Fabrication of Polysilane–Silica Hybrid Thin Films with Controlled Refractive Index

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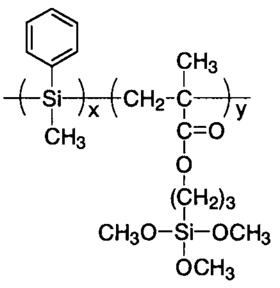
Polysilane–silica hybrid thin films, in which the polysilane segment is encapsulated within the silica matrix, were prepared by a sol–gel method using copolymers, poly[methylphenylsilane-*co*-(methacryloxypropyltrimethoxysilane)]. The hybrid thin films were composed of a wide range of polysilane and silica ratios without phase separation. The observed refractive index of the hybrid thin film was changed from 1.61 to 1.49 with a different composition ratio. Their refractive indexes were decreased with degradation of polysilane segments on UV irradiation.

The organic–inorganic hybrid materials have been recently investigated for optical applications, and their refractive indexes as one of optical properties have become of interest.[1] A sol–gel process can provide a transparent and homogeneous hybrid thin film containing a high refractive index material, such as ZrO_2, and hence the process is suitable for a fabrication of the planar waveguide, optical devices, and so on.[2] The refractive index can be tailored by changing the composition ratio of organic component to inorganic one in the hybrid material.[3] For the optical applications, polysilane also has attracted considerable attention because of the several characteristic photo-functionalities.[4] Although the refractive index of poly(methylphenylsilane) (PMPS) is higher than that of silica,[5] the continuous refractive index change of polysilane by the photo-degaradation has not yet been reported. Therefore, polysilane–silica hybrid thin films would be the promising materials with specific properties due to their refractive index. We have already reported that the preparation of the polysilane–silica hybrid materials via a sol–gel process by using poly[methylphenylsilane-*co*-(methacryloxypropyltrimethoxysilane)] (P(MPS-*co*-MPTMS)) and tetraethoxysilane (TEOS).[5] In this work, we have studied the preparation of the polysilane–silica hybrid thin films with a wide range of composition ratios and their specific refractive index properties. Furthermore, the control of refractive indexes of the polysilane–silica hybrid thin films has been investigated by utilizing the photo-degradation of polysilane.

The P(MPS-*co*-MPTMS) and polysilane–silica hybrid thin film by a sol–gel method are prepared according to the procedure previously reported.[5] The feed ratio for the preparation of the hybrid thin film was P(MPS-*co*-MPTMS)/TEOS = 1/1, 1/3, 1/5, and 1/10 by weight. A thin film of PMPS used as a reference was prepared by spin coating of the toluene solution (PMPS: M_n = 2.73 × 10^4, M_w = 5.64 × 10^4, M_w/M_n = 2.06). The refractive index and the thickness of the thin films on a silicon substrate was measured by an ellipsometer (ULVAC ESM-1) with a He–Ne laser (632.8 nm). These results are summarized in Table 1. The refractive indexes of these hybrid thin films decreased with increasing composition ratios of TEOS. Therefore, it was found that the hybrid thin film with different refractive index from 1.61 to 1.49 could be fabricated easily. The thickness of the thin films before UV irradiation was in the range of 90 to 180 nm. In general, much increase of the silica content in organic–silica hybrid materials tends to result in the formation of opaque and/or brittle films due to the phase separation in the micrometer scale.[6] However, the transparent polysilane–silica hybrid thin films containing a 10 times silica by weight in visible region indicate that P(MPS-*co*-MPTMS) has a good miscibility with TEOS. Assuming that all the TEOS in the composition of P(MPS-*co*-MPTMS)/TEOS = 1/10 ratio were converted to the silica matrix, the weight ratio of the silica to the hybrid material was 88.3 wt%.



M_n = 1.06×10^4
M_w = 2.28×10^4
M_w/M_n = 2.14
x = 114
y = 30

P(MPS-co-MPTMS)

Table 1. Feed ratio[a] of polysilane/silica hybrid thin films and their result of ellipsometry.

Copolymer/TEOS	Refractive index	Film thickness / μm
1/1	1.61	0.17
1/3	1.55	0.17
1/5	1.53	0.18
1/10	1.49	0.11

[a]Feed ratio of P(MPS-*co*-MPTMS)/TEOS by weight for the preparation of polysilane/silica hybrid thin films. A hybrid thin film of 1/x feed ratio was prepared by spin coating (2000 rpm, 1 min) the THF (2 mL) solution of P(MPS-*co*-MPTMS) (50 mg), TEOS (50x mg) with diethylene glycol methyl ether (0.3 mL) and 4.5 M HCl (10 μL).

Figure 1 shows plots of the refractive index of the PMPS and hybrid thin films toward UV irradiation time using a mercury UV light (Ushio SPOT CURE SP-V). The light power was 141 mW/cm^2. The refractive index of the PMPS thin film at an irradiation time of more than 1.0 s could not be measured because the degraded thin film was removed by rinsing with hexane. On the other hand, the hybrid thin films remained on substrates at an irradiation time of 1.0 s and their refractive index decreased with irradiation time to reach almost constant value, 1.45, that of silica. It is especially noteworthy that a refractive index change of 0.043 was seen for a hybrid thin film of P(MPS-*co*-MPTMS)/TEOS = 1/10 ratio at an irradiation time of 7.0 s in spite of a slight decrease (5%) of the film thickness. In the case of a hybrid thin film with 1/1 ratio, the decrease of the film thickness was 16%. Futhermore, the silica matrix in the hybrid thin films was left even after the removal of the decomposed polysilane segment

UV–vis absorption spectra of the PMPS and the hybrid thin

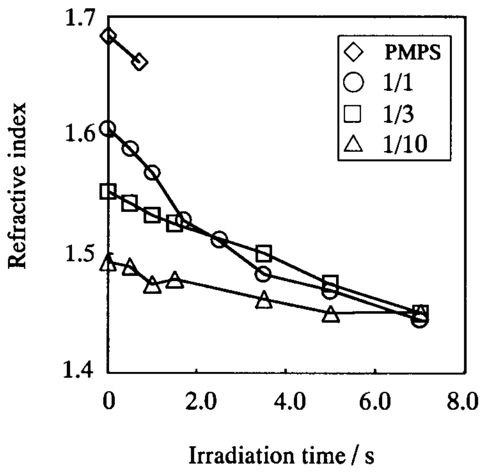


Figure 1. UV irradiation time vs refractive index of PMPS and hybrid thin films with different composition ratios of P(MPS-*co*-MPTMS)/TEOS = 1/1, 1/3, and 1/10. The light power was 141 mW/cm^2.

films before and after the UV irradiation were illustrated in Figure 2. The spectra of both films show σ–σ* transition around 340 nm due to Si–Si bond of polysilane. In the PMPS thin film, the peak disappeared after 1.0 sec irradiation. In the hybrid thin film, on the contray, the peak remained at some extent with the elapse of irradiation time. Figure 3 shows XPS spectra (ULVAC Phi ESCA 5700) of the PMPS and the hybrid thin films before and after the UV irradiation. Si_{2p} peaks of Si–Si and Si–O bond appear at around 99.0 eV and 103.0 eV respectively. Both Si–Si and Si–O bond were observed in the hybrid thin film before the UV irradiation because the polysilane segment as a domain was dispersed in the silica matrix. The Si–Si bond in the PMPS thin film disappeared at an irradiation time of 1.0 s, while the Si–Si bond in the hybrid thin film remained after longer irradiation. From these results, it is found that the hybrid thin films had a certain extent of durability against UV exposure at ambient temperature in comparison with PMPS, as well as the durability of photoluminescence at low temperature.[7].

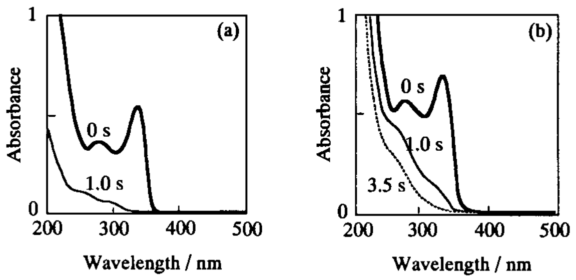


Figure 2. UV–vis absorption spectra of (a) PMPS and (b) polysilane–silica hybrid thin films (P(MPS-*co*-MPTMS)/TEOS = 1/1) after UV irradiation (light power : 141 mW/cm^2).

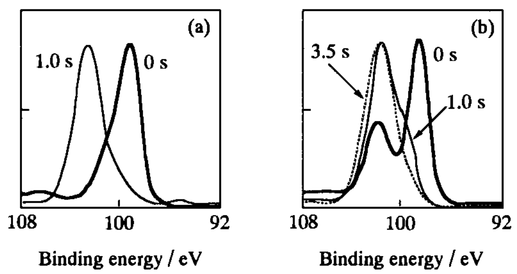


Figure 3. XPS spectra of (a) PMPS and (b) polysilane–silica hybrid thin films (P(MPS-*co*-MPTMS)/TEOS = 1/1) after UV irradiation (light power : 141 mW/cm^2).

In conclusion, the refractive index of polysilane–silica hybrid thin films varied depending on the silica content. Furthermore, the refractive index changing by UV irradiation was observed without considerable decrease of the film thickness. This behavior seems to apply to the fabrication of controlled refractive index pattern, which was formed from a hybrid thin film of P(MPS-*co*-MPTMS)/TEOS = 1/1 ratio by UV irradiation for 7.0 s (see the graphical abstract). The further characterization of the refractive index pattern is currently under investigation.

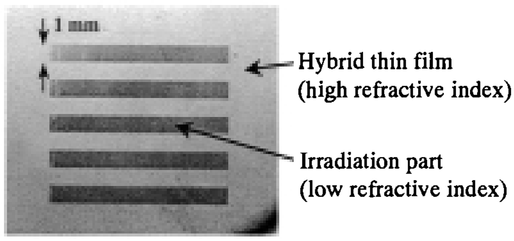


Figure 4. Refractive index pattern of a polysilane–silica hybrid thin films (P(MPS-*co*-MPTMS)/TEOS = 1/1) formed by UV irradiation on silicon substrate.

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