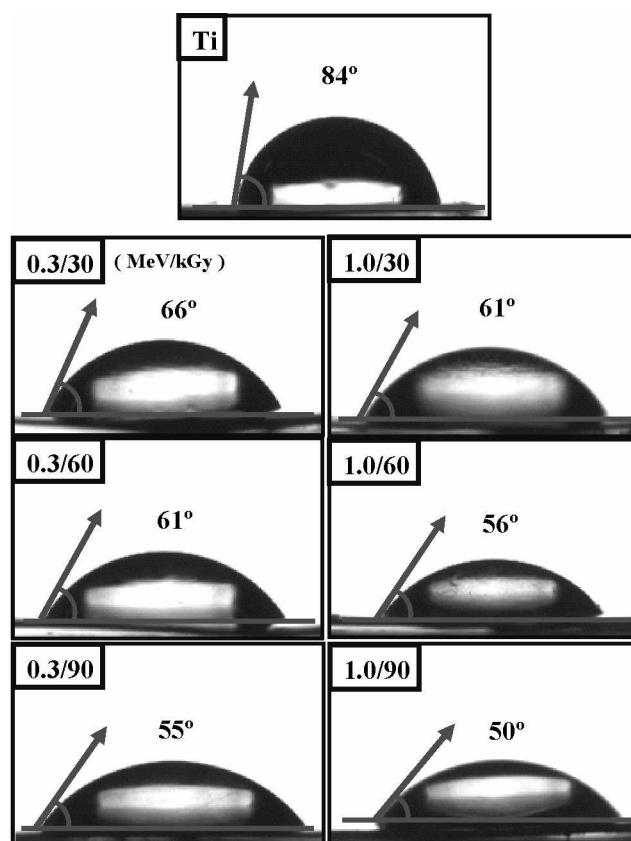

Figure 1. Contact angle measurements of water of TiO_2 surfaces treated with different e-beam exposure conditions. Exposure conditions are given in the figure.
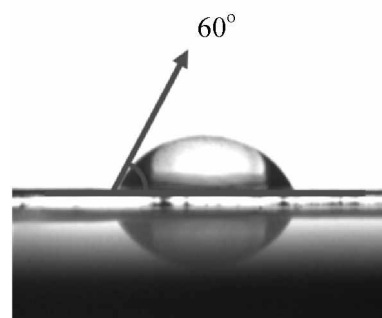

Figure 2. Contact angle of water of TiO_2 surface treated by 1.0 MeV/ 90 kGy of e-beam. The measurement was conducted 3 weeks after the e-beam exposure.

In the introduction, possible change in surface structure by high-energy e-beam was summarized. Combination of different factors should result in diverse surface structures depending on the e-beam exposure conditions.

Fig. 4 compares the O 1s core level spectra of three different samples of Fig. 3. O 1s spectra show two different states centered at 531 and 533 eV, and the relative intensity of both states was varied from sample to sample. Based on previous studies, the higher-binding-energy state should be mostly attributed to the OH-group formed by the dissociative chemisorptions of water existing in air, or formed as a consequence of water dissociation by e-beam.[16] The sample treated with
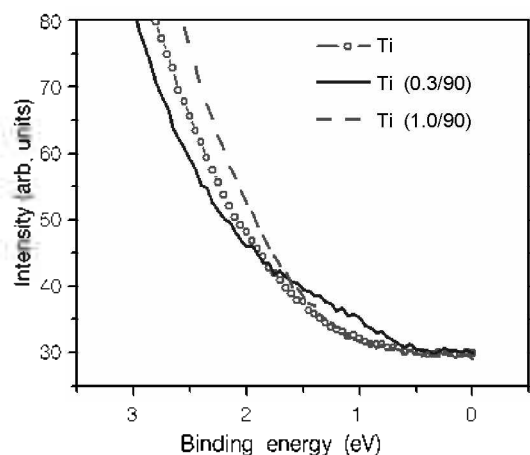
Figure 3. Valence band spectra of three different TiO₂ surfaces 1) non-treated 2) treated by 0.3 MeV / 90 kGy and 3) 1.0 MeV / 90 kGy.
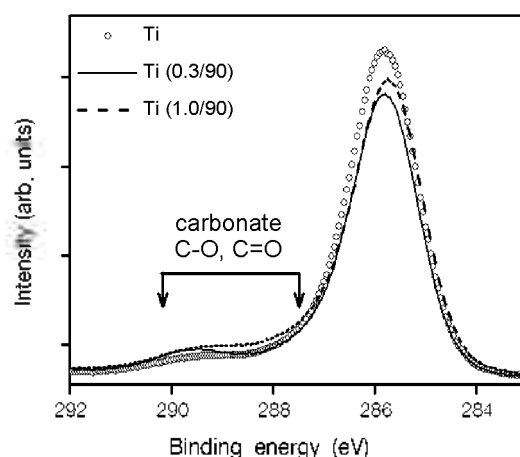

Figure 5. C 1s level spectra of three different TiO₂ surfaces 1) non-treated 2) treated by 0.3 MeV / 90 kGy and 3) 1.0 MeV / 90 kGy.

Spectroscopy (TDS) suggested that oxygen vacancies of TiO₂ surfaces formed by the e-beam exposure lowers probability of the dissociative chemisorptions of water. *i.e.* the water-oxygen vacancy interaction is weaker than that of water-stoichiometric TiO₂ surface.[17] In absence of oxygen vacancies formed by the e-beam treatment. water can dissociatively chemisorb on other defect sites. such as steps. and the dissociated species are stable up to 500 K on TiO₂ surfaces.[17]

Our results in Figs. 1 and 2 show that the water contact angle became smaller upon the e-beam treatment independent of the e-beam energy. In general, a higher content of OH-group is suggested to result in a higher hydrophilicity of TiO₂[11]; however, the OH-contentcan increase or decrease depending on the e-beam exposure conditions. *i.e.* no correlation between OH-concentration and water contact angle could be found.

In order to obtain a deeper insight into the change in the surface structure upon e-beam exposure. C 1s spectra were collected from three different samples of Figs. 3 and 4 (Fig. 5). C 1s spectra show a pronounced peak centered at 285.7 eV. which is positively shifted by about 1.0 eV with respect to the value of the ideal graphite structures.[18] In addition to this state, broad shoulders at higher energies could be found. indicative of the C-O and C=O bonds (286-287 eV) and carbonate species (~289 eV).[18,19] When the surface was exposed to 0.3 MeV/90 kGy of e-beam. increase in intensity of the carbonate state could be identified. When 1.0 MeV was used. additional increase in the intensity of the 286-287 eV states corresponding to the C-O or C=O groups could be found. *i.e.* when a higher energy of e-beam was used. a larger incorporation of oxygen on carbon took place.

Considering that the C-O and C=O species (or COH, COOH groups) can interact with water more strongly than the pure graphite layers, the results of the water contact angle in Figs. 1 and 2 can be rationalized. Using a higher e-beam energy, a higher coverage of C-O and C=O species was found, in line with a lower contact angle of water, when a higher electron-energy was used for the surface treatment. Transformation of hydrophobic graphitic carbon into hydrophilic structure can decrease the contact angle of water. It is worth mentioning that e-beam treatment on a pure hydrocarbon polymer film
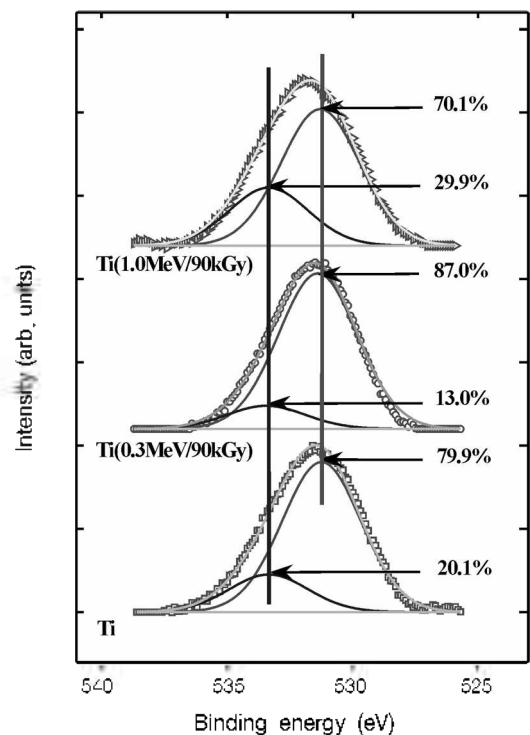

Figure 4. O 1s level spectra of three different TiO₂ surfaces 1) non-treated 2) treated by 0.3 MeV / 90 kGy and 3) 1.0 MeV / 90 kGy.

e-beam with an energy of 0.3 MeV showed a lower relative intensity of O 1s (533). implying that the concentration of OH groups on carbon-contaminated TiO₂ decreased upon the 0.3 MeV e-beam treatment. In contrast. when 1.0 MeV e-beam was used for the sample treatment. O1s (533) / O1s (531) ratio became larger than those of other samples shown in Fig. 4 (samples without and with e-beam treatment of 0.3 MeV). The change in the relative amount of OH-species upon e-beam treatment on the surface can be justified in connection with the results of the valence band spectra in Fig. 3. When 0.3 MeV of e-beam was used. band gap could be identified. which can be an indication of the formation of oxygen vacancies (Fig. 3). and previous studied using Thermal Desorption

resulted in decrease in water contact angle, in line with our suggestion that partial oxidation of carbon impurity on TiO_2 can be responsible for the decrease in water contact angle.[20]

Conclusion

In summary, we found decrease in the water contact angle of TiO_2 surfaces by the high-energy e-beam treatments. Change in the valence band and O 1s spectra representing the overall structural change in the carbon-contaminated TiO_2 surface cannot rationalize the water contact angle change. We suggest that change in the surface structure of carbon layers existing on the surface should be taken into account in order to fully understand the change in the water contact angle.

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