

Wednesday Morning, October 17, 2007

Advanced Surface Engineering

Room: 617 - Session SE-WeM

Photocatalytic Coatings

Moderator: A. Erdemir, Argonne National Laboratory

8:00am **SE-WeM1 High Rate Deposition of Photocatalytic TiO₂ Films by dc Magnetron Sputtering using a TiO_{2-x} Target.** *Y. Sato, A. Uebayashi, N. Ito, Aoyama Gakuin University, Japan, T. Kamiyama, Asahi Glass Ceramics Co., Ltd., Japan, Y. Shigesato, Aoyama Gakuin University, Japan*

Sputter deposition should be the most promising technique for the uniform coatings in large area with very high durability and strong adhesion. However, the deposition rate of TiO₂ films by conventional reactive sputtering using a Ti metal target is very low, because the target surface should be fully oxidized (in "oxide mode") in order to deposit stoichiometric TiO₂ films. Recently, a slightly reduced TiO_{2-x} target (2-x = 1.986, Resistivity: 0.27 Ωcm) has been developed. Using this TiO_{2-x} target TiO₂ film deposition by dc sputtering with rater high rate and high durability should be possible. TiO₂ films were deposited on alkali-free glass substrate at RT-400°C by dc magnetron sputtering using the TiO_{2-x} target under 3.0 Pa. O₂ flow ratio during deposition was controlled from 0 to 100%. The variation in the deposition as a function of O₂ flow ratio did not show hysteresis curve at "transition region" as can be seen in the case of using Ti metal target, indicating that the TiO_{2-x} target surface was gradually oxidized with increasing O₂ flow ratio. The deposition rate using TiO_{2-x} target under 100% Ar gas was about 5 times higher than that using Ti metal target in "oxide mode". XRD patterns of the films deposited at O₂ flow at 0-5% showed entirely amorphous structure. After postannealing in air at higher than 200°C for 1 hour, these films changed to polycrystalline anatase TiO₂ and showed excellent photocatalytic activities such as photodecomposition of acetaldehyde (CH₃CHO) or photo-induced hydrophilicity. Furthermore, we carried out in-situ analyses on the sputtering processes using the different sputtering target. A quadrupole mass spectrometer (QMS, AQ-360, ANELVA) combined with a specially designed energy analyzer revealed that high-energy O⁻ ion flux was detected clearly even in the sputtering with 100% Ar gas in the case of using the TiO_{2-x} target. Whereas in the case of using Ti metal target the O⁻ ion flux was detected only in the "oxide mode". The sputtered fragments mass analyses showed that Ti⁺ and TiO⁺ existed as sputtered particles in case of using the TiO_{2-x} target under O₂ flow ratio from 0 to 100 %, which was the same result as in the case of using the Ti metal target in the "oxide mode".

8:20am **SE-WeM2 Flat-Flame Chemical Vapor Deposition Synthesis of Nanostructured Titania for Visible Light Photocatalyst.** *Y.J. Chen, J.M. Wu, M.S. Wong, National Dong Hwa University, Taiwan ROC*

Anatase is known as the favorable phase of titania as photocatalyst over rutile. However, several reports suggest that a mixed phase of anatase and rutile possesses even better photocatalytic efficiency. In this paper, we report that a mixed phase of anatase and rutile synthesized by low-pressure flat-flame metalorganic chemical vapor deposition does show such phenomenon that the mixed phase with proper proportion has higher photocatalytic efficiency over single phase anatase. 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. The phase of titania powder can be manipulated from almost pure anatase through mixed phases and to pure rutile phase by varying the inert precursor-carrying gas flow rate. The higher the carrier gas flow, the higher the rutile content. From the methylene blue decomposition study we found that the powder with almost pure anatase phase possesses best photocatalytic efficiency under illumination of UV light. However, mixed phase shows best efficiency under visible light illumination. Furthermore, for powder annealed in nitrogen atmosphere at 150 Celsius for 3 hours, the sample of mixed phase further enhanced its methylene blue photodecomposition efficiency. The reaction rate constant is even higher than that of ST-01 titania powder, which is commercially available for photocatalytic applications. While proper annealing process increases the photocatalytic activity of the powder, prolonged or elevated temperature annealing leads to degradation of its power, even the mixed-phase configuration is still retained. It suggest that carbon species play important role in enhancement of mixed-phase photocatalytic activity, since the carbon species will be oxidized during annealing, leaving uncontaminated titania powder, which lose its enhanced catalytic power. Evidence will be

provided to show that the carbon species does evolve with annealing, and the presence of carbon species is in coincident with the presence of visible light absorption.

8:40am **SE-WeM3 Preparation and Characterization of TiO₂/Ferrite Nanocomposites.** *K.S. Lin, W.R. Chen, C.F. Wu, Yuan Ze University, Taiwan, R.O.C.*

A core-shell structured composite, nanophase titania coated Ni-, or Zn-ferrites nanoparticles, not only reserve the characteristics and advantages of TiO₂ but also have the strong ferromagnetism of the ferrites. Therefore, the main objective of this study was to synthesize TiO₂/nickel or zinc ferrite nanocomposites with spinel structure. In addition, it focused on the magnetic characteristics of the TiO₂ surface-modified Zn or Ni-ferrite nanoparticles, which was expected to prepare a magnetically separable TiO₂ photocatalyst. Experimentally, nickel or zinc ferrite core nanoparticles were synthesized under hydrothermal conditions by precipitating from metal nitrates with aqueous ammonia. TiO₂ coated on the surface of the nickel or zinc ferrites were then prepared by hydrolysis of titanium chloride in the presence of ferrite nanoparticles. The optimal synthetic conditions included pH values of 8-9 and sintering at 673-773 K. The obtained ferrites or TiO₂/Ni-, Zn-ferrites samples were characterized by XRD, FE-SEM, and TEM techniques. The results indicated that the size of nanoshell of TiO₂ with anatase structure was 20-50 nm. X-ray absorption near edge structure (XANES) or extended X-ray absorption fine structure (EXAFS) was performed to identify the fine structures and oxidation state of Ni- or Zn-ferrites and anatase-typed TiO₂ coated ferrites nanoparticles. By using XANES spectra, Ni- or Zn-ferrites may exhibit an absorbance feature for the 1s to 3d transition can reveal the occupation of tetrahedral sites within the lattice, it showed that Ni ferrite had the same reverse spinel structure with Fe₃O₄ and the valence of hydrogenated ferrites were between 2 and 3. When the sintered temperature arrive 723 K, the nanoshell of TiO₂ would transform from amorphous to anatase, and the nanoshell of TiO₂ photocatalysts were all Ti (IV). The EXAFS data revealed that the nanoshell TiO₂ photocatalyst had first, second shell of Ti-O, and third shell of Ti-Ti with bond distances of 1.96 ± 0.01, 2.01 ± 0.01, and 3.05 ± 0.01 Å, respectively.

9:00am **SE-WeM4 The Substrate Effect on the TiO₂ Photocatalytic Thin Films.** *J.-Y. Ciou, S.-J. Lin, M.-K. Wei, M.S. Wong, National Dong Hwa University, Taiwan*

Titanium dioxide thin films were deposited on two different substrates of p-typed Si (100) and LaAlO₃ (001) single-crystal in a pulsed laser deposition system via KrF excimer laser ablation of a pure titania target of 99.95% purity. The substrate temperature and oxygen partial pressure were varied at 400-600°C and 0-9.3 Pa, respectively. The mismatch of lattice constant between anatase TiO₂ and LaAlO₃ (001) is less than 0.2%, but that between anatase TiO₂ and Si (100) is much larger. TiO₂ films deposited on LaAlO₃ have much better crystallinity than those deposited on Si. The films on LaAlO₃ also revealed strong preferred orientation, but the films on Si did not. At all substrate temperatures the films on LaAlO₃ compose of only a single anatase phase, while the film on Si composes of mixed phases of anatase and rutile at 600°C, but the crystallinity of the films on both substrates increases with rising substrate temperature. For the surface morphology, the films on LaAlO₃ show mosaic structures of epitaxial growth, but the films on Si are polycrystalline in nature with smaller random grains. The photocatalytic performance is determined by the relative amounts of precipitated silver aggregates on the deposited films from AgNO₃ aqueous solution under illumination of ultraviolet or visible light. The most precipitated silver aggregates were found at the steps or grain edges on the film surfaces. At lower substrate temperatures, the film deposited on Si has better catalytic performance than those deposited on LaAlO₃. It may be due to much more grain edges of the films on Si. At higher substrate temperatures, however, the film deposited on LaAlO₃ has better performance than the film on Si, which may be due to pure anatase phase with better crystallinity in the film on LaAlO₃.

9:20am **SE-WeM5 Structuring Highly Active, Nano-scale Photocatalytic Films using Reactive Sputtering.** *K.A. Gray, L. Chen, M.E. Graham, G. Li, Northwestern University*

INVITED

Since Fujishima and Honda developed the photoelectrochemical cell for H₂O splitting in 1972, heterogeneous photocatalysis has attracted much attention. TiO₂ is among the most extensively studied semiconductor photocatalysts. It is chemically and biologically inert, photocatalytically stable, commercially available, and inexpensive. In the past three 30 years, most of the effort in the photocatalytic field has been focused on energy and environmental applications, which require materials with the following properties: (1) hindered charge recombination and improved photocatalytic

efficiency; (2) targeted reactivity and selectivity that match band energies to the desired reaction, and (3) extended photoresponse into the visible light region. Masakazu Anpo first introduced the notion of "second-generation" TiO₂ photocatalysts, which can absorb visible light and also operate effectively as photocatalysts. We hypothesize that the solid-solid interface in TiO₂-based nanocomposites is key to overcoming these three challenges and are a promising candidates for 2nd-generation photocatalysts. Recent findings in our laboratory and others throughout the world reveal a number of surprising insights as to why TiO₂ nanocomposites tend to display higher photoactivity than pure-phases and point to the critical role of the solid-solid interface as the location of catalytic "hot spots". Yet, efforts to probe the role of the solid-solid interface in photocatalytic activity are stymied by an inability to synthesize under sufficiently controlled conditions and in sufficient quantities the "interface", which would then allow structural characterization and functional interrogation. Advances in photocatalyst synthesis using sputtering technologies promise to revolutionize our ability to engineer the solid-solid interface at the molecular level and thus, to fabricate photoactive nanostructured composite materials having high densities of "defects" designed for energy harvesting and storage. We prepare highly active TiO₂ nanocomposites using chemical and physical methods in our laboratory. By varying key fabrication conditions (target power, substrate bias, oxygen partial pressure, and deposition angle) in reactive DC magnetron sputtering, we synthesize TiO₂ thin films with different microstructures. This paper will report the synthesis and characterization of photocatalytic films and their use to generate solar fuels and oxidize gas phase contaminants.

10:40am **SE-WeM9 Photocatalytic Coating: Present Situation and Future Direction.** A. Fujishima, Kanagawa Academy of Science and Technology, Japan **INVITED**

The recent decade has witnessed the birth and development of photocatalytic coatings.¹ In the early 1990s, we proposed the concept of photocatalytic thin film coatings for deodorizing, self-cleaning, and antibacterial uses.² In 1997, we reported the photo-induced superhydrophilic effect of TiO₂ surface,³ and proposed the concept of antifogging surface, and the concept of self-cleaning based on the photocatalytic and superhydrophilic actions of TiO₂.⁴ Nowadays, these concepts have all born out real products. In Japan, self-cleaning building materials have covered tiles, glass, coatings, polymer films, aluminum sidewalls, and so on. Air-cleaners, equipped with photocatalytic filters, have got recognition of consumers. Antibacterial tiles have been used in hospitals, hotels, and restaurants. Recent news is the carriage of high-speed railway system of Japan will be coated with photocatalytic self-cleaning coating. Besides these matured techniques, we are now studying new applications of photocatalytic coatings; these include anticorrosion coatings,⁵ multichromic coatings,⁶ low reflection self-cleaning coatings,⁷ and heat-transfer applications,² etc. We are also thinking of the development visible-light responsive photocatalytic coatings and the standardization of photocatalytic coatings.¹ Our photocatalyst museum, which started three years ago, provides exhibition for companies' products as well as information service for consumers and researchers.

¹ A. Fujishima, X. Zhang, C. R. Chimie 9 (2006) 750.

² K. Hashimoto, H. Irie, A. Fujishima, Jpn. J. Appl. Phys. 44(2005) 8269.

³ R. Wang, K. Hashimoto, A. Fujishima, et al. Nature 388 (1997) 431.

⁴ R. Wang, K. Hashimoto, A. Fujishima, et al. Adv. Mater. 10 (1998) 135.

⁵ T. Tatsuma, S. Saitoh, Y. Ohko, A. Fujishima, Chem. Mater. 13 (2001) 2838.

⁶ Y. Ohko, T. Tatsuma, A. Fujishima et al., Nature Mater. 2 (2003) 29.

⁷ X.-T. Zhang, A. Fujishima et al., J. Phys. Chem. B 110 (2006) 25142.

11:20am **SE-WeM11 Composition-Spread Carbon-Incorporated Titania Films for Visible Light Photocatalysis.** C.W. Weng, P.W. Chou, K.K. Rao, M.S. Wong, National Dong Hwa University, Taiwan

We adopted a combinatorial approach to develop a series of carbon-incorporated titania (TiO_xC_y) films titania films with composition spread up to 40 at.% of carbon. The films were deposited on silicon and quartz substrates by co-sputtering a metallic titanium target and a graphite target simultaneously onto a stationary long-strip of substrate in a gas mixture of argon and oxygen. The location of substrates in relation to targets and the power of targets are found to be very crucial for the desired result. As the carbon content increases, the film structure and crystallinity transform from anatase to amorphous-like phase and its morphologies and microstructures change from rough surface of columnar grains to smooth surface of nanocomposite. The carbon is present both in the form of substituted Ti-C bonds in anatase grains as well as free graphitic along grain boundaries or in matrix. With increasing carbon content, the film optical absorption in visible region decreases first and then increase, while the film optical bandgap energy varies from 2.6 up to 3.2, and then descends to 2.5 eV. On photocatalysis under visible light, the film with about ~10% carbon exhibits the largest photoreduction of silver-ions to form Ag particles and nano-wires, while the film of the best anatase crystallinity with about 3 at% of carbon has the most degradation of methylene blue. The content and the

nature of carbon as well as the titania crystallinity dominate the visible-light induced photocatalytic activity of the TiO_xC_y films.

11:40am **SE-WeM12 High Rate Deposition of TiO₂ Films by using Two Sputtering Sources.** Y. Hoshi, O. Kamiya, T. Sakai, Tokyo Polytechnic University, Japan

Deposition of TiO₂ films by reactive sputtering of titanium metal target has been reported by many researchers. However, it is very difficult to realize the high rate deposition of TiO₂ films by conventional reactive sputtering, since the surface of the target is covered with titanium oxide layer, which leads to a significant reduction of the sputtering yield of titanium atoms. If we can suppress the formation of titanium oxide layer on the target surface and promote the oxidization of titanium atoms on the film surface during sputtering, high rate deposition of titanium oxide films can be realized by using the reactive sputtering method. In this point of view, we designed a new sputter-deposition system with two sputtering sources. One source, 33mm diameter magnetron sputtering source, is used as the source of titanium atom, and works at the metal mode sputtering condition and supplies the titanium atoms to the substrate. The other source of 100 mm in diameter works as an oxygen radical source and supplies oxygen radicals to the substrate surface to promote the oxidization of the titanium atoms during film deposition. Each sputtering sources are separated from deposition chamber and Ar gas and oxygen gas was introduced through the 33mm sputtering source and 100mm source, respectively. When Ar gas flow rate is fixed at 50 sccm and oxygen gas flow rate was below 8mTorr, the 33mm titanium sputtering source works in metal mode at a discharge current of 1 A. Whereas, the 100 mm oxygen radical source works in an oxide mode at an oxygen gas flow rate below 8 sccm and the sputtering current below 1.5 A. In this deposition method, most of the titanium atoms deposited on the substrate are supplied from the 33 mm sputtering source, and oxygen radicals supplied from 100mm source promote the oxidization of titanium atoms on the substrate. As a result, deposition rate more than 30 nm/min can be easily realized for the deposition of transparent TiO₂ film with transmittance above 90%. These results indicate that the reactive sputtering method with two sputtering sources is effective to realize a high rate deposition of TiO₂ films.

12:00pm **SE-WeM13 Enhancement of Hydrophilicity and Photocatalytic Activities of Nanocrystalline TiO₂ Thin Film Doped with Ruthenium.** R.R. Pandey, K.K. Saini, M. Dhayal, Chanderkant, S.C. Jain, National Physical Laboratory, India, M. Singh, University of Delhi, India

In this study Ru⁺³ ion doped nanocrystalline TiO₂ thin films has been fabricated using dip-coating technique on glass substrates. Surface structure and chemistry of the films was characterized using X-ray diffraction, transmission / scanning electron microscopy, UV-visible spectroscopy, X-ray photoelectron spectroscopy and FTIR. The Ru⁺³ ion doping in the film have significant influence on the morphology and surface chemistry. These nanocrystalline films have shown improved activity on the oxidation of organic pollutants possibly due to enhanced surface area with more active site in presence of Ru⁺³.

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