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Structural colors from TiO_2/SiO_2 multilayer flakes prepared by sol–gel process

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ABSTRACT

Preparation of TiO_2/SiO_2 multilayer flakes and their application to decorative powders were investigated. In contrast to conventional products prepared through the multicoating of core platelets, the coreless TiO_2/SiO_2 multilayer flakes were prepared by detaching multilayer films from their substrates. These flakes exhibited structural colors, when the optical path length of both the TiO_2 and SiO_2 layers are adjusted to be one fourth of the wavelength of visible light. A multicoating of more than five layers resulted in the propagation of cracks, which prevented the preparation of thick flakes. Paint films fabricated using the multilayer flakes and acrylic resins showed reflectance spectra that were comparable with those obtained for multicoatings on substrates.

1. Introduction

Over the past few decades, the sol–gel technique has been successfully applied to the fabrication of optical products such as lenses, mirrors and filters [1,2]. This technique has reduced production costs in comparison with other methods such as high-temperature glass molding or vapor deposition. For optical applications, multicoatings of oxide layers are often important. When the optical path length of the coating thickness is near the wavelength range of visible light, a multicoated film exhibits a specific glossy color, called a structural color. This is caused by optical interference, the reflected color depending on the interference conditions, namely the refractive indices of the materials, the thickness of the layers and the angle of observation. Structural colors can be observed in many natural materials such as beetle outer shells, butterfly wings, feathers and seashells [3].

Particulates that have an internal multilayer structure can also exhibit a structural color. They can be used as optical interference pigments for the decoration of industrial products. Pearlescent effect pigments, for example, have been widely used in cosmetics and automobile paints. Although there are few publications that describe the preparation of these particles, pigment companies report that these interference pigments consist of multicoatings on core materials such as mica or glass flakes. The incorporation of cores, however, causes restrictions in the breadth of application. Firstly, cores usually have a thickness of at least one micron, which accounts for most of the total thickness. Secondly, the nature of the core material determines the physical and chemical properties of the particles, for example, heat resistance, corrosion resistance and hardness.

In our previous work, we developed a novel sol–gel route for the synthesis of multilayered flakes without cores [4]. An advantage of this process is that we can arbitrarily set the sequence of material accumulation and even create flakes with a different chemical makeup on each side. In this paper, this process is applied to the synthesis of interference flakes that exhibit structural colors.

2. Experimental

Sol–gel coatings of TiO_2 and SiO_2 were used as high and low refractive index layers for interference effects. The details of the preparation techniques of the multilayer films and flakes were previously described [4]. Briefly, precursors of TiO_2 and SiO_2 were prepared through the hydrolysis of ethanolic solutions of Ti-tetraisopropoxide (TTIP, Wako) and tetraethyl orthosilicate (TEOS, Tokyo Chemicals). The molar ratios of water, which was introduced as an aqueous solution of 1 M nitric acid, were adjusted to $H_2O/TTIP = 2$ and $H_2O/TEOS = 4$. Triton X-100 (Wako) was added to both solutions at a concentration of 0.1% (v/v) as a wetting agent.

For the preparation of the flakes, these precursor solutions were spin coated onto a glass substrate on which a methylcellulose (MC, Wako) layer was formed in advance. The samples were then immersed in water to dissolve the MC layer. After a few minutes,

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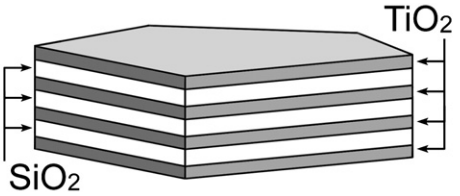

Fig. 1. Schematic of a seven-layer flake.

the oxide films were detached from the substrates, yielding thin floating flakes.

The thickness and configuration of the TiO_2/SiO_2 multilayers were designed using a numerical simulation based on the conventional theory of the optics of multiple reflections [5]. In this study, TiO_2 was used as the outermost layer, as shown in Fig. 1. Once the desired wavelength for maximum reflection, λ_R, is selected, the condition for optical interference at normal incidence can be written as:

$$4n_t t_t = 4n_s t_s = (2m+1)\lambda_R \quad (m = 0,1,2,\ldots) \tag{1}$$

where n_t and n_s are the refractive indices and t_t and t_s are the layer thicknesses of TiO_2 and SiO_2, respectively. We used the $m = 0$ order of interference to form coatings that were as thin as possible. At an arbitrary angle of incidence, n_t and n_s in eq. (1) are replaced by $n_t\cos\theta_t$ and $n_s\cos\theta_s$, where θ_t and θ_s are angles of incidence of the light ray in the TiO_2 and SiO_2 layers measured from the normal direction. This implies that for multilayers that satisfy eq. (1) the wavelength for maximum reflectance should decrease if the incident angle deviates from the normal.

A transmission spectrum for a thin film can be calculated using the Fresnel equations and the theory of multiple reflections, where the refractive index and the film thickness arise as parameters [5]. The parameters n_t and t_t for TiO_2 films were therefore determined by fitting the calculated curves to the experimental transmission spectra. In the fitting procedure, we used spectra over the wavelength range from 500 to 800 nm and ignored the effect of absorption. Borosilicate glass was employed as substrates. Because the refractive index of borosilicate glass (1.524) was near n_s, spectral fits for SiO_2 single-layer films led to estimates of n_s and t_s with poor accuracy. As an alternative, we performed a fit on SiO_2/TiO_2 double layer films to estimate n_s and t_s. In this fit, we used predetermined values of n_t and t_t for the inner TiO_2 layer.

Optical transmission and reflection spectra were measured with a fiber optic spectrometer (HR2000+, Ocean Optics), which was equipped with a reflection probe for specular reflectance measurements. This system was also equipped with an integrating sphere for diffuse reflectance measurements.

3. Results and discussion

The crystallographic properties of the TiO_2 and SiO_2 sol–gel films were examined via X-ray diffraction. It was found that the amorphous TiO_2 gels crystallized into the anatase structure at 400–500 °C, and that SiO_2 remained amorphous below 1100 °C, as previously reported by many researchers [6–8]. Fig. 2 shows the refractive indices and film thicknesses of the TiO_2 and SiO_2 sol–gel films that were spin coated at 2000 rpm onto borosilicate glass. In the figure, two sets of data are plotted as functions of the concentrations of the precursor solutions. One set of data corresponds to 1 h of heating at 140 °C (drying temperature), and the other corresponds to 1 h of heating at 450 °C (crystallizing temperature of TiO_2). It can be seen in Fig. 2 that the film thicknesses increase linearly with increasing concentration for both materials. The least squares lines cross the horizontal axis at positive concentrations, below which films cannot be deposited. These critical concentrations are possibly related to the wettability of the precursors on the substrates. As estimated from Fig. 2, relative errors in thickness control are a few percent in our process.

Thicknesses of both the TiO_2 and SiO_2 films, which were heat-treated at 140 °C, decreased by nearly thirty percent after heating at 450 °C. Simultaneously, the refractive indices of TiO_2 increased from 1.89–1.97 to 2.05–2.09, while those of SiO_2 varied little. In general, the refractive index of a material is positively correlated to its mass density [9]. The increase in the refractive index of TiO_2 can therefore be related to densification and crystallization.

It has been reported that heat treatment induces the condensation reaction in the SiO_2 gel films, but that the refractive index weakly depends on the heating temperature up to 500 °C [10]. Because the condensation process is accompanied by a significant weight loss [10,11], both the density and the refractive index of SiO_2 films may not change markedly after the heat treatment. The weight loss is probably due to the decomposition of residual alkyl groups.

The optical properties of the TiO_2/SiO_2 multilayer films were studied prior to the preparation of the flakes. Borosilicate glass was used as the substrate, and the post-heating temperature was fixed at 140 °C. The deposition conditions were determined according to the

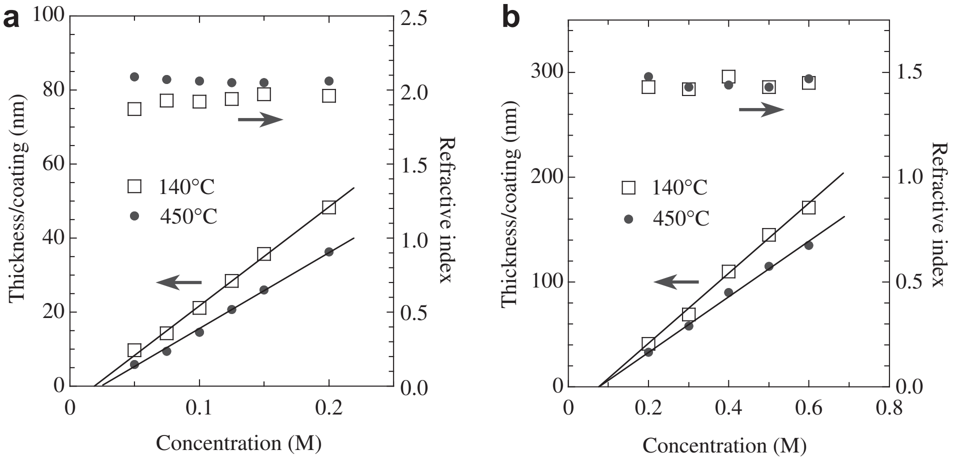

Fig. 2. Refractive indices and thicknesses of spin coated films as functions of the concentration of the precursor solutions: (a) TiO_2; (b) SiO_2. Data for post-heating at 140 and 450 °C are plotted. Least-squares fits (solid lines) are shown for the thickness data.

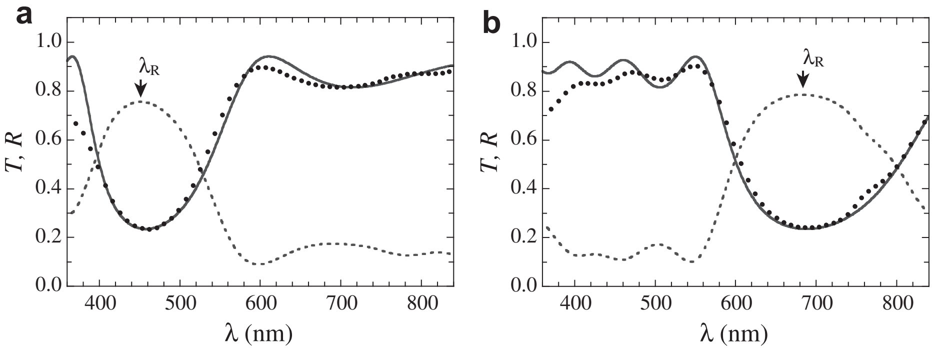

Fig. 3. Transmission (dots) and specular reflectance (broken lines) spectra of the seven-layer films: (a) $\lambda_R = 450$ nm; (b) $\lambda_R = 680$ nm. Parameters for the theoretical curves (solid lines) are described in the text.

data in Fig. 2 to ensure that the thicknesses and refractive indices in eq. (1) correspond to the desired reflection wavelength λ_R.

Fig. 3 shows transmission and reflection spectra of films with $\lambda_R = 450$ (denoted as film A) and 680 nm (film B). During the preparation of film A, the TiO_2 layer was formed by coating twice with a 0.13 M precursor solution, and the SiO_2 layer was formed by coating once with a 0.31 M precursor solution. Film B was similarly deposited using a 0.18 M TiO_2 precursor solution and a 0.43 M SiO_2 precursor solution. The total number of layers of TiO_2 and SiO_2 is seven for both films. The solid lines in Fig. 3 show the theoretical transmission spectra calculated using the Fresnel equations and the theory of multiple reflections. For this calculation, we used the refractive indices $n_t = 1.95$ and $n_s = 1.45$ and the thicknesses calculated from the experimental values of λ_R through eq. (1). The observed transmittance data in Fig. 3 roughly agree with the theoretical curves and the sum of transmittance and reflectance is close to 1, which implies that both the transparency of each layer and the flatness of the interfaces are optically sufficient.

Multilayer flakes were prepared using the same deposition conditions as for films A and B, and we also denote these flakes as A and B. The flakes A and B exhibited cyan and orange as their reflected colors, but red and light blue as their transmitted colors. These colors are consistent with the spectra from the films A and B (Fig. 3). Fig. 4 shows optical micrographs of particles from flake B. The reflection image exhibits the complementary colors (or inverted images in grayscale) of the transmission image, which is a characteristic of structural color.

The maximum number of alternate layers of TiO_2 and SiO_2 deposited in this study was nine. When the total number of layers exceeded five, cracks often appeared in the multicoated films. In the detaching process, the films broke into flakes primarily at the cracks, giving rise to disordered edges. This effect can be observed as the interference fringes in Fig. 4 on some edges of the flakes.

To demonstrate the use of the flakes in decorative paints, we examined the optical properties of paint films made from the multilayer flakes and a transparent acrylic resin. Our test paints were prepared by mixing 10 mg of the flakes with 80 mg of a 25% (w/w) commercial acrylic polymer emulsion paint. Paint films were formed on a glass slide using a spatula. Fig. 5 shows diffuse reflectance spectra of the paint films that contain flakes A and B. The thicknesses of the paint films were 16 and 19 μm for A and B, respectively. Assuming that the flakes tended to orient nearly parallel to the substrates, we estimated that the number of sheets of flakes accumulated in these thicknesses was four or five on average.

Because the angle of incidence varies with the orientation of the flakes in the resins, a misorientation of the flakes may cause both a broadening of the spectral peak and a shift to lower wavelengths for the maximum reflectance. The reflectance peaks observed in Fig. 5 are actually broader than those in Fig. 3, but a systematic shift of the peak positions to lower wavelengths was not observed. The deviation of peak positions between Figs. 3 and 5 may be primarily caused by inaccuracy in the control of the layer thickness of the flakes.

The minimum reflectances observed for the paint films of flakes A and B (Fig. 5) were significantly larger than those for the individual multilayer films (Fig. 3). Because platelets tend to align parallel to one another and the transparency of the acrylic resin is excellent, it is expected that flakes in the paint films act as parallel reflectors. Two parallel reflectors with reflectances R_a and R_b, and

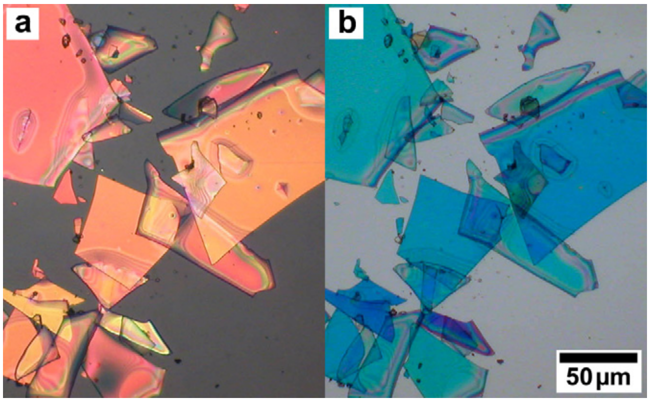

Fig. 4. Optical micrographs of individual platelets (flake B) observed by (a) reflection and (b) transmission.

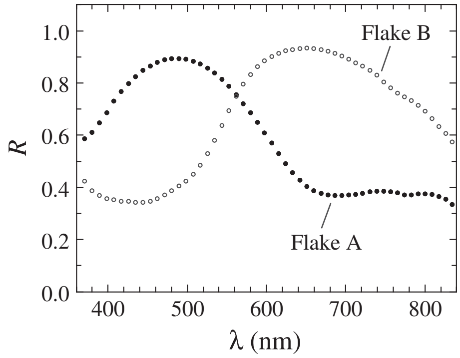

Fig. 5. Diffuse reflectance spectra of the paint films composed of multilayer flakes and acrylic resin.

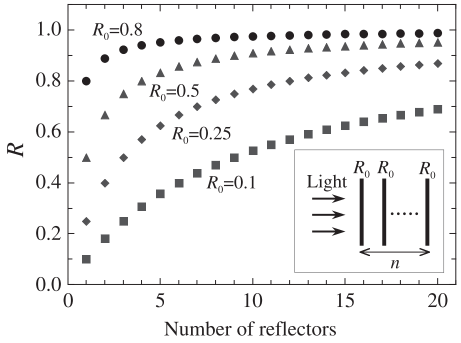

Fig. 6. Theoretical plots of reflectance from a number of parallel reflectors calculated using eq. (2). The inset shows a layout of reflectors with identical reflectances R_0, which is a model for the accumulated flakes in the paint film.

transmittances $1 - R_a$ and $1 - R_b$, give a reflectance: $R = (R_a + R_b - 2R_aR_b)/(1 - R_aR_b)$, which can be derived from an intensity summation of multiple reflections between the two reflectors. The reflectance R_n from n sheets of identical reflectance R_0 (the inset in Fig. 6) can be written as a recursion formula:

$$R_n = \frac{R_0 + R_{n-1} - 2R_0R_{n-1}}{1 - R_0R_{n-1}} \quad (2)$$

which is obtained using the substitutions $R_a = R_0$ and $R_b = R_{n-1}$ in the formula for two reflectors. The numerical result for several values of R_0 is shown in Fig. 6. As estimated above, the paint films in Fig. 5 contain four or five sheets of flakes across their thicknesses, if the flakes are oriented parallel to each other. The calculation in Fig. 6 predicts that the maximum and minimum reflectance values, which are about 0.8 and 0.1 for a single sheet shown in Fig. 3, will increase to 0.9 and 0.35 for five sheets in the paint films. The experimental data in Fig. 5 agrees fairly well with this prediction, which confirms that the flakes in the paint films act as parallel reflectors. In addition, reflectance differences at different R_0 (Fig. 6) decrease with increasing reflector number. This means that if the number of accumulated flakes is very large, the paint film should have a flattened spectrum. Thin paint films are therefore favorable for retaining the original color of a single flake.

The sharpness of the reflectance peaks observed in Figs. 3 and 5 is insufficient to yield the primary colors of light: red, green and blue. All the flakes hitherto prepared showed reflected colors near the secondary colors of light: cyan, magenta and yellow. The theory of optics [5] dictates that sharp spectral peaks necessary for primary colors can be attained by either increasing the number of layers of flakes or by using higher-order interference spectral peaks ($m = 1, 2, \ldots$ in eq. (1)). For either approach to succeed, however, the problem of cracking described above must be addressed. The use of a low surface energy solvent or a polymer binder for precursor solutions, which is often applied in sol–gel techniques [1], might allow for the preparation of thick crack-free multicoatings.

4. Conclusions

Optical interference flakes were prepared by detaching sol–gel TiO_2/SiO_2 multicoatings from substrates. The two fabricated types of seven-layer flakes, which had reflected colors of cyan and orange, exhibited red and light blue as their transmitted colors. Paint films fabricated from these flakes and acrylic resins had nearly the same colors as the individual flakes. Our spectral analysis indicated that the accumulated sheets of flakes in the paint films tended to orient parallel to each other, which results in a flattened spectrum for a thick paint film. The reflectance peaks for all of the flakes prepared in this study were not sufficiently sharp to yield the primary colors of light. To obtain flakes with a wide variety of colors, thicker crack-free coatings must be fabricated.

Acknowledgments

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