

Monday Morning, November 9, 2009

Advanced Surface Engineering

Room: B1 - Session SE1-MoM

Photocatalytic Coatings

Moderator: H. Barankova, Uppsala University, Sweden

8:20am **SE1-MoM1 Development of Highly Functional Visible Light-responsive TiO₂ Thin Film Photocatalyst Materials by a RF Magnetron Sputtering Method and their Applications for our better Environment and Production of Clean Energies using Sunlight.** *M. Anpo, M. Matsuoka, M. Takeuchi*, Osaka Prefecture University, Japan **INVITED**
Titanium oxide-based catalysts have attracted a great deal of attention for their application in photocatalytic materials with high reactivity, thermal stability and nontoxic properties¹. However, unlike natural photosynthesis in green plants, they can make use of only 3-4% of solar light, necessitating the use of a UV light source. Recently, we have successfully applied a RF magnetron sputtering deposition method to design unique and efficient titanium oxide photocatalysts which enable the absorption of visible light of longer than 550 nm. These newly developed titanium oxide catalysts were found to work as environmentally-friendly photocatalyst, leading to the efficient use of solar energy for the production of clean H₂ and O₂ from water with a separate evolution and other significant reactions²⁻⁴.

In the present lecture, the results obtained for the photocatalytic decomposition of H₂O with the separate evolution of H₂ and O₂ under sunlight irradiation of the visible light-responsive titanium oxide thin film photocatalysts will be presented.

References

- 1) M. Anpo, et al., in "Annu Rev. Mater. Res.", Eds. J. M. Thomas and P. L. Gai, **35**, 1 (2005).
- 2) M. Kitano, M. Takeuchi, M. Matsuoka, M. Anpo, et al., *Catal. Today*, **120**, 133 (2007).
- 3) M. Kitano, M. Matsuoka, J. M. Thomas, M. Anpo, et al., *Top. Catal.*, **49**, 24 (2008).
- 4) S. Fukumoto, M. Kitano, M. Takeuchi, M. Matsuoka, M. Anpo, *Catal. Lett.*, **127**, 39 (2009).

9:00am **SE1-MoM3 The Effect of Nb Additions on the Synthesis, Photo-Response, and Photo-Activity of TiO₂ Thin Films.** *P.A. DeSario, M.E. Graham, K.A. Gray*, Northwestern University

A deeper understanding of the relationships between synthesis, structure and function is needed to improve the design of materials tailored to solar energy conversion and storage. The objective of this research is to synthesize TiO₂ composites with properties tailored to the harvesting and conversion of solar energy. Unbalanced reactive dc magnetron sputtering with partial pressure control of oxygen was utilized to synthesize a series of pure and mixed phase TiO₂ films. Films were doped with Nb (Ti_{1-x}Nb_xO₂) in the range of 0<x<0.45 to evaluate the effect of cation doping on optical, chemical and physical properties. The films were interrogated structurally and functionally using SEM, EDX, XPS, AFM, UV-Vis absorption spectroscopy, and XRD. Selected films were evaluated with respect to gas phase CO₂ reduction and gas phase oxidation of acetaldehyde and the action spectra were determined.

Improvements in catalytic efficiency can be made by shifting the photo-response of titania-based materials to utilize a larger portion of the solar spectrum. Many attempts have been made to red-shift the photoresponse of TiO₂ through cation doping or anion doping. It is not yet proven, however, if the shift in photoresponse correlates to enhanced photoactivity under visible light or simply the creation of color centers. Preliminary findings show that Nb doping enhances oxidative reactivity under visible light. Reductive chemistry does not seem to be enhanced, however, which suggests how Nb substitution is altering band gap structure.

While earlier work established the relationships between sputtering process parameters and the film structure, including phase identity and distribution in pure TiO₂, this work is focused on how the addition of Nb cations change the film growth and phase formation relative to the pure material. The work also tries to characterize the cation valence and location in the TiO₂ lattice. The parametric response of film structure still suggests that in the mixed phase system greater energy input favors the formation of rutile and lower energy favors anatase, but Nb additions shift the regions of phase stability compared to pure TiO₂ and favor the growth of rutile. The shift in optical absorption to the visible wavelength range as a function of Nb concentration and anatase-rutile phase distribution is also presented.

Our work on pure TiO₂ indicates that the films with the highest photoreactivity were nanocrystalline, mixed phase structures (~70% anatase) with substoichiometric oxygen concentration. Results are presented comparing the photoreactivity of the Nb doped films with the pure TiO₂ mixed phase films of similar structure and phase proportions.

9:20am **SE1-MoM4 Identification of Carbon Sensitization for the Visible Light Photocatalytic Titanium Oxide.** *Y. Chen, G. Jhan, G. Cai, T. Lin, M.S. Wong, C. Cheng*, National Dong Hwa University, Taiwan

Titania nanopowders synthesized by low-pressure flat-flame metalorganic chemical vapor condensation method are known to possess visible light photocatalytic ability even they are produced without intentional doping. While the visible-light absorption of the powder is convincing, the cause of visible light absorption is still inconclusive. There are 3 main possible causes for visible light absorption discussed earlier. First is the anatase/rutile interface that generates defect levels for visible light absorption. Second is the nitrogen doping that forms the absorption center. Third is the carbon doping that forms the absorption center. In order to confirm that carbon doping is the major cause for the visible light absorption of the powder, we modify the process using helium in place of nitrogen to eliminate the nitrogen doping possibility. Helium in place of nitrogen is used as the titanium precursor carrier gas, where the precursor is titanium isopropoxide. Using acetylene and oxygen as fuel and oxidizer for the flame, the titanium isopropoxide was decomposed and oxidized, and the nanoparticles of titania were formed. From the methylene blue decomposition study we found that the powder synthesized under low precursor feed rate possesses high photocatalytic efficiency under illumination of visible light. Since nitrogen is avoided in the process, the visible light absorption cannot be due to nitrogen doping. We also found that the nanopowder formed has a single phase of anatase. Thus the nanopowder does not have anatase/rutile interface, and we can eliminate the possibility of visible light absorption by the anatase/rutile interface. The visible light absorption should thus be resort to the carbon doping. XPS studies show the presence of several carbon related bonds except Ti-C bond. This suggests that the carbon does not incorporate into the TiO₂ crystal and should locate on the surface of the nanopowder. Thus the carbon species act as a visible light sensitizer for the titania as a photocatalyst. Among all carbon bonds the C-C bond is believed to be responsible for the light absorption, since all other carbon related bonds are not chromophores. The carbon should be in the cluster form to become colored. The visible light TiO₂ photocatalysis induced by carbon doping is confirmed and explained.

9:40am **SE1-MoM5 Effects of Oxygen Vacancies on Electro-Optic Properties of Reactively Co-Sputtered Nb-doped Titania Films.** *H.C. Hsing, H.T. Chang, T.Y. Lu, C.C. Mo, M.S. Wong*, National Dong Hwa University, Taiwan

Transparent conducting niobium-doped titania was prepared by reactive co-sputtering of Ti and Nb metal targets in oxygen and argon plasma. The as-deposit films were annealed at 650°C under air atmosphere for 8 hr and then hydrogen annealed. Two different H₂-annealing procedures were executed to generate different concentration of oxygen vacancies: the H₂-annealing time ranges from 10 min to 4 hr under constant temperature and H₂-annealing temperature ranges from 200°C to 800°C under constant time. From the XPS spectra, the concentration of oxygen vacancies was observed, and directly affects the carrier concentrations in the thin film. The thin film's structure and optical properties was also measured and discussed.

10:00am **SE1-MoM6 Micro-Structure of Photo-Catalytic TiO₂ Films Deposited by Oxygen Ion Assist Reactive Evaporation Method and Reactive Sputtering.** *Y. Hoshi, D. Ishihara, H. Lei, T. Sakai*, Tokyo Polytechnic University, Japan

TiO₂ films were deposited on glass slide substrates by using oxygen ion assist reactive evaporation method(IARE) and reactive sputtering method(RS), and their micro-structure was investigated by using FE-TEM.

The films of above 1um thick deposited by IARE at the substrate temperature of 300 °C and ion accelerating voltage of 200 V has excellent photo-catalytic properties. However, the films with thickness lower than 1um shows poor photo-catalytic properties. In these films, the crystallization in the initial layer on the substrate was suppressed so that the film near the substrate contains large amount of amorphous phase. As the film grew, crystallization was enhanced and clear columnar structure was developed in the films. As a result, most of the amorphous phase was disappeared at the thickness above 600 nm. In addition, the column were separated each other with clear spaces at the thickness above 800 nm. This may be the reason why the photocatalytic properties improved significantly as the film thickness increased above 1um. These results suggest that the

poor crystal structure is the main reason why the film with thickness below 800nm has poor photo-catalytic properties.

On the other hand, compared with the films deposited by IARE, crystallization was enhanced in the deposition of the films by using a reactive sputtering. As a result, crystallized film with thickness below 200 nm can be obtained at 300 °C. This may be due to the fact that the depositing atoms in the sputtering process have much larger kinetic energy than in IARE. The film, however, has much dense structure and smooth surfaces, which results in a poor photo-catalytic organic decomposition properties.

10:40am **SE1-MoM8 Enhancement of Visible-Light Activities of Photocatalytic WO₃ Films Deposited by Sputtering.** *A. Murata, M. Kikuchi, N. Oka, Y. Sato, S. Nakamura, H. Yamaguchi, Y. Shigesato*, Aoyama Gakuin University, Japan

We have been reported on photoinduced superhydrophilicity and oxidative decomposition of organic compounds under visible light irradiation on polycrystalline WO₃ films deposited by reactive magnetron sputtering at the substrate temperature at 800 °C [1,2,3]. On the other hand, Abe, et al. reported that WO₃ powder loaded with Pt nanoparticles exhibits high efficiency for the decomposition of organic compounds under visible light irradiation, certainly due to promotion of multielectron O₂ reduction [4].

In this study, we deposited the photocatalytic WO₃ films with visible-light-activity on fused silica glass substrates by dc reactive magnetron sputtering using a W metal target. The substrate temperatures and total gas pressure during the deposition were 800 °C and 5.0 Pa, respectively. In addition, Pt was deposited on WO₃ film surfaces at RT by sputtering with various sputtering power and deposition time. In the case of Pt deposited on WO₃ films, 3D growth mode (Volmer-Weber) should be expected in general, because atoms or molecules in the deposit are more strongly bound to each other than to the substrate. The surface coverage of Pt on the WO₃ films were estimated by X-ray photoelectron spectroscopy (XPS), which implied that the Pt film followed Volmer-Weber type film growth process, i.e., after an initial nucleation, an island structure grew and coalesced with each other with increasing film thickness. High resolution electron microscopy (HREM) revealed that Pt nano-particles with diameter of about 2 nm were generated at the early stages of the Pt film growth, which dispersed uniformly on the columnar polycrystalline WO₃ films possessed of large surface area.

The photocatalytic activity was evaluated by photodecomposition of acetaldehyde under the irradiation of visible light (Xe lamp with a 410-500 nm band pass filter, 1.0 mW/cm²). With increasing in the Pt deposition time upto 10 sec, the decomposition rates for the Pt loaded WO₃ films were higher than that on the pristine WO₃ film. Especially, for the WO₃ films deposited with the Pt by 7 sec, acetaldehyde was completely decomposed within 150 min, on which the surface coverage of Pt indicated about 60%.

[1] M.Ebihara, Y.Shigesato,et al., Proceedings of the 3rd ICCG (2000) 137.

[2] M. Kikuchi, Y. Shigesato, et al., Abstract of the 21st IUPAC SYMPOSIUM (2006) 496.

[3] M. Kikuchi, Y. Shigesato, et al., Proceedings of the 6th ICCG (2006) .

[4] R. Abe, B. Ohtani, et al., J. Am. Chem. Soc. 130, (2008) 7780.

11:00am **SE1-MoM9 Optimization of Photovoltaic Performance through the Integration of Electrodynamic Dust Shield Layers.** *S. Nason, K. Davis, N. Hickman*, Florida Solar Energy Center, *E. Arens, J. McFall, C. Calle*, Kennedy Space Center

The viability of photovoltaics on the Lunar and Martian surfaces may be determined by their ability to withstand significant degradation in the Lunar and Martian environments. One of the greatest threats is posed by fine dust particles which are continually blown about the surfaces. In an effort to determine the extent of the threat, and to investigate some abatement strategies, a series of experiments were conducted outdoors and in the Moon and Mars environmental chamber at the Florida Solar Energy Center .

Electrodynamic dust shield prototypes based on the electric curtain concept have been developed by our collaborators at the Kennedy Space Center [1]. These thin film layers can remove dust from surfaces and prevent dust accumulation. Several types of dust shields were designed, built and tested under high vacuum conditions and simulated lunar gravity to validate the technology for lunar exploration applications.

Gallium arsenide, single crystal and polycrystalline silicon photovoltaic integrated devices were designed, built and tested under Moon and Mars environmental conditions as well as under ambient conditions. Photovoltaic efficiency measurements were performed on each individual cell with the following configurations; without an encapsulation layer, with a glass covering, and with various thin film dust shields. It was found that the PV efficiency of the hybrid systems was unaffected by these various thin film

dust shields, proving that the optical transmission of light through the device is virtually uninhibited by these layers.

The future goal of this project is to incorporate a photovoltaic cell as the power source for the electrodynamic dust shield system, and experimentally show the effective removal of dust obstructing any light incident on the cell, thus insuring power production is maximized over time.

[1] C.I. Calle, C.R. Buhler, J.G. Mantovani, S. Clements, A. Chen, M.K. Mazumder, A.S. Biris, A.W. Nowicki, Electrodynamic dust shield for solar panels on Mars, Lunar and Planetary Science XXXV, 2004, p. 2014.

Authors Index

Bold page numbers indicate the presenter

— A —

Anpo, M.: SE1-MoM1, 1
Arens, E.: SE1-MoM9, 2

— C —

Cai, G.: SE1-MoM4, 1
Calle, C.: SE1-MoM9, 2
Chang, H.T.: SE1-MoM5, 1
Chen, Y.: SE1-MoM4, **1**
Cheng, C.: SE1-MoM4, 1

— D —

Davis, K.: SE1-MoM9, 2
DeSario, P.A.: SE1-MoM3, **1**

— G —

Graham, M.E.: SE1-MoM3, 1
Gray, K.A.: SE1-MoM3, 1

— H —

Hickman, N.: SE1-MoM9, 2

Hoshi, Y.: SE1-MoM6, **1**

Hsing, H.C.: SE1-MoM5, 1

— I —

Ishihara, D.: SE1-MoM6, 1

— J —

Jhan, G.: SE1-MoM4, 1

— K —

Kikuchi, M.: SE1-MoM8, 2

— L —

Lei, H.: SE1-MoM6, 1

Lin, T.: SE1-MoM4, 1

Lu, T.Y.: SE1-MoM5, 1

— M —

Matsuoka, M.: SE1-MoM1, 1

McFall, J.: SE1-MoM9, 2

Mo, C.C.: SE1-MoM5, 1

Murata, A.: SE1-MoM8, 2

— N —

Nakamura, S.: SE1-MoM8, 2

Nason, S.: SE1-MoM9, **2**

— O —

Oka, N.: SE1-MoM8, 2

— S —

Sakai, T.: SE1-MoM6, 1

Sato, Y.: SE1-MoM8, 2

Shigesato, Y.: SE1-MoM8, 2

— T —

Takeuchi, M.: SE1-MoM1, **1**

— W —

Wong, M.S.: SE1-MoM4, 1; SE1-MoM5, **1**

— Y —

Yamaguchi, H.: SE1-MoM8, 2