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Journal of Organometallic Chemistry 611 (2000) 40–44

Journal of Organo metallic Chemistry

Optical properties of organic–inorganic hybrid thin films containing polysilane segments prepared from polysilane–methacrylate copolymers

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Received 28 February 2000; accepted 31 March 2000

Abstract

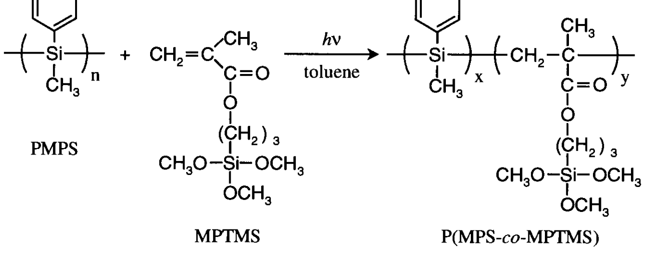
Optical properties of polysilane–silica hybrid thin films have been studied to examine confinement effects of polysilane segments in silica matrices. Polysilane–methacryloxypropyltrimethoxysilane copolymers are synthesized from photo-radical copolymerization of 3-methacryloxypropyltrimethoxysilane and using polymethylphenylsilane. Organic–inorganic hybrid thin films with homogeneously dispersed polysilane segments are successfully prepared from the copolymers by a sol–gel method. It is found that UV light-induced degradation of photoluminescence of the polysilane–silica hybrid thin films is suppressed in comparison with that of polymethylphenylsilane at 10 K, and that UV light exposure decreases the refractive index of the polysilane–silica hybrid thin film from 1.60 to 1.40 at room temperature. It is also found that the degree of the anisotropy of the linearly polarized photoluminescence approaches to the theoretical upper limit with decreasing polysilane content in the polysilane–silica hybrid thin films. These results indicate that the fabrication of polysilane–silica hybrid thin film is a new approach for future polysilane based opto-electronic devices. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Organic polysilane; Organic–inorganic hybrid film; Sol–gel method; Photoinduced effect; Polarization memory

1. Introduction

Organic polysilanes are chain-like polymers with a silicon backbone and organic substituent groups, and exhibit a variety of unique and interesting properties, such as high quantum efficiency of photoluminescence (PL) and high hole drift mobility. These properties are associated with σ conjugation along the Si backbone [1–5]. Recently, the applicability of the materials to future opto-electronic devices has been extensively studied [6–8].

Molecularly dispersed polysilane composites, i.e. organic–inorganic hybrid materials, attract much attention to fabricate a new class of organic confinement structures. For the preparation of the hybrid materials, polysilane copolymers are important components. Although polysilane–vinyl block copolymers have been prepared by anionic polymerization using 'masked disilylene' [9], there are difficulties to prepare the monomers. We have found that since the photolysis of polysilanes produces silyl radicals, which can be used as



Scheme 1.

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PII: S0022-328X(00)00297-7

Table 1
Photo-polymerization of MPTMS using PMPS as a macro-photoinitiator

	Feed ratio (wt%) MPTMS/PMPS	P(MPS-*co*-MPTMS)						
		Yield (%)	M_n	M_w	M_w/M_n	x	y	Si chain length
Run 1	33/67 [a]	45	9.3×10^3	16.6×10^3	1.78	122	8	94
Run 2	50/50 [a]	36	11.6×10^3	19.4×10^3	1.67	127	17	100
Run 3	60/40 [a]	36	1.26×10^3	24.3×10^3	1.93	148	27	97
Run 4	60/40 [b]	38	10.5×10^3	18.2×10^3	1.73	96	18	81

[a] Molecular weight of PMPS; $M_n=2.54\times10^4$, $M_w=5.94\times10^4$, $M_n/M_w=2.34$.

[b] Molecular weight of PMPS; $M_n=2.07\times10^4$, $M_w=4.54\times10^4$, $M_n/M_w=2.19$.

a radical polymerization initiator of vinyl monomers [10], polysilane copolymers are prepared from the photo-radical polymerization of acrylic monomers [11]. These copolymers are miscible with tetraethoxysilane (TEOS) as an inorganic silica matrix for a sol–gel process. In this paper, we report the synthesis of polysilane–methacryloxypropyltrimethoxysilane copolymers [P(MPS-*co*-MPTMS)], the preparation of organic–inorganic hybrid thin films using copolymers by a sol–gel method, and optical properties of the hybrid thin films. We find the unique optical properties of the polysilane–silica hybrid thin films such as photoinduced large refractive index changes and linear polarization memory of photoluminescence.

2. Experiment

2.1. Synthesis

Polymethylphenylsilane (PMPS), which was prepared by the Wurtz coupling reaction of methylphenyldichlorosilane in THF [11], was used for a macro-photoinitiator. In a typical photo-polymerization of 3-methacryloxypropyltrimethoxysilane (MPTMS), PMPS (1.0 g) and MPTMS (1.0 g, 50 wt%) were dissolved in toluene (10 ml) in a Pyrex tube, the mixture was sufficiently degassed by the freeze–thaw method. After sealing the tube under reduced pressure, photo-polymerization was carried out by irradiation with UV light (high-pressure Hg lamp of 10 mW cm^{-2}) for 6 min, as shown in Scheme 1. Copolymers, P(MPS-*co*-MPTMS), were obtained after reprecipitating from hexane, and the results of copolymerization are summarized in Table 1. The molecular weights of P(MPS-*co*-MPTMS) were measured by GPC calibrated with polystyrene standards. The composition, x and y in Scheme 1, was determined by ^{1}H-NMR spectra. The appearance of absorption maxima around 3.67 eV in UV absorption spectra of P(MPS-*co*-MPTMS) in tetrahydrofuran (THF) indicates that polymeric Si–Si bonds exist after photo-polymerization. The Si chain length of the copolymers was estimated from our own calibration curve for absorption maximum. From these results, P(MPS-*co*-MPTMS) was found to be mainly A–B block copolymers whose Si chain length was slightly smaller than x.

2.2. Preparation of the hybrid thin films

Diethylene glycol monomethyl ether and HCl were added to a THF solution of P(MPS-*co*-MPTMS) from Run 4 in Table 1 and TEOS with different compositions (75, 33, 24 and 7.5 wt% of P(MPS-*co*-MPTMS)/TEOS) [11]. After thoroughly mixing in the dark at room temperature (r.t.) for 1 h, the thin films were prepared by spin-coating the solution on substrates at 2000 rpm for 60 s. By the heat treatment of the spin-coated substrates at 120°C for 1 h, the solution gelled to hybrid thin films. The hybrid thin films prepared in this way were transparent in visible region and insoluble in solvent such as toluene and THF. These results suggest that P(MPS-*co*-MPTMS) is highly dispersed in silica. The thickness of the hybrid films was between 60 and 70 nm, and thereby the thickness can be controlled stepwise by repeated spin coats of the solution.

2.3. Optical measurements

The optical absorption spectra and the PL spectra of the thin films were measured with a Shimadzu UV-3100PC spectrometer and a Shimadzu RF-5300PC spectrometer, respectively, at r.t. For PL measurements at 10 K, a 3.814-eV He–Cd laser was used as an excitation source, and the PL spectra were measured using a 30-cm monochromator (Actron Research Corporation SpectraPro-300i) and a CCD camera (Princeton Instrument RTE/CCD-128) in order to minimize the photoinduced change of the optical properties of polysilanes.

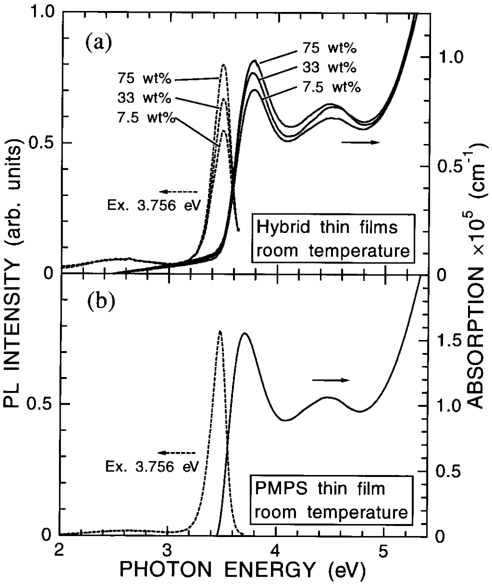

Fig. 1. Optical absorption spectra (solid lines) and PL spectra (broken lines) of (a) the hybrid thin films (75, 33 and 7.5 wt% of P(MPS-*co*-MPTMS) to TEOS) and (b) the PMPS thin film at r.t.

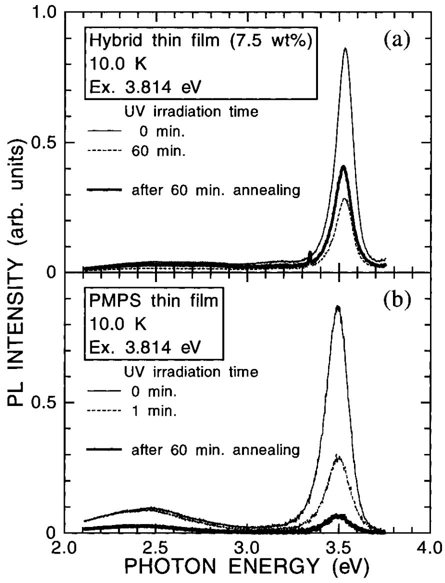

Fig. 2. Photoinduced degradation of PL spectra (broken lines) in (a) the hybrid thin film (7.5 wt% of P(MPS-*co*-MPTMS) to TEOS) and (b) the PMPS thin film by UV light exposure (3.814 eV excitation of 2.5 W cm^{-2} at 10 K under vacuum). PL spectra after the samples were kept at 10 K for 1 h in dark are also shown (bold lines).

Table 2
Refractive index of the hybrid thin film (24 wt% P(MPS-*co*-MPTMS) to TEOS)

Hybrid thin film	Refractive index *n*
(a) Before UV irradiation	1.60
(b) After UV irradiation	1.53
(c) Rinsing (b) with hexane	1.40

3. Results and discussion

3.1. Optical absorption and photoluminescence

Fig. 1 shows optical absorption and PL spectra of the PMPS thin film ($M_w = 3.1 \times 10^4$) and the hybrid thin films under the 3.756 eV excitation at r.t. It can be seen that the optical absorption and PL spectra of the hybrid thin films are essentially the same as those of the PMPS thin film. We find out from these results that organic polysilanes are embedded in inorganic silica matrices by means of the sol–gel method without any significant spectrum-change in their optical properties.

3.2. Photoinduced effect

Photoinduced change of PL spectra in the PMPS thin film and the hybrid thin film (7.5 wt% of P(MPS-*co*-MPTMS) to TEOS) by UV light exposure (3.814 eV excitation of 2.5 W cm^{-2} at 10 K under vacuum) is shown in Fig. 2. The PL intensities of both PMPS thin film [12] and hybrid thin film decays with UV irradiation, but the decay rate of the hybrid thin film is much lower than that of PMPS. After the samples were kept at 10 K for 1 h in dark, PL spectra of these thin films were again measured. It was found from Fig. 2 that the PL intensity of the PMPS thin film decreases further, while that of the hybrid thin film recovers slightly. These results indicate that the silica matrix in the hybrid thin film acts as a passivation cage which prevents from photocreating dangling bonds and from photodegrading irreversibly, thus improving the durability of organic polysilanes.

When the hybrid thin films are irradiated with UV light in air at r.t. for a few minutes, photoscission of polysilane segments occurred, as confirmed by the disappearance of 3.67 eV absorption in UV spectra and Si–Si bond (Si_{2p}: 101.2 eV) in X-ray photoelectron spectroscopy. The refractive index *n* of the hybrid thin film (24 wt% of P(MPS-*co*-MPTMS) to TEOS) on a silicon wafer substrate was measured before and after UV irradiation by ellipsometry. As shown in Table 2, before irradiation, the refractive index of the hybrid film is $n = 1.60$, and that of PMPS is $n = 1.67$. After irradiation, the refractive index of the hybrid film becomes lower, $n = 1.53$. A further decrease in the refractive index, $n = 1.40$ is observed after rinsing the irradiated hybrid thin film with hexane for removing photodegradation products. The value of the refractive index of 1.40 is comparable to that of silica glass, which means only silica glass remains on the substrate. These results suggest the wide application of the hybrid thin film to opto-electronic devices such as distributed feedback lasers.

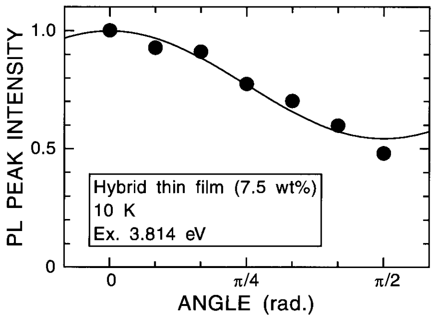

Fig. 3. Angular dependence of the normalized PL peak intensity in the hybrid thin film (7.5 wt% of P(MPS-*co*-MPTMS) to TEOS) at 10 K under 3.814 eV laser excitation. The angle is made between the polarizers in the excitation and the PL beam.

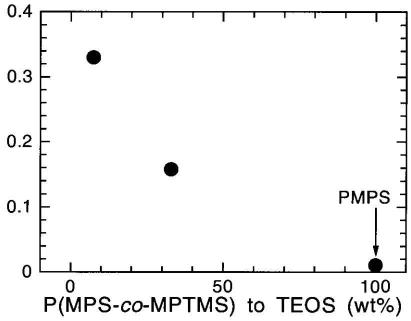

Fig. 4. Dependence of the degree of anisotropy *r* at 10 K under 3.814 eV laser excitation on the weight ratio of P(MPS-*co*-MPTMS) to TEOS.

3.3. Polarization memory

Polarized PL spectra have been examined in order to gain insight into excitation energy migration [13]. We show the normalized PL peak intensity at different angles between the polarizers in the excitation and the PL beam at 10 K under 3.814 eV laser excitation in Fig. 3. The degree of anisotropy r is obtained from $r = (I_{vv} - I_{vh})/(I_{vv} + 2I_{vh})$, where I is the PL intensity, and indices v and h denote the vertical and horizontal position of the polarizer in the excitation and the PL beam, respectively. Fig. 4 shows the dependence of the degree of anisotropy on the weight ratio of P(MPS-*co*-MPTMS) to TEOS. It is found from Fig. 4 that with decreasing polysilane concentration the degree of anisotropy is increased. The value of r of 7.5 wt% of P(MPS-*co*-MPTMS) to TEOS is close to a theoretical upper limit of 0.4 in the case of an isotropic film containing non-interaction molecular emitters [13], indicating that the interchain energy migration erasing the polarization memory is considerably suppressed in the hybrid thin films. We note that the polarization memory observed here is an indication of P(MPS-*co*-MPTMS) being homogeneously dispersed in silica.

4. Conclusions

We have synthesized polysilane–methacryloxypropyltrimethoxysilane copolymers from the photo-radical copolymerization of 3-methacryloxypropyl-trimethoxysilane by using PMPS as a macro-photoinitiator, fabricated the organic–inorganic hybrid thin films with highly dispersed polysilane segments from the copolymers by a sol–gel method, and studied their optical properties. We find that the degradation of the polysilane–silica hybrid thin films induced by UV light is significantly suppressed in comparison with that of PMPS thin films at 10 K. We also find that UV irradiation to polysilane–silica hybrid thin films changes their refractive index from 1.60 to 1.40. In addition, linear polarization memory of PL is found in the polysilane–silica hybrid thin films, and is due to the increase in the interchain separation and homogeneous dispersion of polysilane chains in the inorganic silica matrix. The results show that organic polysilanes embedded in an inorganic silica matrix is a new approach to improve the durability of organic polysilane based devices and to fabricate opto-electronic devices such as distributed feedback lasers utilizing large changes in the refractive index upon UV exposure.

Acknowledgements

Part of this work at Nara was supported by a Grand-in-Aid for Scientific Research on Priority Areas (A) ‘The Chemistry of Inter-element Linkage’ from the Ministry of Education, Science, Sport and Culture of Japan.

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