Controlling Transmittance of Visible Light by the Incident Light Angle Using Needle-like TiO_2 Particle Arrayed Composite Films

Hidetoshi Miyazaki (Corresponding author), Masato Miyoshi, Takaaki Otsuka & Shin-ichi Kikitsu
Department of Material Science, Interdisciplinary Faculty of Science and Engineering
Shimane University, 1060, Nishikawatsu, Matsue, Shimane, 690-8504, Japan
E-mail: miya@riko.shimane-u.ac.jp

Hisao Suzuki
Graduate School of Science and Technology, Shizuoka University
3-5-1, Johoku, hamamatsu, Shizuoka 432-8561, Japan

Toshitaka Ota
Ceramic Research Laboratory, Nagoya Institute of Technology
10-6-29, Asahigaoka, Tajimi, Gifu, 507-0071, Japan

Received: November 18, 2011 Accepted: December 1, 2011 Published: January 1, 2012
doi:10.5539/jmsr.v1n1p123 URL: http://dx.doi.org/10.5539/jmsr.v1n1p123

Abstract

Composite films with an array of needle-like TiO_2 particles in urethane resin matrix were fabricated by applying a 1 kHz AC bias with a square wave. In the resulting film, needle-like TiO_2 particles were arrayed in the composite films in a direction normal to the film surface. The composite films showed angular dependence of transmittance in the visible-NIR range. For the composite film with arrayed 0.1 vol% TiO_2 needle-like particles, the transmittance changed by 16.6% between 0° and 60° at a wavelength of 500 nm.

Keywords: Needle-like particle, Arraying, TiO_2, Transmittance, Angular dependence

1. Introduction

Many energy-efficient window materials have been investigated, including heat mirror materials (Granqvist, 2007; Shanthi et al., 1982; Jie C et al., 1998), thermochromic materials (Granqvist, 2007; Miyazaki & Yasui, 2006; Takahashi, I. Hibino & M. Kudo, 1996), and photochromic materials (Granqvist, 2007; Armlstead & Stookey, 1964; Scarminio & Gorenstein, 1997). These observations imply that the level of sunlight transmitted through the window materials is dependent on the environmental conditions. Therefore, energy efficiency can be improved using these window materials.

Energy efficiency in an office can be improved between summer and winter by controlling transmittance with light angles, as transmittance changes depending on the angle of irradiated light. Thus, there is a great deal of interest in angular selective materials for the development of new windows, and can provide energy-efficient properties to blinds, glazing, and domes. Angularly dependent transmittance films have been reported, which were formed by multilayer coatings (Karlsson et al., 2001; Rubin & Rottkay, 1999) and Cr-base(Palmer et al., 1996; Wbise et al., 1995) or Ti-oxide base (Bellac et al., 1995, 6145-6151; 94-95) columnar structure films. On the other hand, we have reported fabrication of arrayed needle-like TiO_2 particles by applying AC bias with a low frequency of 0.1 Hz, and described the weak transmittance anisotropy in the visible-NIR wavelength region of these materials (Miyazaki et al., 2011; Kikitsu et al., 2011).

In this study, arraying of needle-like TiO_2 particles was carried out at high frequency with a square wave. Figure 1 shows a schematic illustration of a sine wave and a square wave. A square wave electric field is more effective for applying a bias to materials than a sine wave. Thus, the arraying of needle-like particles was carried out under a square wave electrical field in the present study. Furthermore, the transmittance anisotropy of the resulting TiO_2−resin composite film was examined at various incident light angles.

2. Experimental Procedure

Needle-like TiO_2 particles (FT-1000, 1.68 μm length, 0.13 μm in diameter; Ishihara Sangyo, Osaka, Japan) were used as the filler, and liquid urethane polymer (APR M-40; Asahi Kasei Chemicals Corp., Tokyo, Japan), which can be cured by UV irradiation, was used as the matrix. An SEM image of the TiO_2 particles was shown in figure 2. The composites were prepared as follows. The liquid polymer, TiO_2 particles and ethanol (using 0.1 vol% to lower the viscosity of the resin) were mixed at TiO_2 mixing ratios of 0.1 and 0.5 vol%. The mixture was degassed under a pressure of 1 kPa for 1 h to remove the dissolved air introduced during the mixing process. The mixed precursor slurry was placed between flat ITO glasses (with a sheet resistance of about 10 Ω/square), controlling the precursor film thickness to 80 μm. These procedures were carried out in a dark room to prevent exposure of the precursor film to room light. Electrical bias was then applied to the precursor composite at 1 kHz (square wave) with a bias voltage of ±10 V using a universal source (HP-3245A; Agilent Technologies, Santa Clara, CA). After applying bias to the precursor composite, the composite was cured by irradiation with 1-kW low-pressure Hg lamp (UV-visible light) and TiO_2−urethane polymer composite films were obtained. The resulting composite films were removed from the ITO glasses.

The microstructure of the composite, which was sliced normal to the film surface, was evaluated by scanning electron microscopy (SEM) (Hitachi S-2100; Hitachi, Tokyo, Japan). The optical properties of the composite films were measured using a Shimadzu UV-1600 spectrophotometer (wavelength range 200 – 1100 nm) (Shimadzu. Kyoto, Japan). Furthermore, the angular dependence of transmittance was measured from 0° to 60° at 10° intervals by rotating the film, where the measured angle was between the direction of irradiated light and a line normal to the composite film surface.

3. Results and Discussion

The composite films were fabricated with a TiO_2 content of 0.5 vol% with application of 1-kHz AC bias for 0, 30, or 60 min. Figure 3 shows SEM images of the composite films fabricated under the conditions described above. For all films, TiO_2 particles did not aggregate and were dispersed homogeneously in the composite films. TiO_2 particles in the composite film without application of bias showed a random array, while those in composite films with bias applied for 30 and 60 min showed slight arraying or arraying of the needle-like particles normal to the film surface, respectively. In a previous investigation (Kikitsu et al., 2011), the arraying of needle-like particles took over 4 h under conditions of AC 10 V, 0.1 Hz, with a sine wave. Therefore, to array needle-like TiO_2 particles, AC bias with high frequency and a square wave was more effective than that at low frequency with a sine wave.

Figure 4 shows the visible-NIR transmittance of the composite films with different film angles from 0° to 60° normal to the irradiated light. For all charts, discontinuous points were observed at 365 nm, and these points represented the change in light source from a tungsten iodide lamp to a D_2 lamp. Little angular dependence of transmittance was observed for films without application of bias, and slight angular dependence was observed due to the difference in path distance between angles of 0° and 60°. For composite film with bias applied for 30 min, the transmittance in the visible light region (400−700 nm) changed at angles between 0° and 60°. Furthermore, the transmittance of the sample with bias applied for 1 h exhibited a large angular dependence between 0° and 60°. For the composite film with bias applied for 1 h, 10.0% of the transmittance changed between 0° and 60° at a wavelength of 500 nm. These results reflected the angular dependence of transmittance was due to the arraying of needle-like particles in the composite films. In previous investigations (Miyazaki et al., 2011; Kikitsu et al., 2011), the composite films with arrayed needle-like TiO_2 particles were fabricated with a low frequency of 0.1 Hz. For these composite films, [14,15)] TiO_2 particles deposited close to the film surface, and the transmittance were not high at wavelengths in the region from 200 to 1100 nm because of scattering by segregated TiO_2 particles at the film surface. Therefore, the results indicated that an AC bias with high frequency was effective for fabrication of composite films with arrayed needle-like TiO_2 particles.

The composite films were fabricated with a low TiO_2 content of 0.1 vol%, with application of bias at 1 kHz for 1 h. Figure 5 shows the visible-NIR transmittance of the composite film with changing film angle from 0° to 60° normal to the irradiated light. The inset photographs indicated that the film was (a) placed parallel and (b) tilted 60° from the surface. The film exhibited a large degree of angular dependence between 0° and 60° in the visible light wavelength region. The transmittance changed by 16.6% between 0° and 60° at a wavelength of 500 nm, and this changed by 0.8% between 0° and 60° at a wavelength of 1100 nm.

From the inset photographs in Fig. 5, the letters written on the paper can be seen clearly beyond the film placed parallel to the paper. On the other hand, the letters written on the paper could not be seen beyond the film tilted

60° from the paper. These results also indicated angular dependence in this wavelength region.

The refractive indexes n_p and n_s of TiO_2 (rutile) are 3.03 and 2.71 at 500 nm, and 2.74 and 2.48 at 1100 nm (Palik, 1997). The refractive indexes in the small wavelength region were higher than those in the large wavelength region. This is because TiO_2 particles cause interaction with the light of shorter wavelength, and the transmittance of the film with an angle of 60° was greater at a wavelength of 500 nm than that at 1100 nm (see Fig. 5).

4. Conclusion

In summary, needle-like TiO_2 particles were arrayed normal to the film surface by applying an AC bias of ± 10 V with a square wave to the precursor slurry composite for 1 h. The resulting composite film with arrayed TiO_2 particles showed angular dependence of transmittance. For the film with a TiO_2 content of 0.1%, the transmittance was 20% higher for an angle of 0° to the incident light compared to that for 60°. This study suggested an improvement in the energy efficiency of the material through the angular dependence of transmittance in the visible-near-infrared range.

References

Armlstead, W. H., & Stookey, S. D. (1964). Photochromic silicate glasses sensitized by silver halides. *Science, 144,* 150-154.

Bellac, D. Niklasson, G. A., & Granqvist, C. G. (1995). Angular selectivity of the infrared transmittance through obliquely sputter-deposited Ti-oxide-based films. *Thin Solid Films, 266,* 94-95. http://dx.doi.org/10.1016/0040-6090(95)06813-9

Bellac, D. Niklasson, G. A., & Granqvist, C. G. (1995). Angular-selective optical transmittance of anisotropic inhomogeneous Cr-based films made by sputtering. *J. Appl. Phys, 77,* 6145-6151. http://dx.doi.org/10.1063/1.359140

Granqvist, C. G. (2007). Transparent conductors as solar energy materials: A panoramic review. *Sol. Energy Mater. Sol. Cells, 91,* 1529-1598. http://dx.doi.org/10.1016/j.solmat.2007.04.031

Jie, C., Shi, G. X., & Fang, H.X. (1998). Single-layer heat mirror films and an improved method for evaluation of its optical and radiative properties in infrared. *Sol. Energy Mater. Sol. Cells, 55,* 323-329. http://dx.doi.org/10.1016/S0927-0248(98)00094-4

Karlsson, J., Rubin, M., & Roos, A. (2001). Evaluation of predictive models for the angle-dependent total solar energy transmittance of glazing materials. *Sol. Energy, 71,* 23-31. http://dx.doi.org/10.1016/S0038-092X(01)00024-X

Kikitsu, S., Otsuka, T., Miyazaki, H., Suzuki, H., & Ota, T. (2011) Arraying needle-like TiO_2 particles in a composite film by applying ac bias and its transmittance anisotropy. *Key Engineer. Mater., 484,* 177-182. http://dx.doi.org/10.4028/www.scientific.net/KEM.484.177

Miyazaki, H., Kikitsu, S., Ota, T., & Suzuki, H. (2011). Arraying needle-like TiO2 particles in a composite film by applying ac bias and its transmittance anisotropy. *Adv. Pow, Technol, 22,* 544-547. http://dx.doi.org/10.1016/j.apt.2010.10.017

Miyazaki, H., & Yasui, I. (2006). Effect of buffer layer on VOx film fabrication by reactive RF sputtering. *Appl. Surf. Sci., 252,* 8367-8370. http://dx.doi.org/10.1016/j.apsusc.2005.11.040

Palik, Edward. (1997). *Handbook of Optical Constants of Solids.* Academic Press, Inc.

Palmer, S., Mbise, G. W., Niklasson, G. A., & Granqvist, C. G. (1996). Angular selective optical properties of thin films: Measurement of polar and azimuthal transmittance. *Sol. Energy Mater. Sol. Cells, 44,* 397-403. http://dx.doi.org/10.1016/S0927-0248(95)00176-X

Rubin, M., Powles, R., & Rottkay, K. (1999). Evaluation of predictive models for the angle-dependent total solar energy transmittance of glazing materials. *Sol. Energy, 66,* 267-276. http://dx.doi.org/10.1016/S0038-092X(99)00029-8

Scarminio, J., Loureno, A., & Gorenstein, A. (1997). Electrochromism and photochromism in amorphous molybdenum oxide films. *Thin Solid Films, 302,* 66-70. http://dx.doi.org/10.1016/S0040-6090(96)09539-9

Shanthi, E., Banerjee, A., Dutta, V., & Chopra, K. L. (1982). Electrical and optical properties of tin oxide films doped with F and (Sb+F). *J. Appl. Phys., 53,* 1615-1621. http://dx.doi.org/10.1063/1.330619

Takahashi, I., Hibino, M., & Kudo, T. (1996). Thermochromic V1-xWxO2 Thin Films Prepared by Wet Coating

Using Polyvanadate Solutions. *Jpn. J. Appl. Phys., 35,* L438-440. http://dx.doi.org/10.1143/JJAP.35.L438

Wbise, G. W., Niklasson, G. A., & Granqvist, C. G. (1995). Angular-selective optical transmittance through obliquely evaporated Cr films: Experiments and theory. *J. Appl. Phys., 77,* 2816-2818. http://dx.doi.org/10.1063/1.363476

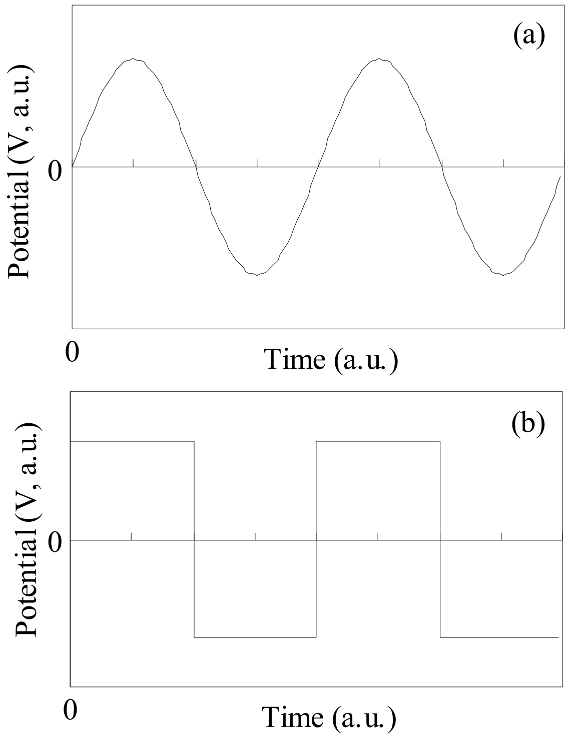


Figure 1. Schematic illustrations of (a) a sine wave and (b) a square wave

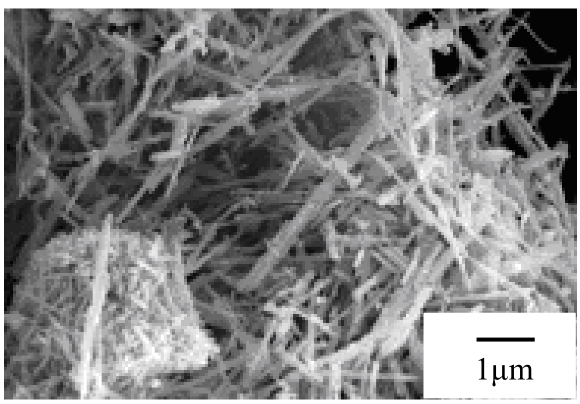


Figure 2. An SEM photograph of Needle-like TiO_2 particles

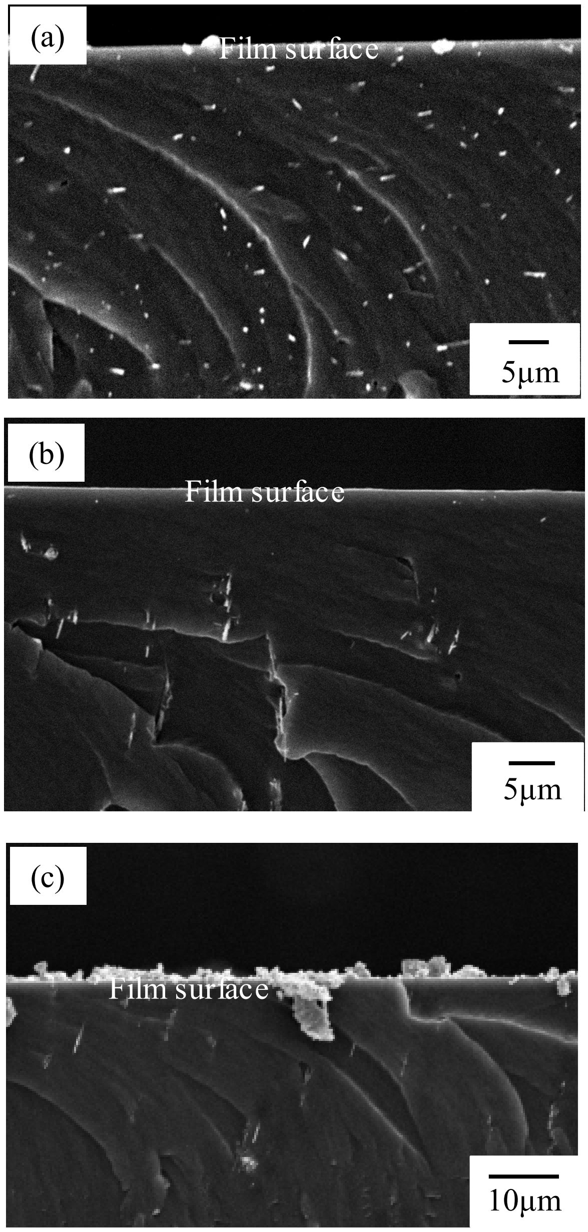
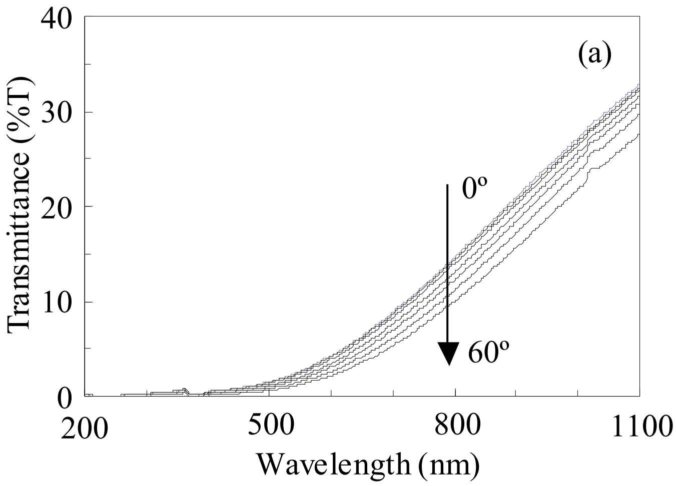
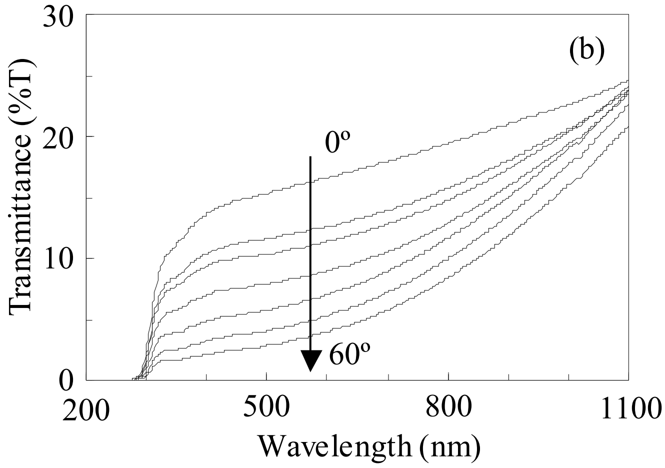


Figure 3. SEM photographs of the resulting composite films, to which an AC bias of ±10 V was applied before curing for (a) 0 min (no applied bias), (b) 30 min, and (c) 60 min





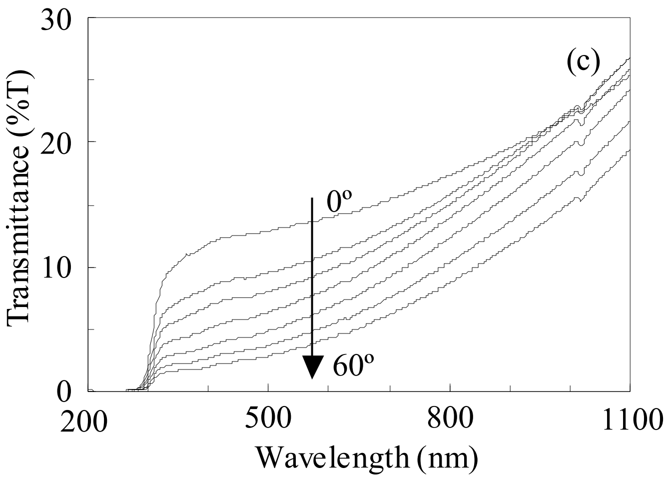


Figure 4. Transmittance for composite films at various incident angles where the bias was applied for (a) 0 min, (b) 30 min, and (c) 60 min at film fabrication

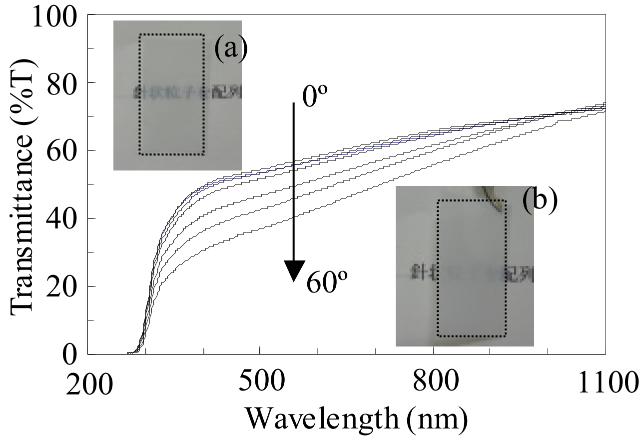


Figure 5. Transmittance for the composite films with TiO_2 content of 0.1%. The film was fabricated at 0.1 Hz, square wave, 1 h. The inset photographs show the film (a) placed parallel and (b) tilted by 60° from the paper surface