Orientation of Polysilanes along the Film Thickness and their Properties

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Abstract

The method to prepare polysilane films aligning along their thickness has been developed. Oriented polysilane films of $(MeSiPh)_n$ and $(n\text{-}Hex_2Si)_n$ with the respective aligning of 84% and 94% of Si chains are demonstrated and their molecular orientations are investigated. The plane of phenyl rings are perpendicular to the aligned Si chains in the oriented $(MeSiPh)_n$ film and the plane of trans-planar of *n*-hexyl side chains is also perpendicular to the aligned Si chains in the oriented $(n\text{-}Hex_2Si)_n$. The carrier transport measurement indicates that the hole drift mobility is improved in the oriented films of $(MeSiPh)_n$. However, it is not sufficient and its reason is discussed in terms of the energetic and positional disorders of the carrier hopping sites.

Introduction

The local carrier-mobility in polysilane films has been estimated to be higher than 10^{-1} cm^2/Vs by a pulse radiolysis time resolved microwave conductivity measurement.[1] This implies that polysilanes have a high potential as a carrier transport material. Although which of electron or hole mainly contributed to the conductivity was not determined in that experiment, the estimated value is two or three orders of magnitudes higher than the hole drift mobilities[2] measured by a time-of-flight (TOF) technique for ordinary polysilane films in which polysilanes were unoriented. A big issue appears. It is whether such a high mobility can be measured or not in oriented films by a conventional TOF technique.

We have reported the anisotropy of photoconduction for the oriented films of $(c\text{-}HexSiMe)_n$ which were prepared by an electric field induced method[3,4] and an air-flow dipping (AFD) method.[5,6] The photoconductivity is one order of magnitude higher along the Si chains and two orders of magnitude less perpendicular to the Si chains than for unoriented films. A TOF measurement perpendicular to the Si chains in the oriented films of $(c\text{-}HexSiMe)_n$[7,8)] and $(n\text{-}Hex_2Si)_n$[8)] prepared by an AFD method has been carried out. The results show that the orientation reduces the potential disorder and the preexponential factor of the hole drift mobility perpendicular to the Si chains is more than two orders of magnitude lower than that in unoriented films. This suggests that the hole drift mobility along the Si chains is ~10^{-1} cm^2/Vs at room temperature for these polysilanes,[9] which is consistent with the measurement of a local mobility. In this work, we have developed a method to align polysilanes along the film thickness for a TOF measurement along the Si chains. We will report the structure of the resultant oriented films of $(MeSiPh)_n$ and $(n\text{-}Hex_2Si)_n$ and the primitive result of the carrier transport property in $(MeSiPh)_n$ films.

Experimental

Polysilanes used were $(MeSiPh)_n$ and $(n\text{-}Hex_2Si)_n$ and their molecular weights were 30,800 and 250,000, respectively.

Polysilanes were spin-casted or simply casted on substrates to form films. The film was sandwiched with a spacer and a cover glass plate as shown in Fig. 1. The cover glass plate was forced to press the film once and then the force was released to stretch the film along its thickness. This process, so called the method of stretching along the thickness (SAT), was carried out in vacuum at a temperature higher than the glass transition temperature of polysilanes.

Absorption spectra for ultraviolet (UV) light and infrared (IR) light were measured for polysilane films prepared on quartz plates and Si wafers, respectively.

Hole transport properties were measured by a TOF technique. Samples had a sandwich structure consisting of semitransparent Au electrode / stretched $(MeSiPh)_n$ film / bisazo film / indium-tin-oxide film coated on glass substrate, where holes were photogenerated at the bisazo layer with 10 ns pulsed light (480 nm) and injected into the polysilane film.

Results and Discussion

Orientation of $(MeSiPh)_n$ and $(n\text{-}Hex_2Si)_n$ films

Figure 2(a) shows the thickness profile of the $(MeSiPh)_n$ film after the SAT process. The original film thickness was 400 nm and the central region of ~ 3 × 6 mm^2 was stretched to have the thickness of ~750 nm. Its stretching rate is ~190%. The edge of a part adsorbed on to the cover glass plate during the stretching process was observed by a tapping-mode atomic-force-microscope as shown in Fig. 2(b). The edge is quite sharp and appears with a 150 nm step. The dark and lower part, which had not contacted the cover glass plate, corresponds to the steep slope in Fig. 2(a). The unevenness of the stretched region is caused by the spatial fluctuation of the absorption force to the cover glass plate. The circumference of the stretched region forms a groove with the width of 0.8 mm and the depth of 150 nm to serve the polysilanes to the stretched region. It is believed that the polysilanes are stretched uniformly in the film.

Figure 3 shows the UV absorption spectra of the stretched and unstretched films of $(MeSiPh)_n$ and $(n\text{-}Hex_2Si)_n$. Here the stretching rates of these films are 210 and 230%, respectively. The unstretched film of $(MeSiPh)_n$ has a sharp peak at 3.68 eV due to the σ–σ^* transition in the Si chains and a broad peak at 4.5 eV due to the π–π^* transition in the phenyl substituents. However, for the stretched film the sharp peak and broad peak become small by factors of 0.23 and 0.37, respectively. The decrease in the sharp peak indicates that 84% of Si chains align along the film thickness, i. e. the stretching direction, because its transition moment is along the Si backbone. The decrease in the broad peak indicates that the plane of more than 90% of the phenyl substituents is perpendicular to the aligned Si chains. A possible molecular orientation based on these results is illustrated in Fig. 5.

For $(n\text{-}Hex_2Si)_n$, the absorption peak due to σ–σ^* transition in the Si chains, which appears at 3.68 eV, decreases by a factor of 0.09 by stretching the film, indicating that 94% of the Si chains align along the film thickness. This high value corresponds to the high stretching ratio.

Figure 4 shows the IR absorption spectra of the stretched and unstretched films of $(MeSiPh)_n$ and $(n\text{-}Hex_2Si)_n$. Their respective stretching ratios are 144 and 230%. A considerable change in the spectra by the SAT process of $(MeSiPh)_n$ is seen as a 1.5 times increase in peaks at 3049 and 3067 cm^{-1} attributable to the stretching vibration of CH bonds$^{10)}$ in the phenyl substituents. This indicates that the plane of the most phenyl substituents is parallel to the substrate surface in the stretched film, consistent with the molecular orientation as estimated from the UV absorption spectra, shown in Fig. 5. It is noticed that the peak at 460 cm^{-1} due to the Si-Si stretching vibration$^{10)}$ does not decrease for the stretched film, suggesting that its IR activity is strengthened.

For $(n\text{-}Hex_2Si)_n$, the SAT process increases the IR absorption peaks at 670 and 2857 cm^{-1} due to the SiC stretching vibration and the symmetric CH_2 stretching vibration$^{11)}$, respectively, while it decreases the peak at 2923 cm^{-1} due to the asymmetric CH_2 stretching vibration.$^{11)}$ This indicates that the stretched film has predominantly Si-C bonds parallel to the substrate surface and CH_2 bonds with the H to H direction perpendicular to the substrate surface in the *n*-hexyl side chains. This molecular orientation is also illustrated in Fig. 5, where the trans-planar plane of the *n*-hexyl side chains is parallel to the substrate.

These results indicate that the SAT process is a simple method to realize polysilane films highly oriented along the thickness.

Carrier Transport In Oriented (Mesiph)$_N$ Films

Figure 6 shows the electric field dependence of hole drift mobility in the oriented and unoriented films of $(MeSiPh)_n$. The data for the unoriented film are referred from Ref. 12, where the sample is free from the residual solvent in terms of the hole transport. The oriented film shows higher hole drift mobility by about one order of magnitude and the stronger field dependence than the unoriented film.

These differences are analyzed based on the disorder model. The disorder model gives a drift mobility written as$^{13)}$

$$\mu_d = \mu_0 \exp\left[-\left(\frac{2}{3}\frac{\sigma}{kT}\right)^2\right]\exp\left[c\left\{\left(\frac{\sigma}{kT}\right)^2 - \Sigma^2\right\}F^{1/2}\right], \qquad (1)$$

where μ_0 is the preexponential factor which reflects the average hopping distance, σ is the width of the density of states in hopping sites, Σ is a parameter that characterizes the degree of positional disorder, F is the electric field, k is the Boltzmann constant and T is the measurement temperature.

Applying the formalism to the data in Fig. 6, we have estimated the values of μ_0, σ and Σ listed in Table I. It is evidenced that the orientation of polysilanes along the carrier transport pass increases the μ_0 value by about two orders of magnitude. However, the values of σ and Σ also increase by the orientation. This indicates that the average hopping distance of carriers become short but the energetic and positional disorder of the hopping sites increases. The change in the disorder parameters is in the opposite tendency to the expectation that we have reached from the carrier transport experiment perpendicular to the orientation of polysilane.^{11} This reason is unclear and is the subject for further study.

Table I. Preexponential factor and disorder parameters for oriented and unoriented films of $(MeSiPh)_n$.

$(MeSiPh)_n$	μ_0 (cm^2/Vs)	σ (meV)	Σ
unoriented	2.7×10^{-2}	97.4	2.12
oriented	2.03	114	3.79

Summary

The method to prepare polysilane films oriented along their thickness has been developed, where the two dimensional stretching technique has been employed. The aligning of

84% and 94% of Si chains has been demonstrated for $(\mathrm{MeSiPh})_n$ and $(n\text{-}\mathrm{Hex}_2\mathrm{Si})_n$, respectively. In the oriented films of $(\mathrm{MeSiPh})_n$ the plane of the phenyl substituents is presumably perpendicular to the aligned Si chains. For the oriented films of $(n\text{-}\mathrm{Hex}_2\mathrm{Si})_n$, the *n*-hexyl side chains are aligned with their trans-planar plane perpendicular to the aligned Si chains. The preexponential factor of the hole drift mobility along the orientation of $(\mathrm{MeSiPh})_n$ has been measured to be about two orders of magnitude higher than that in the unoriented film. However, the hole drift mobility does not increase so much as being expected because of the higher energetic and positional disorders.

Acknowledgments

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Biography

Yoshikazu Nakayama received his B.S. degree in Electric Engineering from Osaka Prefecture University in 1972 and a Ph.D. in Applied Physics from Osaka University in 1985. In 1972, he joined Matsushita Electric Industry Co., Ltd. where he worked on research in optical memory using holograms. In 1979, he moved to Osaka Prefecture University and has worked on solid-state physics, especially photoconductive materials, and plasma processing for electronic materials. He was appointed to the position of professor in 1995. He is a member of the IS&T and the Material Research Society. E-mail: nakayama@pe.osakafu-u.ac.jp

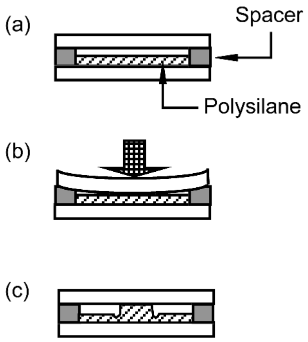

Figure 1: Process to prepare polysilane films oriented along the thickness

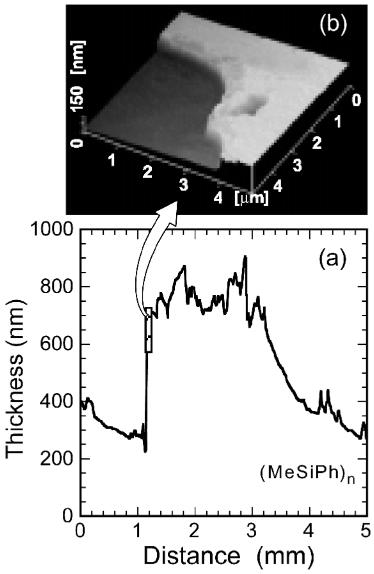

Figure 2: (a) Thickness profile of the $(MeSiPh)_n$ film after stretching along its thickness and (b) AFM image of the edge of the stretched portion.

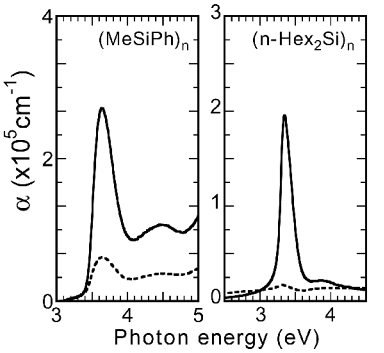

Figure 3: UV absorption spectra of the stretched (dotted line) and unstretched (solid line) films of $(MeSiPh)_n$ and $(n\text{-}Hex_2Si)_n$

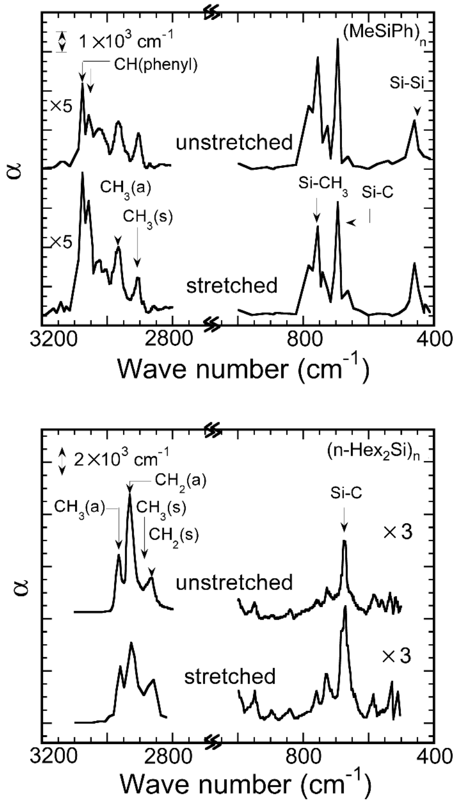

Figure 4: IR absorption spectra of the stretched and unstretched films of of $(MeSiPh)_n$ and $(n\text{-}Hex_2Si)_n$

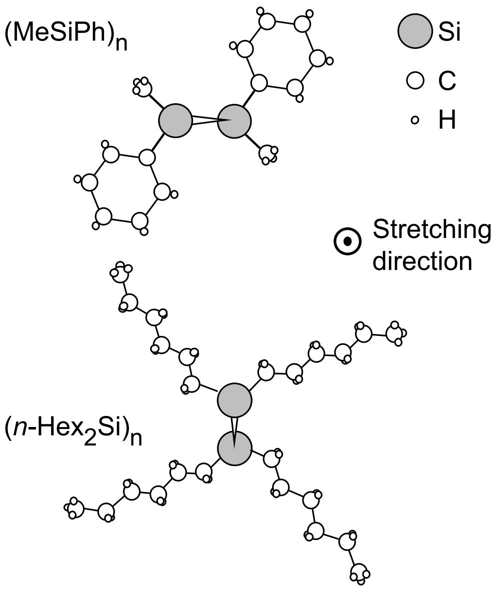

Figure 5. Molecular orientation in the oriented films of $(MeSiPh)_n$ *and* $(n\text{-}Hex_2Si)_n$.

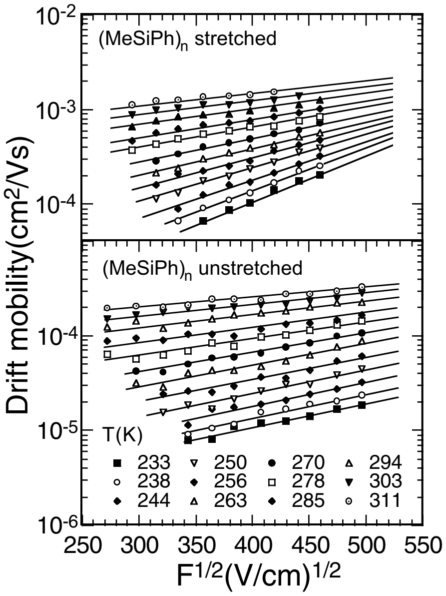

Figure 6. Eelectric field dependence of hole drift mobility in the oriented and unoriented films of $(MeSiPh)_n$.