Modulation of Polymer Refractive Indices with Diamond Nanoparticles for Metal-Free Multilayer Film Mirrors

Tomonari Ogata,*[†,‡] Ryohei Yagi,[‡,§] Nozomi Nakamura,[⊥] Yutaka Kuwahara,[‡,§] and Seiji Kurihara*[‡,§]

[†]Innovative Collaboration Organization and [§]Graduate School of Science and Technology, Kumamoto University, 2-39-1 Kurokami, Kumamoto 860-8555, Japan

[‡]JST, CREST, 7 Gobancho, Chiyoda-ku, Tokyo 102-0076, Japan

[⊥]Department of Applied Science for Electronics and Materials, Kyushu University, 6-1 Kasugakoen, Kasuga, Fukuoka 816-8580, Japan

Ⓢ Supporting Information

ABSTRACT: Modulation of the refractive index of a polymer was achieved by combining it with diamond nanoparticles (NDs). The increase in the refractive index was controlled by the amount of NDs added, according to the Lorentz−Lorenz equation. The refractive index of poly(vinyl alcohol) (PVA), which was used as the base polymer, increased from 1.52 to 1.88. A multilayer film consisting of alternating layers of ND−PVA composite and poly(methyl methacrylate) exhibited ca. 80% reflectance with 10 bilayers.
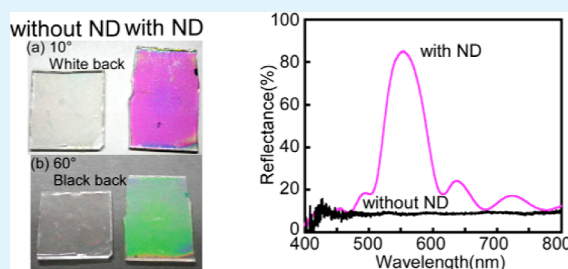
KEYWORDS: *nanodiamond, refractive index, polymer composite, photonic crystal, polymer multilayer, Bragg diffraction*

INTRODUCTION

Control of the refractive indices of materials has attracted much interest and is in demand for optical applications such as lenses, prisms, optical filters, and optical fibers. In particular, the refractive index is an essential property for photonic crystal materials functioning as optical confinement structures, light-extraction materials, optical waveguide materials, and optical resonators. Multilayer films, one kind of photonic crystal, consisting of alternating layers of different materials, are widely used as antireflective coatings,[1,2] mirrors,[3,4] and tunable flexible mirrors.[5] These multilayer films are constructed from metals or metal oxides and the film thickness is controlled precisely. The reflection wavelength is related to the refractive index as well as the film thickness, according to the Bragg equation.[6] Polymeric photonic crystals with orderly periodic structures have characteristic structural colors, and photonic crystal fibers are used in decorative fabrics.[7] Thomas et al. reported innovative multilayer structured photonic crystals fabricated by self-assembly using silica and block copolymers.[8,9]

Míguez et al. have made an important achievement by producing multilayer film mirrors consisting of silica and titania nanoparticles, fabricated using a spin-coating technique.[10] They achieved not only wide variations in the reflection band[11] and high reflectance, but also flexibility.[12] Their multilayer films are rich in metal-oxide nanoparticles, giving greater contrast in the refractive indices.

If nanoparticles of metal oxides such as titania[13−15] or zirconia[16] are used to increase the refractive index of a polymer, the composite will be almost transparent in the visible wavelength region, and the modulation width will be arbitrary and depend on the amount of additive. However, mixing of nanoparticles and polymers to produce a homogeneous composite without aggregation is difficult because of the high surface energies of the particles.[17,18] As Balazs et al. has reported, the nanoparticles tend to aggregate during preparation and will negate the advantages of nanoscale composites, and modification of the particle surface is one way of preventing aggregation.[19]

In addition, titania has photocatalytic activity, which will accelerate photodeterioration of the polymer matrix, and this is a disadvantage in optical applications.[20,21]

Metallic materials are unsuitable for high-frequency circuits because of their high dielectric constants and low insulation resistances. In these cases, organic materials, especially polymers, will be suitable materials. However, polymers show small variations in their refractive indices, and changing the constituent atoms to modulate the refractive index, while maintaining other functions such as a photoresponsivity, is very difficult.

The refractive index of a diamond, which consists of only carbon, is 2.42, the highest value for a nonmetallic material. However, incorporating the characteristic properties of a diamond in polymers is not simple. Recently, diamonds consisting of single-digit nanoparticles, produced by a detonation method, with various functional groups such as carboxyl, hydroxyl, and amino groups on a graphite surface layer, have been reported.[22−26] These functional groups give reactivity and affinity to the diamond nanoparticles (NDs).

Table 1. Conditions for ND−PVA/PMMA Multilayer Films Containing NDs in the PVA Layers

| concn of ND-PVA solution used in spin-coating (wt %) | | ND fraction in the composite (vol %) | $n_C{}^a$ | thickness of single layer in the multilayer film (nm) | | peak^c (nm) | reflectance^d (%) |
ND	PVA			ND−PVA	PMMA^b		
1	4	8.4	1.58	45	121	518	27
1.91	3.35	17	1.63	49	118	532	58
3.5	3	30	1.71	44	123	554	76

$^a n_C$ is a refractive index of the ND−PVA composite layer at 589 nm. ^{b}The concentration of PMMA toluene solution was 2 wt %. ^{c}The peak of a reflection spectrum of 10 bilayer multilayer film. ^{d}The reflectance shows difference in the peak and the baseline level of a reflection spectrum of 10 bilayer multilayer film.

NDs can be dispersed not only in water, but also in aqueous solutions of hydrophilic polymers, as primary particles, even if the mixture solution is dried to a solid.[27] A composite of a polymer and NDs instead of metal-oxide particles will show a very low dielectric constant and a high dielectric strength voltage as a result of the primary attributes of diamonds. These properties will be advantages in the use of ND−polymer composites in microwired circuit electronics combined with optical circuits, such as in high-speed optical communication devices working at high frequencies.

In this work, we prepared composites of NDs with poly(vinyl alcohol) (PVA) to modify the refractive index as the primary objective. Furthermore, multilayer film mirrors were fabricated from poly(methyl methacrylate) (PMMA) and PVA, which have very similar refractive indices.

■ EXPERIMENTAL SECTION

PVA (Wako Pure Chemical Industries Ltd., Osaka, Japan; n = 500, degree of saponification = 88 mol %) was dissolved in water to a level of 10 wt % at 60 °C. The PVA solution and an aqueous dispersion containing 10 wt % of detonation NDs (supplied as an aqueous dispersion by Nippon Kayaku Co., Ltd., Tokyo, Japan; average diameter = 5 nm) were diluted to a prescribed concentration after mixing (Table1), and the concentration of each solution was adjusted based on the results of gravimetric analysis of the drying loss of the solution. The weight fractions were converted using the specific gravity of the NDs (d = 3.14 g/cm³).[28] The PVA solution was slowly added to the ND dispersion, and the resulting mixture was sonicated and filtered using a membrane filter with a pore diameter of 0.2 μm to remove dust contaminants; a blackish transparent solution was obtained. The ND−PVA mixture solution was applied to a glass or silicon substrate by spin-coating at 4000 rpm. After drying in air at room temperature, ND−PVA composite films were obtained on the substrates. The resulting ND−PVA composite films were characterized by optical microscopy, UV−vis spectrometry, and spectroscopic ellipsometry. Multilayer films were prepared by alternately spin-coating PVA aqueous solutions containing NDs and 2 wt % PMMA toluene solutions on glass substrates for specific times. The reflection spectra of the multilayer films were measured using a fiber-optic spectrometer.

■ RESULTS AND DISCUSSION

As mentioned above, the NDs had functional groups on their surfaces and this assisted embedding in the polymer. Scorsone et al.[29] used PVA as a dispersion agent to avoid aggregation of ND particles, and they used scanning electron microscopy to confirm the dispersion of NDs cast on a silicon substrate. In

this study, we also dispersed the NDs in a PVA solution, and the PVA was used as a binder for the layer structure.

The resulting ND−PVA composite films had a mirror surface, and were transparent, with a slightly yellow color. In all cases, ND aggregation was not observed by optical microscopic observation at 1000-fold magnification. The ND−PVA composite films (normalized to thickness = 3 μm) containing 8.4, 17, and 30 vol % NDs showed weak absorptions in the visible spectral range because of their blackish color, and strong absorptions in the region of wavelengths shorter than 400 nm (Figure 1). These colors come from the graphite surface layer
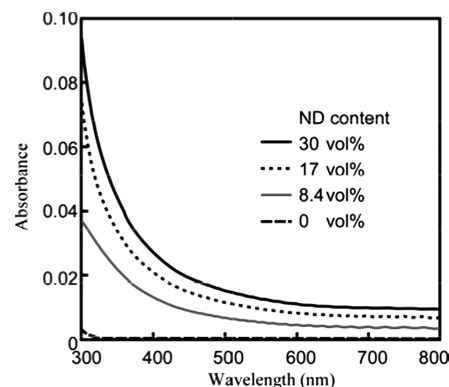

Figure 1. UV−vis absorption spectra of PVA and ND−PVA composite films on the glass substrate. The lines are in the order ND = 30, 17, and 8.4 vol% PVA, from the top.

on the diamond particles[30−32] (see the Supporting Information for detection of graphite in ND in this study by means of Raman spectroscopy and XRD).

However, absorption was observed over a wide range of wavelengths, all the films were blackly transparent, and no particles and clouds were observed. The results indicate that the NDs could be well dispersed in PVA, even if the ND volume fraction was higher than 30 vol %. A transparent film was obtained from ND−PVA (6:4 volume ratio), and the refractive index of the film was determined using ellipsometry. Figure 2 shows the dependence of the refractive index at 589 nm on the ND fraction in the composite films.

The refractive index increased with increasing ND fraction in the composites. The closed circles in Figure 2 indicate the experimentally observed values, and the solid line indicates the values calculated by curve-fitting to the Lorentz−Lorenz equation[33]

$$\frac{n_c^2 - 1}{n_c^2 + 2} = f_{ND} \frac{n_{ND}^2 - 1}{n_{ND}^2 + 2} + f_{PVA} \frac{n_{PVA}^2 - 1}{n_{PVA}^2 + 2} \tag{1}$$
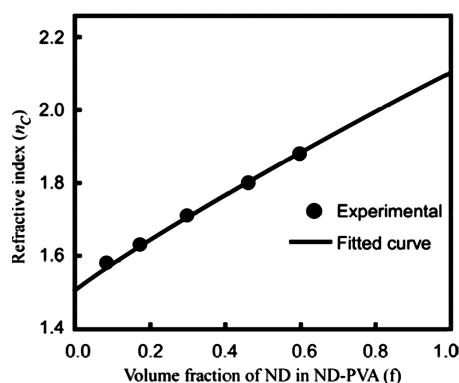
Figure 2. Dependence of refractive index on ND fraction. Closed circles are the refractive indices at 589 nm for various volume fractions of NDs in PVA films. The solid line is the curve fitted to eq 1. The refractive indices of the raw materials are estimated from each *y*-intercept of the line.

where n_c is the refractive index of the composite measured, n_{ND} is the refractive index of the NDs, n_{PVA} is the refractive index of PVA, and f_{ND} and f_{PVA} are the volume fractions of the composites in the feed. The calculated line was in good agreement with the experimental values. This agreement demonstrated the validity of the measurements and estimations of the refractive indices by extrapolation. The refractive index of the ND−PVA (6:4 volume ratio) composite film reached 1.88, which was an increase from that of 1.52 for PVA (n_{PVA}). The refractive index of the NDs (n_{ND}) was estimated to be 2.08 using curve-fitting with eq 1, and this value is lower than the refractive index of crystalline diamond, which is 2.42.[34] The impurities contained in the NDs, such as graphite and organic side groups, may contribute to the low estimated refractive index.[30−32] However, it is noteworthy that the refractive index of the polymer composite increased by 0.36, using only a carbon material without heavy atoms.

A multilayer film of regularly alternating laminated layers of two different materials is one type of one-dimensional photonic crystal showing a Bragg reflection. The reflectance of the multilayer film is closely related to the contrast between the refractive indices of the two layers and the number of layers.[35] Multilayer films with high reflectances will therefore be obtained by alternately laminating two materials that have very different refractive indices. A polymeric multilayer film consisting of PMMA and PVA shows very low reflectance because of the small difference between their refractive indices: $n_{PMMA} = 1.49$,[36] $n_{PVA} = 1.52$. Consequently, in the case of a PMMA and PVA multilayer film mirror, lamination of over 60 bilayers is required to attain a reflectance of over 80%. If one can increase the difference between the refractive indices of the PMMA and PVA layers, the number of layers required to obtain more than 80% reflectance would decrease. As a result of a greater difference between the refractive indices of the two component layers, the reflectance increases. Multilayer films were prepared on a glass substrate by alternately spin-coating PVA aqueous solutions and PMMA toluene solutions. ND−PVA mixture solutions with various volume fraction of NDs (8.4, 17, 30, 46, and 60 vol % based on solid) were used to fabricate multilayer films by alternating spin-coating. However, the surface of the film became rough during spin-coating using a volume ratio of 46 vol% or higher. Although the reason is not clear at this point, a rich nanoparticle dispersion under a higher shear might reduce flowability. Multilayer films of good

appearance were obtained using ND−PVA solutions with 8.4, 17, and 30 vol % NDs. The effects of the ND fraction in the PVA layers on the reflectances of PVA/PMMA multilayer films with 10 bilayers are shown in Table 1 and Figures 3 and 4.
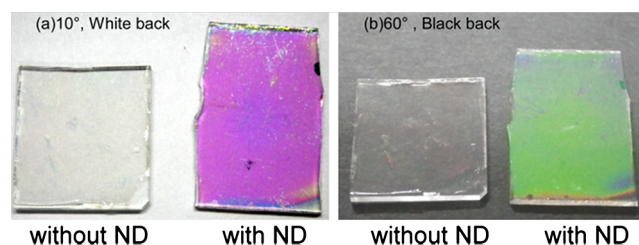

Figure 3. Optical images of 10-bilayer multilayer films consisting of PMMA and PVA without NDs and containing 30 vol % NDs: (a) observation angle = 10°, white back; and (b) observation angle = 60°, black back.
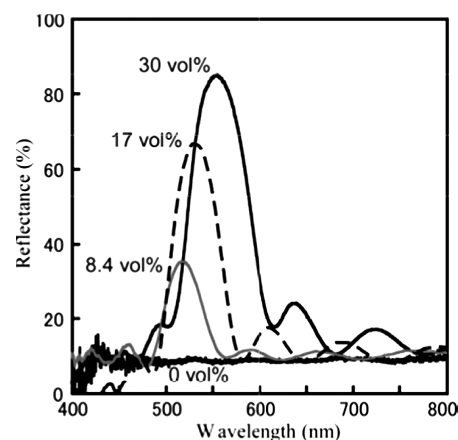

Figure 4. Changes in the reflection spectra with varying ND fractions in the PVA layer of an ND−PVA/PMMA multilayer film on a glass substrate.

Figure 3 shows optical images of the PVA/PMMA and PVA−ND (30 vol %)/PMMA 10-bilayer multilayer film on a glass substrate. The films in a and b differ only in their back color and observation angle; a is an image of a white-backed film taken from an incident angle of 10°, to observe the transmitted light, and b is an image of a black-backed film taken from an incident angle of 60° to observe the reflected light. The ND−PVA/PMMA multilayer film has a mirror-finished surface and is transparent, and purple was observed in the transmitted light, i.e., the complementary color of the reflected band at around 550 nm, based on the structural color.

Figure 4 shows the reflection spectra of PVA/PMMA multilayer films with various contents of NDs in the PVA layers. These reflection spectra were corrected to remove the absorption effect of the ND color, using the results shown in Figure 1, and the total thickness of the ND−PVA layers.

As mentioned above, no distinct reflection was observed for the PVA/PMMA multilayer film with 10 bilayers without NDs, as shown in Figure 3 (left-hand side films in both images) and Figure 4 (lowest line). In contrast, the reflectance clearly increased with increasing ND fraction as a result of the increasing contrast between the refractive indices of the PMMA and PVA layers. The reflection band shifted toward a longer wavelength region as a result of the higher average refractive index of the whole film.[6] In addition, there was no change in

the absorbance of the baseline as a result of increasing the ND fraction. The ND particles were well-dispersed, even in the multilayer films, indicating neither segregation nor aggregation by contact with the poor solvent during the alternating spin-coating process.

CONCLUSION

Well-dispersed ND−PVA mixture solutions were obtained by a simple process using detonation ND particles. ND−PVA composite films were fabricated on substrates without significant aggregation of nanoparticles, even near the theoretical closest packing content of ND particles. The refractive index of the ND−PVA composite increased with increasing ND content and reached 1.88. Clear and highly refractive polymeric composite films were obtained, and the increased refractive index would be helpful in designing optical devices without metallic materials, which means that the highly refractive part could be incorporated without using costly vacuum processes. Multilayer films consisting of PVA and PMMA did not show clear reflection with 20 bilayers; in contrast, 10-bilayer multilayer films consisting of ND−PVA and PMMA exhibited strong reflection as a result of the increased refractive index. These materials with large contrasts in their refractive indices enhance the reflectance of a multilayer film, and sufficient reflection can be obtained with fewer layers. Furthermore, the reflection band can easily be tuned by changing the thickness of each layer. The increase in refractive index was achieved without modification of the constituent atoms and/or structure of the molecules, and the resulting composites are applicable as optical materials.

ASSOCIATED CONTENT

Ⓢ Supporting Information

Raman spectrum and XRD pattern of the NDs. This information is available free of charge via the Internet at http://pubs.acs.org/.

AUTHOR INFORMATION

Corresponding Author

*E-mail: t_ogata@kumamoto-u.ac.jp (T.O.); kurihara@kumamoto-u.ac.jp (S.K.).

Notes

The authors declare no competing financial interest.

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