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Energy transfer in highly oriented permethyl-dodecasilane and -octadecasilane films

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Abstract

Heterostructured films of permethyl-dodecasilane (DM12) and permethyl-octadecasilane (DM18) were prepared on silicon and fused quartz plates under ultrahigh vacuum conditions and the films were characterized by optical absorption and photoluminescence spectroscopy, and atomic force microscopy. The molecules were found to form highly oriented films in a layer-by-layer growth mode with their molecular chains perpendicular to the substrate surface. Moreover, it was found on the basis of optical measurement that the energy transfer progressed effectively from the optically excited state of DM12 generated by the σ–σ^* one-electron transition to that of DM18 through the interface between the layers. © 2000 Published by Elsevier Science S.A. All rights reserved.

Keywords: Origosilane; σ–σ^* Transition; Molecular orientation; Heterostructure; Layer-by-layer growth; Energy transfer

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1. Introduction

Rapid progress is being made in chemical synthesis of interelement linkages, by which a wide variety of novel compounds have been developed [1]. Among the various materials synthesized so far, organopolysilanes and their derivatives have attracted considerable attention, since they exhibit interesting optical and electronic properties arising from σ-electrons delocalized over Si chains [2]. Polysilanes are known to have intense light absorption and emission in the near-ultraviolet region, which is attributed to the σ–σ^* one-electron transition. The energy and strength of this optical transition are known to depend on the length and conformation of the Si-backbone [3]. The optical properties of σ-conjugated polymers and oligomers in the solid state have also been studied and are found to be affected significantly by molecular orientation and molecular packing in the aggregates [4].

In our previous works [5], we examined film growth of poly(dimethylsilane) (PDMS) and permethyl-dodecasilane, $CH_3\{Si(CH_3)_2\}_{12}CH_3$ (DM12) on fused quartz plates and cleaved faces of alkali halides, and studied the correlation between the molecular orientation and the optical characteristics. PDMS and DM12 molecules formed thin layers on quartz with their molecular chains perpendicular to the surface, while the molecules stayed parallel on alkali halides. The films grown on quartz and alkali halides showed quite different optical properties from each other as a result of differences in molecular orientation on the substrates.

The molecules were found to form large grains in a layer-by-layer mode at appropriate growth conditions. The methods established make it possible to prepare heterostructures and super lattices composed of highly oriented ultrathin layers. Heterostructures with layered materials in nanometer scale are of particular interest because of their potential applications to optical devices. In the present study, we prepared heterostructures composed of DM12 and permethyl-octadecasilane, $CH_3\{Si(CH_3)_2\}_{18}CH_3$ (DM18) and studied their optical properties. Since the energies for the σ–σ^* transitions differ from each other depending on the chain length, the energy transfer in the heterostructured films is feasible.

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2. Experimental

Film growth was carried out in an ultrahigh vacuum chamber at a base pressure of about 2×10^{-8} Pa. DM12 and DM18 were synthesized by reductive coupling of 1,6-dichloropermethylhexasilane and 1-chloropermethylhexasilane with potassium and sodium in toluene [6]. After purification by silica gel column chromatography, HPLC, and recrystalization, pure DM12 and DM18 were obtained with yields of 5 and 2%, respectively. DM12 and DM18 powders thus prepared were charged into Knudsen-cells without further purification. Silicon wafers with a naturally formed oxide layer and fused quartz plates with a typical size of $15 \times 10 \times 1$ mm^3 were used as substrates. They were washed with acetone and introduced into the chamber. The substrates were kept at room temperature during film growth in the present experiment. The growth rate and average thickness of the film were measured with a quartz oscillator located near the substrate. The growth rate was controlled to be 0.1 nm min^{-1} by keeping the temperature of DM12 and DM18 powders at 75 and 110°C, respectively.

The UV–vis light absorption spectra were measured for the films grown on quartz with a Hitachi U-3500S spectrometer. The photoluminescence (PL) and photoexcitation (EX) spectra of the films on silicon were recorded on a Hitachi Fluorescence Spectrophotometer 850. The surface morphology of the specimen was observed by the contact mode atomic force microscopy (AFM) with SEIKO SPI 3700.

3. Results and discussion

Fig. 1 shows optical absorption spectra of ultrathin DM12 and DM18 films grown on quartz. No absorption peak was observed at normal incidence (curve a), while sharp peaks appeared at 287 nm (4.32 eV) for DM12 and at 297 nm (4.18 eV) for DM18 when the substrates were tilted by 45° with respect to the incident light beam (curves b and c). These absorption peaks are attributed to the electron transition from the highest molecular orbital (HOMO) to the lowest unoccupied MO (LUMO). Since the symmetry of MOs shows that the transition dipole moment is along with the molecular chain, the dichroism observed here for DM12 and DM18 films indicates that the molecules oriented perpendicular with respect to the substrate surface.

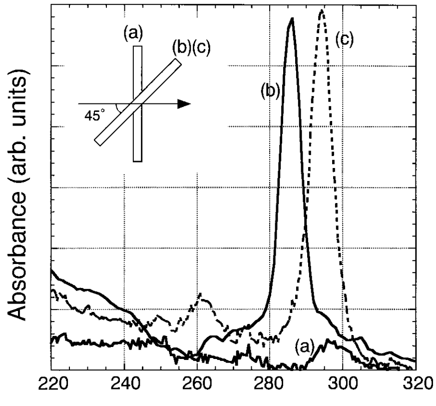

Fig. 1. UV–vis light absorption spectra of DM12 (b) and DM18 (a, c) films grown on quartz. Curve (a) was recorded with normal incidence and curves (b) and (c) were recorded when the sample was tilted by 45° with respect to the light path.

The perpendicular orientation of molecules in the films was also ascertained by AFM examinations. Fig. 2(a) and (b) show contact mode AFM images of DM12 and DM18 films, respectively. The darkest areas labeled A in both images are the substrate surface, while the areas labeled B indicate the first molecular layers of which the heights correspond to the length of molecules; 2.6 nm for DM12 and 3.9 nm for DM18. The areas C are the second layer with the height of molecular length. It was thus concluded that the molecules formed films in the layer-by-layer mode with their molecular chains perpendicular to the substrate surface. It is interesting that the upper layers grow at the edge of the underlying layers, as is indicated by arrows. The mean free path of migration of the molecules is so long that the nucleation occurs at the edge. The area D in Fig. 2(a) consists of five layers. DM12 tends to form thick layers easily at the present growth conditions.

Fig. 3 shows EX and PL spectra of DM12 and DM18 films. The PL spectra were recorded using the excitation lights tuned at the wavelength of absorption maxima. DM12 films give the emission peak centered at 332 nm (3.73 eV), while DM18 films give the emission at 342 nm (3.63 eV). The Stokes shifts observed for DM12 and for DM18 were 0.59 and 0.55 eV, respectively. The EX spectra for emission maxima are similar to the absorption spectra shown in Fig. 1. The excited states generated by the HOMO–LUMO transitions are found to be dominant origins of the light emissive states. The states originating from the transitions observed around 270 nm (4.59 eV) in the EX spectra of both films give some contributions to the emission peaks. These are possibly attributed to the transition from one level below HOMO to one level above LUMO. Fig. 4 shows the energy diagram illustrated on the assumption that the states concerned are singlet. The S_0, S_1 and S_2 indicate the ground state, the first excited state and the second excited state, respectively. Since the S_1 state of DM12 is located at slightly higher energy than that of DM18, energy transfer from DM12 to DM18 is feasible through the S_1 states in the appropriate molecular configuration. The energy transfer progressed in the heterostructured films composed of

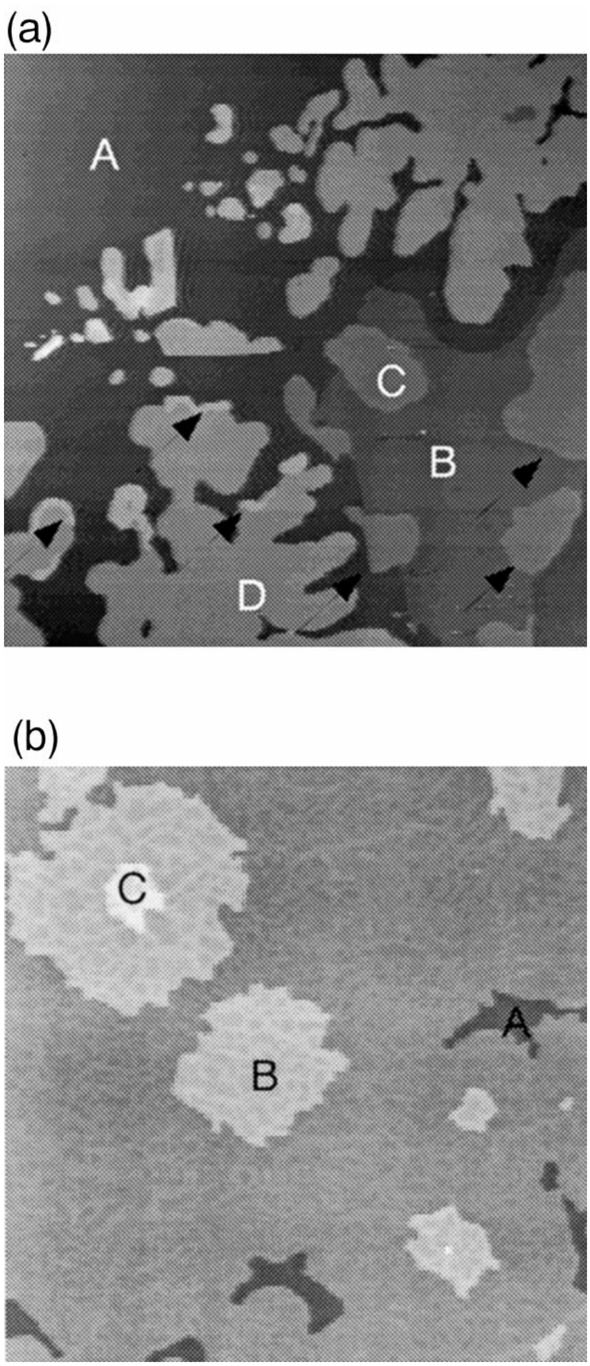

Fig. 2. AFM images of DM12 (a) and DM18 (b) films on silicon; area (A), substrate surface; area (B), the first monolayer; area (C), the second layer; and area (D), the grains composed of five layers. The scan size is 10 × 10 μm.

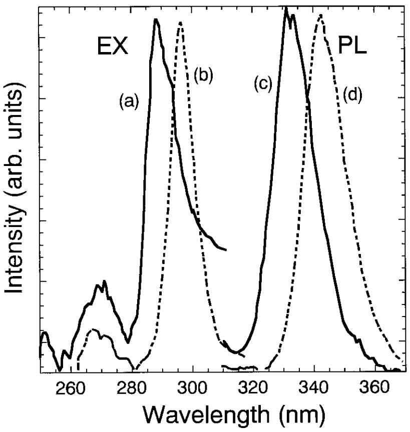

Fig. 3. The EX and PL spectra of DM12 (a, c) and DM18 (b, d) films on silicon. Curves (a) and (b) were the EX spectra for the emission at 332 and 342 nm, respectively. Curves (c) and (d) were obtained when the films were excited with the light at the wavelength of 287 and 297 nm, respectively.

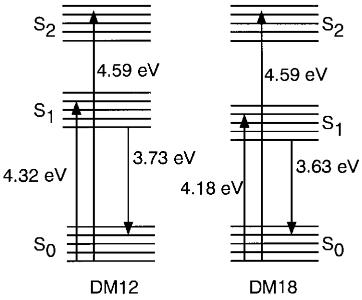

Fig. 4. The energy diagram illustrated on the basis of the present results.

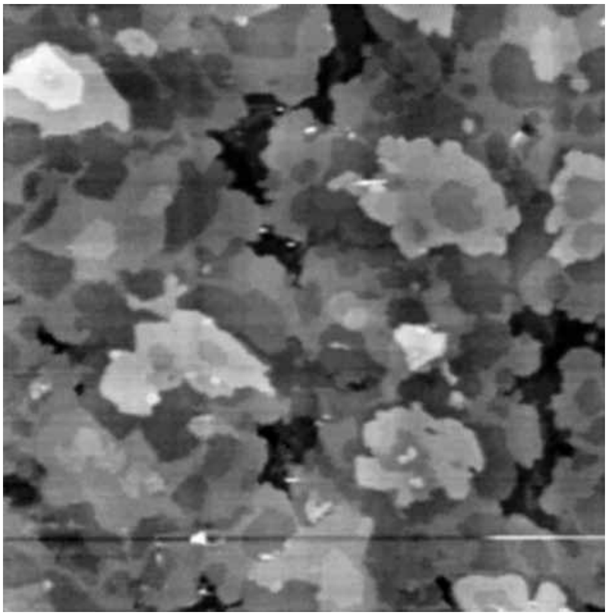

Fig. 5. AFM image of a heterostructured film composed of DM12 films on DM18 ultrathin films. The scan size is 15 × 15 μm.

DM12 and DM18 layers will be demonstrated in the following sections.

Fig. 5 shows an AFM image of a heterostructured film consisting of DM12 layers on DM18 ultrathin films. DM12 molecules are found to form layers on DM18 with perpendicular orientation. Fig. 6 shows absorption spectra of the heterostructured film. Curve (a) was obtained at normal incidence, and curve (b) was

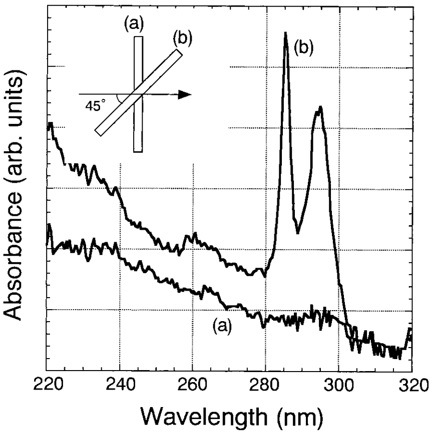

Fig. 6. Optical absorption spectra of a heterostructured film with normal incidence (a) and grazing incidence (b).

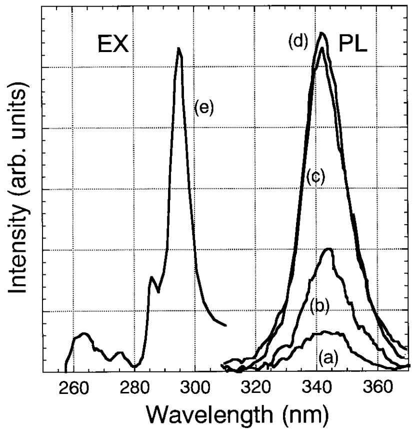

Fig. 7. The EX and PL spectra of a heterostructured film. The curves (a), (b), (c) and (d) were recorded with the excitation light at the wavelength of 282, 287, 292 and 297 nm, respectively. The EX spectrum (e) was for the emission at 342 nm.

recorded when the substrates were tilted by 45° with respect to the light path. The molecules are confirmed to have perpendicular orientation. The spectrum is composed of the overlapping of absorption spectrum of DM12 and DM18 films.

Fig. 7 shows EX and PL spectra of the film. The curves (a), (b), (c) and (d) were recorded with the excitation light at the wavelengths 282, 287, 292 and 297 nm, respectively. All curves have the peak centered at 342 nm, which corresponds to the emission from DM18 molecules. Noticeable emission from DM12 was not detected around 332 nm, even when the films were excited with the light at wavelengths shorter than 287 nm. In the EX spectrum recorded for the DM18 emission, the contribution of the state originating from DM12 is clearly seen. The energy transfer from the excited state of DM12 to that of DM18 is found to occur effectively in the films. The interface between the layers is thought to play important roles in smooth energy transfer. Time resolved measurement for various types of heterostructures is in progress to reveal the mechanism of energy transfer. It is helpful and interesting to use such well defined systems as highly oriented molecular layers in order to study the mechanism.

In summary, we have prepared heterostructured films of DM12 and DM18 and studied their optical properties. The molecules formed highly oriented films in the layer-by-layer growth mode with their molecular chains perpendicular to the substrate surface. It was found that the energy transfer progressed effectively from the excited state of DM12 to that of DM18.

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