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Band-selective Mirror Characteristics of Polymer/Metal Multilayer Films

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The optical characteristics of polymer/metal composite films having metal nanoparticles periodically aligned in rows were explored. They were prepared by irradiating ultraviolet light on the polymer films containing metal complex spin-coated on a reflective surface. The films were found to exhibit band-selective mirror characteristics. The wavelength of maximum reflection can be controlled by changing the incident angle of the irradiating light.

The ability to exhibit precise structural control in materials enables us to design well-defined structures having cutting-edge functions. Among such materials, dielectric/metal multilayer has been widely studied and used for optical devices.[1–3] Conventionally, layer-by-layer coating techniques, like sputtering, vacuum deposition, and ion-beam deposition, have been used to prepare these multilayers. They are powerful and promising methods to achieve desired optical characteristics for materials by repeating the thin layer formation at a nanometer level precision.[4] However, it is not cost- and time-effective.

We have recently reported a new method based on optical interference to prepare highly structured materials based on polymer films containing periodically aligned metal nanoparticles in rows.[5] The main claim of the reference was how nanoparticles could be periodically aligned. With this technique, the spacing between two successive metal layers can be controlled by changing the wavelength or incident angle of the irradiating monochromatic ultraviolet (UV) light. Given that the films obtained exhibit similar optical characteristics observed in well-defined dielectric/metal multilayers, our newly developed method would be more efficient than any of conventional layer-by-layer coating methods. In this paper, we explored the optical characteristics of the polymer/metal composite films prepared using our proposed methodology.

The composite films of polymer and metal nanoparticles were prepared using random copolymer of poly(methyl methacrylate) (PMMA) and poly(methacrylic acid) (PMAA), hereby referred to as PMMA-*ran*-PMAA, and $AgClO_4$. The weight fraction of the PMMA and the PMAA in the copolymer is 75:25. The copolymer has a weight-average molecular weight (M_w) of 420000 g mol^{-1} and a polydispersity index (PDI) of 4.4. $AgClO_4$ was dissolved in a 10 wt % tetrahydrofuran solution of PMMA-*ran*-PMAA. The amount of the metal complex in the polymer solution was fixed at 1 wt %. The composite films were prepared by spin-coating this solution onto a reflective substrate at 1500 rpm. A soda-lime glass covered with a 200-nm thick aluminum layer was used as the reflective substrate. The samples were vacuum-dried at room temperature for 3 h. These were then irradiated with UV light (center wavelength being 365 nm) from the free surface side at incident angles of 0 and 60° using the *i*-line emission of a mercury vapor lamp (PM50C-80A1, Ushio, Japan) at room temperature for 2 h. The irradiation intensity for the wavelength of 365 nm at the film surface was 26 mW cm^{-2}.

The samples for TEM were prepared by using a focused-ion-beam (FIB) apparatus (FB-2000A, Hitachi, Japan) operated at 30 keV. The polymer film and the rigid reflective substrate were directly cut into cross-sectional pieces without detaching them from each other. To minimize damage to the samples during the FIB process, the spin-coated films were initially covered with a protective resin layer and then a tungsten layer. For TEM observation, a JEM-200CX, JEOL, Japan operated at 100 keV was used. To characterize the optical attributes of the multilayers, reflection spectra of the PMMA-*ran*-PMAA/Ag films were obtained using a UV–vis–NIR spectrophotometer (V-570, JASCO, Japan).

Figure 1 shows the cross-sectional TEM image of the PMMA-*ran*-PMAA/Ag film on a reflective substrate, which was vertically irradiated by UV light. The darker regions in the TEM micrograph correspond to the Ag nanoparticles with a diameter of 7 ± 3 nm contained in the films after the reduction of $AgClO_4$.[6] The average distance between the rows of aligned nanoparticles in the films was approximately 108 nm, as indicated by d_{TEM}. When UV light was applied at an incident angle of 60°, the observed spacing d_{TEM} was 122 nm (TEM picture is not shown here). These regularly spaced darker

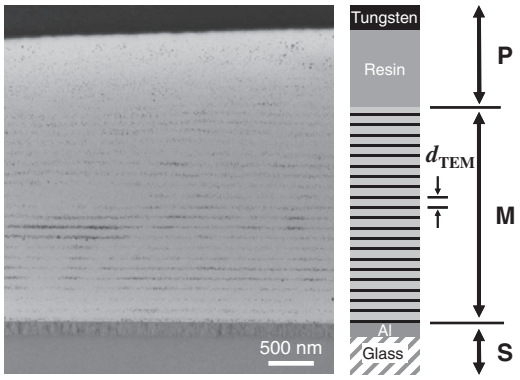

Figure 1. Cross-sectional TEM image of a UV-irradiated PMMA-*ran*-PMAA/$AgClO_4$ film previously spin-coated on a reflective substrate. The figure on the right is a schematic representation of the observed structure at same magnification. The PMMA-*ran*-PMAA/$AgClO_4$ film, the reflective substrate, and the protecting layer are denoted as M, S, and P, respectively.

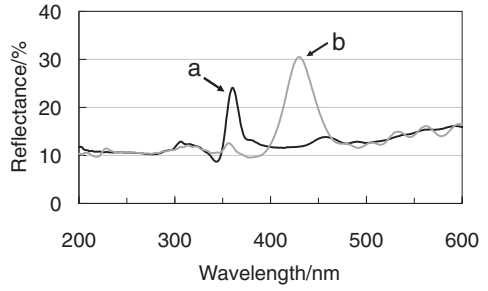

Figure 2. Reflection spectra for the PMMA-*ran*-PMAA/Ag films prepared using a 365-nm UV light at incident angles of (a) 0 (vertical) and (b) 60°.

regions indicate that the nanoparticles were aligned in rows with a periodic pattern. We have reported the same observation as published elsewhere using PMAA homopolymer.[5] This suggests that this technique of multilayer preparation can be extended to various kinds of copolymers containing PMAA segments.

When UV light irradiates onto a polymer film containing metal complex supported on a reflective substrate, both irradiated and reflected light generate a standing wave field in the film. The intensity of the light varies depending on the distance from the reflective substrate. The spacing d_{opt} of the intensity maxima for the interference light is given by $d_{opt} = \lambda/(2n \cdot \cos\theta)$, where λ, n, and θ are the light wavelength in vacuum, the refractive index of the film, and the angle of incidence,[7] respectively. The n value for the PMMA-*ran*-PMAA matrix containing $AgClO_4$ at 365 nm was determined to be 1.54 by spectroscopic ellipsometry. Hence, when UV light with a wavelength of 365 nm was applied to the film at incident angles of 0 and 60°, the corresponding d_{opt} values are 119 and 143 nm, respectively.

The PMMA-*ran*-PMAA films containing layers of Ag nanoparticles were removed from the reflective substrates, floated off onto the water surface, and then vacuum-dried for several hours resulting in free standing films. The films were sandwiched between two quartz plates for shaping flat. Figure 2 shows the reflection spectra of the PMMA-*ran*-PMAA/Ag films irradiated at incident angles of 0 (vertical) and 60°. Both of the films clearly exhibit band-selective mirror characteristics. When the UV light irradiated vertically (0°), the spectrum showed the maximum reflection at 360 nm, which was comparable to the wavelength of light employed. On the other hand, when the UV light was applied at an incident angle of 60°, the wavelength of the maximum reflection shifted to 430 nm. This was simply because the space between two neighboring layers of aligned nanoparticles became wider.

A multilayer repeating a sequence of two layers with different refractive indices with the same spacing is well-known as a Bragg mirror. The wavelength of the light reflected on the Bragg mirror is given by $2n \cdot d$, where d is the spacing of the periodical structure.[8] Hence, the observed wavelength of the maximum reflection λ_{max} was converted to the spacing d_{RM}. When light with a wavelength of 365 nm was applied at incident angles of 0 and 60°, the corresponding d_{RM} values are calculated to be 118 and 140 nm, respectively.

Table 1. Experimental and calculated values of spacing

Incident angles of UV light/°	Spacing/nm		
	d_{TEM}[a]	d_{opt}[b]	d_{RM}[c]
0 (vertical)	108	119	118
60	122	143	140

[a]The observed spacing between the rows of aligned nanoparticles in the films by TEM. [b]The spacing of the intensity maxima for the interference light given by $\lambda/(2n \cdot \cos\theta)$. [c]The spacing calculated by $d_{RM} = \lambda_{max}/2n$.

Table 1 summarizes the spacing discussed above. The d_{RM} values are equal to d_{opt} within our experimental accuracy and are quite different from d_{TEM}. Thus, it can be claimed that the metal nanoparticles were ordered in rows with a period of d_{opt} rather than d_{TEM} in the atmosphere. This discrepancy can be understood by taking into account that the sample should have shrunk under high vacuum in the TEM chamber due to the evaporation of water molecules adsorbed in the hydrophilic PMAA.[5] This was actually confirmed by measuring the thicknesses of a UV-irradiated PMAA/$AgClO_4$ film in air and under vacuum as well. These results clearly show that the wavelength of the maximum reflection with the composite films can be controlled as desired on the basis of the spacing d_{opt}.

In our proposed method, we have shown that it is possible to prepare films with band-selective mirror characteristics. The optical characteristics desired can be easily achieved by changing the irradiation conditions. This technology will open the door to a one-shot production of dielectric/metal multilayer films with band-selective mirror characteristics.

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