Preparation and Characterization of Highly Oriented Films of Poly(di-*n*-hexylsilane)

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ABSTRACT: We have found a simple method for the preparation of oriented films of poly(di-*n*-hexylsilane) (PDHS). The highly oriented PDHS film can be prepared by rubbing the as-cast film with a wiping paper, by which the Si-backbone chains were oriented along the rubbing direction. The differences in the structure of the PDHS film before and after the rubbing treatment was investigated by measurements of polarized electronic absorption and IR vibrational absorption spectra, AFM images, and X-ray diffraction. In the oriented film of PDHS with a *trans*-planar conformation, the *n*-hexyl side chains stand almost perpendicular to the substrate surface. This rubbing method can also be applied to thin films of other polysilanes and polygermanes.

Introduction

Polysilanes, which have unique characters of one-dimensional semiconductors with wide electronic gaps, have drawn growing interest recently.[1] A variety of physical properties, such as fluorescence with a high quantum yield,[2] a large nonlinear optical effect,[3,4] and photoconductivity with a high hole mobility,[5] have been found in polysilanes. These are attributed to the delocalized nature of σ-electrons on the Si-backbone chains.

The preparation of single crystals or highly oriented films is desirable for the investigation of electronic properties and their anisotropy of polysilanes. However, there are only a few reports on the preparation of a single crystal[6] and oriented films.[2,7] For example, oriented thin films of polysilanes are prepared by the Langmuir–Blodgett technique, which is only applicable to the specific polysilanes having hydrophilic parts in their side groups.

In this paper, we report a new simple method for the preparation of oriented films of poly(di-*n*-hexylsilane) (PDHS): rubbing the film repeatedly along a fixed direction with a wiping paper. Microscopic structures of the oriented films have been investigated by measurements of polarized absorption and IR spectra. In the oriented film the Si-backbone chain was proved to lie along the rubbing direction. In addition, we have revealed that the alkyl side chains attached to the Si backbone stand perpendicular to the substrate in the oriented film.

Experimental Section

Sample Preparation. Poly(di-*n*-hexylsilane) (PDHS) was synthesized by the Wurtz coupling method with slight modifications from that described previously.[8] The weight-average molecular weight (M_w) calibrated by a polystyrene standard was 2.44×10^5. Thin films were prepared by spin-coating from a heptane solution on fused quartz plates. The spin-coated films were first heated at 380 K for 15 min and were then allowed to stand overnight at room temperature. Anisotropic orientation of the thin films was accomplished by a rubbing method. The films were gently rubbed several times along a fixed direction with a wiping paper (e.g., a sheet of Kimwiper S-200, Kimberly-Clark Corp.). The oriented thin films, in which polysilane backbones are oriented along the rubbing direction, were obtained by this procedure. The anisotropy of the absorption due to the lowest exciton transition[9,10] was observed to increase with the number of times of rubbing and reached a constant value above a certain number of rubbing times which depended on the thickness of the thin film. In addition, we have observed no substrate dependence of the electronic spectra and the orientation characteristics for the oriented films.

Characterization. Absorption spectra of electronic transitions were measured using a deuterium discharge lamp equipped with a monochromator. The polarized light was made to pass normal to the sample surface, and the transmitted light was detected by a photomultiplier tube. For the measurements of the polarized absorption spectra, the light vector (**E**) was set to be either parallel or perpendicular to the rubbing direction of the thin films. The temperature of the sample was controlled to within ±1 K. Polarization angular dependences of absorption spectra of the oriented thin film were measured with polarized light by rotating the sample around the surface normal.

IR spectra of thin films were measured by Fourier transform spectroscopy to study the vibrational modes and their anisotropy. CaF_2 plates were used as the substrates for transmission measurements. To detect vibrational modes polarized normal to the surface, reflection–absorption (RA) spectra were measured at the grazing incidence. For the RA measurements, substrates precoated with aluminum films were utilized. The angle of incidence was set at 80°.

X-ray diffraction patterns of thin films at room temperature were obtained between 2° and 60° (2θ) with a diffractometer in step-scan mode (0.02°) using nickel-filtered Cu Kα irradiation. The surface structures of the films were investigated by atomic force microscopy (AFM). The AFM images were obtained with a Nanoscope II, Digital Instrument, in air at room temperature.

Results and Discussion

Polarized Electronic Spectra and Thermochromism in an Oriented Thin Film. In order to evaluate the orientation of the Si-backbone chains in the oriented PDHS films by the rubbing treatment, the angular dependence of polarized absorption was studied with normal incident polarized light. In Figure 1, we show the angular (θ) dependence of the absorption due to the lowest exciton[9,10] at 3.4 eV for the oriented PDHS film, θ being the angle between the polarized light and the rubbing direction. The angular dependence shows a maximum at $\theta = 0°$ and minima at $\theta = \pm 90°$. The dashed line in Figure 1 represents a simulated curve of angular dependence for the case of the perfect orientation of the transition moment along the rubbing direction. The observed values are almost on the simulated curve apart from some residual absorption at $\theta = \pm 90°$. Considering that the transition moment lies along the *trans*-planar Si-backbone chain,

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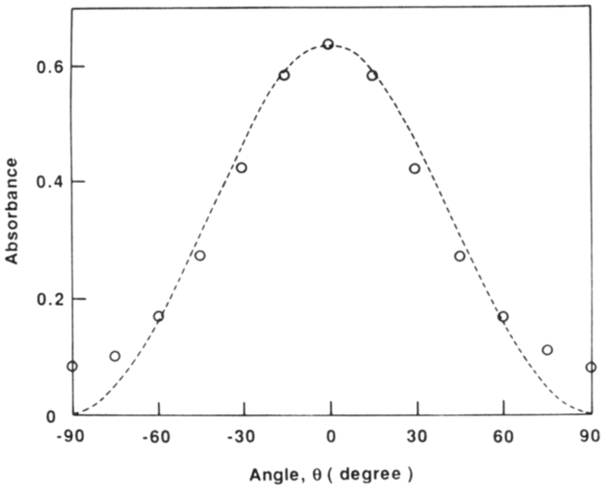

Figure 1. Angular dependence of the absorption due to the lowest exciton at 3.4 eV for the oriented PDHS film. The dashed line shows a simulated curve of angular dependence for the perfect orientation of a transition moment along the rubbing direction.

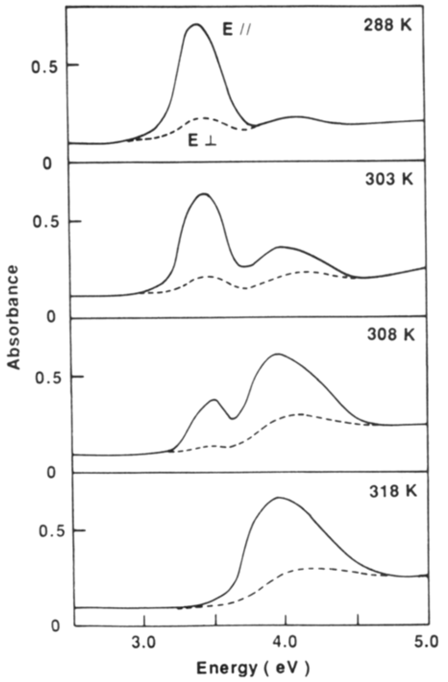

Figure 2. Change of polarized absorption spectra of the oriented film of PDHS around the phase transition temperature. Solid and dashed lines represent the spectra obtained with the light vector (**E**) parallel and perpendicular to the rubbing direction, respectively.

the Si backbones in the oriented film of PDHS are well oriented, though not perfect, along the rubbing direction.

The Si-backbone conformation in thin films of PDHS has been known to change from the *trans*-planar form to the *gauche*-like disordered one around ca. 316 K.[11] Temperature variation of polarized absorption spectra for the lowest exciton around the phase-transition temperature is shown in Figure 2. The energy shift of the absorption peak from 3.4 to 4.0 eV was observed upon the conformational transition of the Si backbone, which indicates a decrease in the delocalization of the σ-electrons along the Si backbones. From polarized absorption spectra in Figure 2, we can estimate an anisotropic ratio of the absorbance for the lowest exciton, $I_{\parallel}/I_{\perp}$, where $I_{\parallel}$ and $I_{\perp}$ are the integrated absorption over the peak region for the polarization parallel and perpendicular to the rubbing direction, respectively. The ratio is very large (amounting to ca. 15) in the ordered *trans*-planar conformation (low-temperature phase). However, the ratio was observed to decrease to ca. 2.8 in the *gauche*-like disordered state. This result is perhaps due to the decrease of delocalization of σ-electrons along the Si-backbone chains upon the conformational transition. For example, the transition dipoles of the localized exciton in the short conjugation region of the PDHS chain are likely to cant from the orientation of the original regular chains (i.e., the rubbing direction). It is also notable that the anisotropy of the absorption for the lowest exciton remains in the *gauche*-like disordered state. The lower but still persistent anisotropy of the absorption in the *gauche*-like disordered state may be essential for the thermally reversible phase transition: The spectral profile and the high anisotropy characteristic of the *trans*-planar form are completely restored with lowering the temperature for the rubbing-oriented films. Incidentally, it has been found that Ge-backbone chains of poly(di-*n*-hexylgermane) (PDHG)[12] can be oriented by the same rubbing method and show a very similar spectroscopic and thermochromic behavior to the case of PDHS.

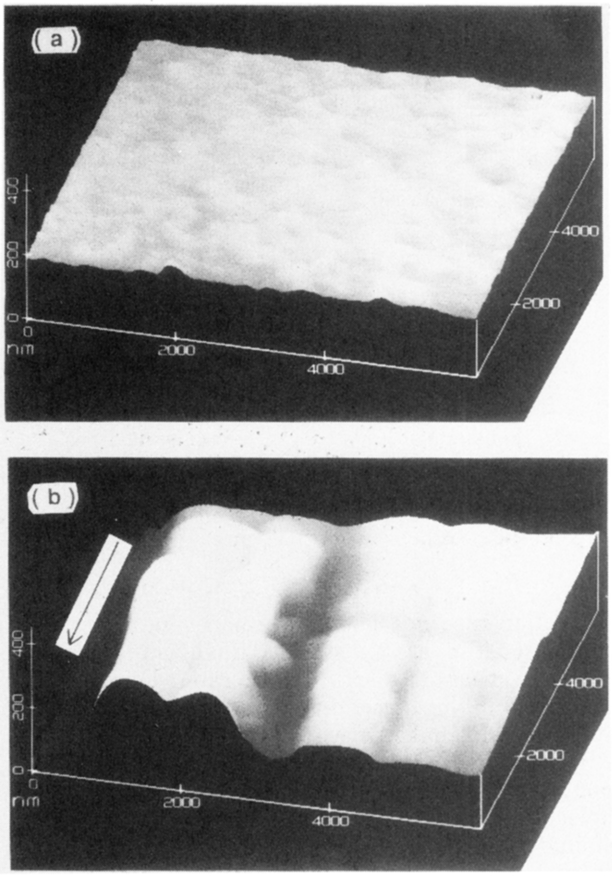

Figure 3. AFM images of the film (a) before and (b) after the rubbing treatment. The arrow indicates the rubbing direction.

Change in the Surface Structure with Rubbing Treatments. We have investigated the surface structure of the oriented PDHS film by atomic force microscopy (AFM), by comparing it with that of the unoriented films. Figure 3 shows the AFM images of thin films on the substrates before and after the rubbing treatment, corresponding to the unoriented and the oriented films, respectively. The surface of the unoriented films is fairly flat over a wide area. With the rubbing treatment, the oriented film shows ridges and grooves on the surface along the rubbing direction, which is indicated by an arrow in Figure 3b. This direction coincides with that of the

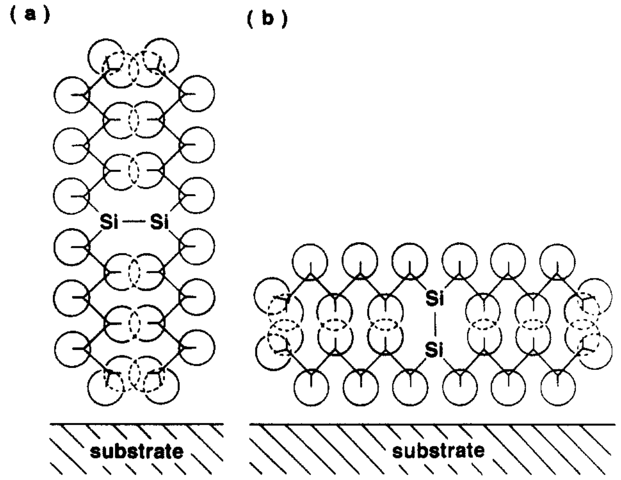

Figure 4. Two possible molecular orientations of *trans*-planar PDHS in the oriented film. The *trans*-planar Si backbones orient perpendicular to the plane of the figure.

polymer chains of PDHS as revealed by the polarized absorption spectra. The AFM images indicate that the unoriented films are transformed finally into the oriented films by a shear or a plastic deformation. Faint striations along the rubbing direction are observed for the oriented film even with naked eyes.

Structure of Oriented Thin Films. PDHS forms a monoclinic structure with a unit cell containing two molecules.[13] According to the literature,[14] the *n*-hexyl side chains, which exist in the *trans*-planar structure, are oriented perpendicular to the plane containing the *trans*-planar Si backbone. Since it is obvious from the polarized absorption spectra for the oriented film that *trans*-planar Si-backbone chains are disposed parallel to the substrate, two possible models are expected for the molecular arrangement of *trans*-planar PDHS as schematically shown in Figure 4. In the both cases the direction of the Si-backbone chain is perpendicular to the plane of the figure, corresponding to the rubbing direction.

We have investigated the structure of the oriented thin films by measurements of infrared transmission and RA spectra. The light **E** vector lies in the film plane for the transmission mode, whereas **E** is along the surface normal for the RA mode.[15] Therefore, the transmission and RA spectra for the vibrational bands of the *n*-hexyl side chains,[16] which show up in the infrared region above 800 cm^{-1}, can bring about useful and complementary information in determining the orientation of the alkyl side chains in the oriented PDHS film. The infrared transmission and RA spectra of the oriented film are shown in Figure 5.

Concerning the vibrational modes of alkyl chains, the IR spectra of polysilanes with alkyl substituents[16] and polyethylenes[17,18] have been studied in detail and their vibrational assignments have been made thoroughly. In the CH stretching region (2800–3000 cm^{-1}) there are a number of bands attributable to methyl ($-CH_3$) and methylene ($-CH_2-$) stretching vibrations. The transition moments of the symmetric and the asymmetric CH_2 stretching vibrations ($\nu_s(CH_2)$ and $\nu_a(CH_2)$), which are prependicular to the alkyl side-chain axis, have been proved to correspond to the directions parallel and perpendicular to the plane of the alkyl chains, respectively.[17,18] As for the symmetric and asymmetric CH_3 stretching vibrations ($\nu_s(CH_3)$ and $\nu_a(CH_3)$), the transition moment of $\nu_s(CH_3)$ is in a direction connecting the methyl carbon and the adjacent methylene carbon, while $\nu_a(CH_3)$ has in-plane and out-of-plane transition moments. By applying these vibrational assignments to the presently observed transmission and RA spectra, we could determine the orientation of the *n*-hexyl side chains in the oriented PDHS film. We have compared relative intensities ($R_1 = \nu_a(CH_2)/\nu_a(CH_3)$ and $R_2 = \nu_s(CH_2)/\nu_s(CH_3)$) of asymmetric and symmetric stretching bands, for the three infrared spectra, i.e., the transmission spectrum of powder dispersed in KBr pellet and the transmission and RA spectra of the oriented film. The powder spectra of polysilane stand for a randomized orientation of the Si backbones. These results are summarized in Table I.

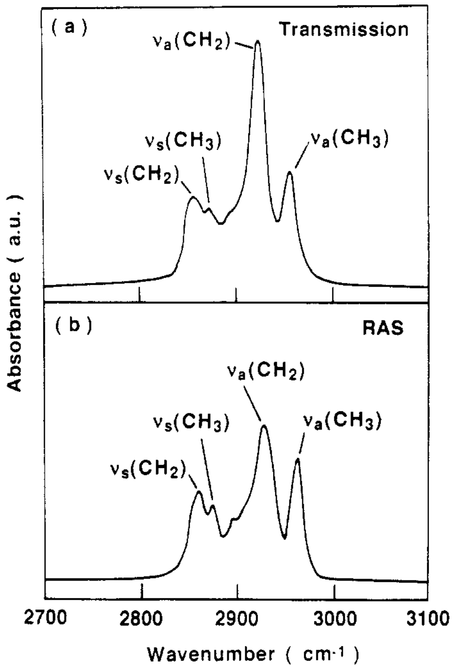

Figure 5. Infrared (a) transmission and (b) RA spectra for the oriented film of *trans*-planar PDHS.

Table I. Relative Intensities of Asymmetric and Symmetric Stretching Bands for IR Transmission and Reflection–Absorption (RA) Spectra of the Oriented Film and IR Transmission Spectra of Powder Dispersed in KBr Pellet

	transmission	RA	powder
$R_1 = A(\nu_a(CH_2))/A(\nu_a(CH_3))$	2.10	1.25	1.45
$R_2 = A(\nu_s(CH_2))/A(\nu_s(CH_3))$	1.85	1.59	1.69

The value of R_1 in the transmission spectra of the oriented film is larger than that in the spectra for the powder. R_1 in the RA spectra of the oriented film shows a further smaller value. This indicates that the transition moment of $\nu_a(CH_2)$ is almost parallel to the film surface, indicating the validity of the two models shown in Figure 4. The value of R_2 behaves similarly to the case for R_1, which shows that the transition moment of $\nu_s(CH_2)$ inclines more than the transition moment of $\nu_s(CH_3)$ with respect to the surface normal. As is seen from Figure 4, the transition moment of $\nu_s(CH_2)$ is disposed parallel to the surface in model (a) while it is perpendicular to the surface in model (b). These results indicate that model (a) is more probable, in which the orientation of the *n*-hexyl side chains is almost perpendicular to the substrate and hence both transition moments of the asymmetric and symmetric CH_2 bands lie parallel rather than perpendicular to the substrate.

Figure 6 shows polarized infrared transmission spectra in the CH_2 and CH_3 stretching regions for the oriented film. Solid and dotted lines represent the polarized spectra for the light vector parallel and perpendicular to the rubbing direction, respectively. The anisotropy of the two

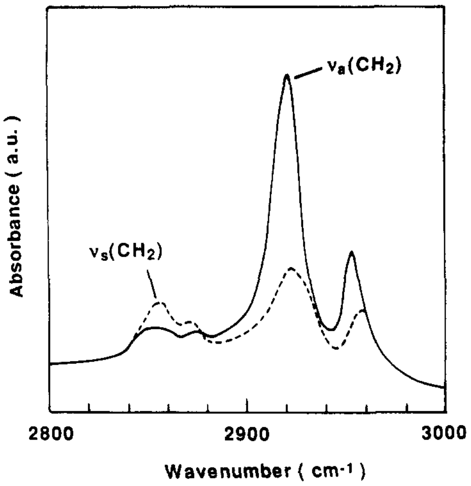

Figure 6. Polarized infrared transmission spectra for the oriented film of *trans*-planar PDHS. Solid and dashed lines represent the spectra obtained with the light vector parallel and perpendicular to the rubbing direction, respectively.

bands at ca. 2920 and 2850 cm^{-1}, which are respectively assigned to the asymmetric and symmetric CH_2 stretching bands, shows a different polarization dependence. Since the transition moments of the two bands are orthogonal to each other and are perpendicular to the alkyl side-chain axis, this fact gives further evidence for almost perpendicular orientation of the *n*-hexyl side chains with respect to the substrate surface.

All the results shown above indicate that the molecular orientation of PDHS with the *trans*-planar conformation in the oriented film is described by model (a) rather than model (b) in Figure 4. If we assume that *trans*-planar Si backbones are crystallized in a monoclinic form, the *n*-hexyl side chains may be inclined to some extent due to the interaction between the *n*-hexyl side chains of the neighboring polysilane.

Further insight into the structure of the oriented thin films was provided by X-ray diffraction measurements. For the unoriented films, a set of diffraction peaks were observed at $2\theta = 7.4°, 14.8°$, and $22.2°$. The corresponding spacing is consistent with the interplanar distance between Si-backbone chains.[13] The X-ray diffraction pattern of the oriented film prepared by the rubbing treatment is nearly identical with that of the unoriented film, indicating that the lattice constants do not change with the rubbing treatment. It is concluded that the rubbing treatment allows the Si-backbone chains to orient along the rubbing direction, maintaining the original crystal lattice structure.

Summary

We have demonstrated that the oriented films of PDHS can be easily prepared by the rubbing treatment, by which *trans*-planar Si-backbone chains are oriented along the rubbing direction. The difference in the structures of PDHS thin films before and after the rubbing treatment has been investigated by polarized electronic absorption and IR vibrational spectra, AFM, and X-ray diffraction. A decrease in the anisotropy of the absorption for the lowest exciton was observed upon the conformational change of the Si backbones from the *trans*-planar form to the *gauche*-like disordered one. This is attributed to the canting of the exciton dipoles in the short conjugation regions of the PDHS chain. From the infrared transmission and RA spectra, it was concluded that the *n*-hexyl side chains of PDHS stand almost perpendicular to the substrate. The rubbing method can provide a simple and convenient way for the preparation of the oriented films of PDHS. This method can also be applied to the thin films of a variety of polysilanes and polygermanes.

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