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RESEARCH NEWS FOR IMMEDIATE RELEASE

Hiroshima University Research on Thin Films of Nanoparticles Wins Award

By Caitlin E. Devor
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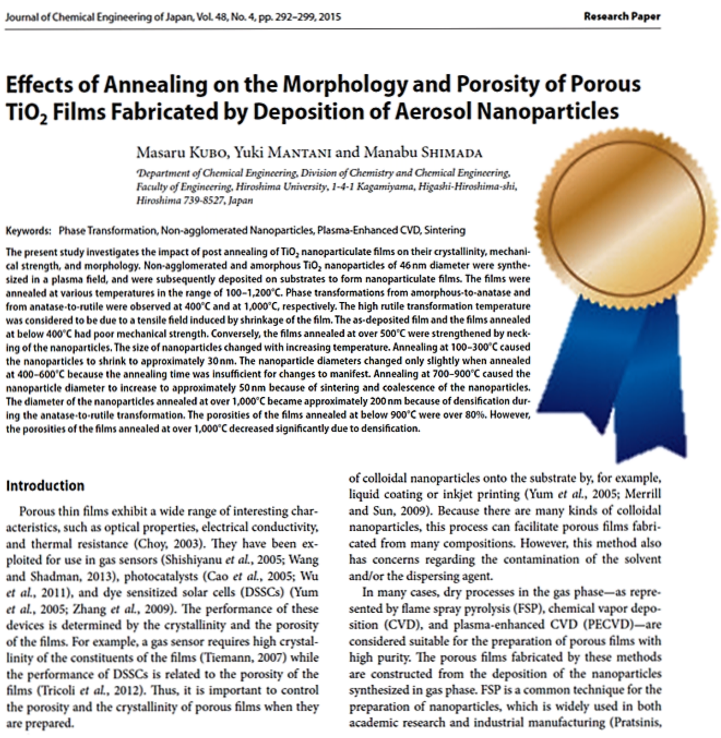
Results from Hiroshima University researchers earned an Outstanding Paper award from the Journal of Chemical Engineering of Japan. The research was completed by Assistant Professor Masaru Kubo, Yuki Mantani, and Professor Manabu Shimada. Mantani was a Masters student at the time of the research.



Journal of Chemical Engineering of Japan, Vol. 48, No. 4, pp. 292–299, 2015 **Research Paper**

Effects of Annealing on the Morphology and Porosity of Porous TiO_2 Films Fabricated by Deposition of Aerosol Nanoparticles

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The present study investigates the impact of post annealing of TiO_2 nanoparticulate films on their crystallinity, mechanical strength, and morphology. Non-agglomerated and amorphous TiO_2 nanoparticles of 46 nm diameter were synthesized in a plasma field, and were subsequently deposited on substrates to form nanoparticulate films. The films were annealed at various temperatures in the range of 100–1,200°C. Phase transformations from amorphous-to-anatase and from anatase-to-rutile were observed at 400°C and at 1,000°C, respectively. The high rutile transformation temperature was considered to be due to a tensile field induced by shrinkage of the film. The as-deposited film and the films annealed at below 400°C had poor mechanical strength. Conversely, the films annealed at over 500°C were strengthened by necking of the nanoparticles. The size of nanoparticles changed with increasing temperature. Annealing at 100–300°C caused the nanoparticles to shrink to approximately 30 nm. The nanoparticle diameters changed only slightly when annealed at 400–600°C because the annealing time was insufficient for changes to manifest. Annealing at 700–900°C caused the nanoparticle diameter to increase to approximately 50 nm because of sintering and coalescence of the nanoparticles. The diameter of the nanoparticles annealed at over 1,000°C became approximately 200 nm because of densification during the anatase-to-rutile transformation. The porosities of the films annealed at below 900°C were over 80%. However, the porosities of the films annealed at over 1,000°C decreased significantly due to densification.

Introduction

Porous thin films exhibit a wide range of interesting characteristics, such as optical properties, electrical conductivity, and thermal resistance (Choy, 2003). They have been exploited for use in gas sensors (Shishiyanu *et al.*, 2005; Wang and Shadman, 2013), photocatalysts (Cao *et al.*, 2005; Wu *et al.*, 2011), and dye sensitized solar cells (DSSCs) (Yum *et al.*, 2005; Zhang *et al.*, 2009). The performance of these devices is determined by the crystallinity and the porosity of the films. For example, a gas sensor requires high crystallinity of the constituents of the films (Tiemann, 2007) while the performance of DSSCs is related to the porosity of the films (Tricoli *et al.*, 2012). Thus, it is important to control the porosity and the crystallinity of porous films when they are prepared.

of colloidal nanoparticles onto the substrate by, for example, liquid coating or inkjet printing (Yum *et al.*, 2005; Merrill and Sun, 2009). Because there are many kinds of colloidal nanoparticles, this process can facilitate porous films fabricated from many compositions. However, this method also has concerns regarding the contamination of the solvent and/or the dispersing agent.

In many cases, dry processes in the gas phase—as represented by flame spray pyrolysis (FSP), chemical vapor deposition (CVD), and plasma-enhanced CVD (PECVD)—are considered suitable for the preparation of porous films with high purity. The porous films fabricated by these methods are constructed from the deposition of the nanoparticles synthesized in gas phase. FSP is a common technique for the preparation of nanoparticles, which is widely used in both academic research and industrial manufacturing (Pratsinis,

“Using our method, individual particles fall like snow,” said Professor Manabu Shimada, a chemical engineer in the Graduate School of Engineering. This project attracted positive attention from the scientific community previously; in 2013, Assistant Professor Masaru Kubo won a best poster presentation honor at a scientific conference in Sydney, Australia.

“I believe our results get this attention because they are relevant to so many other researchers. We systematically identified the basics of how aerosolized nanoparticles move and the parameters to fine-tune their motion. These techniques are applicable to many fields and applications using nanoparticles, and also for scientists who want to remove unwanted dust particles from ultraclean or sterile environments,” said Shimada.

The “snow fall” is noteworthy because the particles, only 50 nanometers in diameter, land individually on the base of a thin film. Shimada’s research group uses specialized equipment, including a custom built plasma reactor and deposition chamber, to aerosolize the particles and then control the flow rate, the number of particles, and even electric fields to build a uniform layer of particles about 20 micrometers tall. Other techniques cause the nanoparticles to clump together before they are deposited on the base, altering the final physical and chemical characteristics of the film.

The aerosol technique of the Hiroshima University team allows researchers to build thin, porous films with very large surface areas proportional to the size of the base. The researchers have already used their technique with particles from 50 to 5 nanometers in diameter. The total surface area of the film can be even further increased by using nanoparticles of smaller sizes. Large surface areas give the films increased sensitivity or functional capacity.

For the Outstanding Paper winning project, Shimada and his team worked with pure titanium dioxide, a ceramic material used in applications ranging from solar power cells to white food coloring. Thin, porous films of titanium dioxide could be used to build new types of solar cell electrodes because of the material's photoelectric properties, or could be used to make grime-resistant building materials because titanium dioxide can decompose other substances.

The major focus of the project was identifying how different heat treatments can alter the final crystal structure of titanium dioxide nanoparticles. Different crystal structures have different chemical and physical properties, giving the final thin films different potential applications.

"The most difficult part of this work was building the approximately 50 films we needed for the experiments. The films needed to be identical so we could accurately compare the different heat treatments," said Kubo.

Shimada agreed, saying, "Yuki Mantani built most of the films while he was a student in our lab. He was a very good student! It takes much dedication and patience to do that part of the work."

Since publishing their award-winning research paper in April 2015, the research team has started investigating how to make composite films (films made with more than one material) using their aerosolized nanoparticle method.

"Now we are combining titanium dioxide and metal particles, so it is like building films with black and white snow. Precisely made composite films could have even more diverse applications because of the combination of different types of nanoparticles," said Shimada.

"We look forward to continuing to refine our nanoparticle films with collaborators at the Hiroshima University Center for Research on Environmentally Friendly Smart Materials to use their expertise in developing innovative functional materials," said Shimada.

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The award-winning academic research article is available with the following citation information:
Kubo M, Mantani Y, Shimada M. Effects of Annealing on the Morphology and Porosity of Porous TiO_2 Films Fabricated by Deposition of Aerosol Nanoparticles. Journal of Chemical Engineering of Japan, Vol. 48, No. 4, pp. 292–299 (2015). DOI: 10.1252/jcej.14we197.

Full citation of the article detailing the merits of the 2015 Outstanding Paper Award winners:
Itaya Y, Shimada M. JCEJ Outstanding Paper Award of 2015. Journal of Chemical Engineering of Japan, Vol. 49, No. 8, pp. 735-736 (2016). DOI: 10.1252/jcej.opa2015.

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Their English webpage will soon be accessible at this address: http://smartm.hiroshima-u.ac.jp/index_en.html

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