Finite chain-length effect on nonlinear optical response in polysilane as investigated by electroabsorption spectroscopy

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We have investigated the electroabsorption spectrum for a thin film of the silicon oligomer $Si_{10}(CH_3)_{22}$, a finite-chain analog of quasi-one-dimensional semiconductor polysilanes. The obtained spectrum can be well reproduced by a four-level model in which a one-photon-forbidden state is located between two one-photon-allowed states. By comparison with the spectra of polysilanes, it was found that the transition dipole moment between the excited states decreases significantly with a decrease of chain length. This can be ascribed to the confinement of the excited states. [S0163-1829(96)53640-4]

Silicon-based polymers provide us with opportunities for study of various optical properties depending on the Si-skeleton structures. In polysilanes with linear Si chains, the linear as well as nonlinear optical properties in the near-UV-region are characterized by the one-dimensional Wannier exciton model.[1–4] The finite-size analogs of the polysilanes, silicon oligomers, have also been studied[5–14] and the various finite-size effects in absorption spectra have been observed.[14] The confinement of the excited states causes various kinds of effects on optical spectra such as the shift of the absorption peak energy, the decrease of the oscillator strength of the lowest absorption band, and the increase of the linewidth of the absorption peak. Among them, the size effect on the optical nonlinearity is expected to show up even more conspicuously, since the change of wave function affects more significantly, in general, nonlinear optical susceptibilities rather than linear susceptibility.

As for polydihexylsilane (PDHS) among various polysilanes, optical nonlinearity has been observed in various experimental configurations such as third-harmonic generation (THG),[2] electric-field-induced second-harmonic generation (EFISHG),[4] and electroabsorption (EA).[3] A series of studies have revealed that the nonlinear optical response can be reproduced quantitatively in terms of the one-dimensional Wannier excitonic system. In particular, it is characteristic of the one-dimensional system that the states which cannot be observed by the normal one-photon absorption measurements are greatly contributory to the spectra of third-order nonlinear susceptibility. In this sense, the finite-size effect for the higher excited states and its influence to nonlinear optical process are of particular interest. In this paper, we have investigated the EA spectrum of silicon oligomer, $Si_{10}(CH_3)_{22}$, and discuss the contribution of the higher excited states to nonlinear optical response in comparison with the case of polysilanes.

Silicon oligomer $Si_{10}(CH_3)_{22}$ was synthesized as follows: Using Li metal as a catalyst, smaller molecules, Si_2Me_6 and cyclo-Si_6Me_{12}, were synthesized from trimethylchlorosilane and dimethylchlorosilane. $Si_6Me_{12}Cl_2$ and $Si_2Me_4Cl_2$ were obtained by chlorination of cyclo-Si_6Me_{12} and Si_2Me_6, respectively. Finally, $Si_{10}(CH_3)_{22}$ was polymerized from $Si_6Me_{12}Cl_2$ and $Si_2Me_4Cl_2$ with Na metal and was obtained in the form of powder. By a similar synthetic procedure, we could prepare a series of Si oligomer, $Si_n(CH_3)_{2n+2}$ with $n=2-16$, and have already reported the systematic n dependence of the energy, linewidth, and oscillator strength of lower-lying one-photon transition, in the form of solution.[14] For the EA measurement, we need the thin solid film and encountered the difficulty of preparing film samples, especially for the low-$n(\leqslant 6)$ oligomers. Practically, only the $n=10$ (and also $n=8$) oligomers enabled us to make a spectroscopic quality of thin film. The $Si_{10}(CH_3)_{22}$ $(n=10)$ oligomer film is free from some structural change upon cooling which was observed for the $n=16$ film.

The film was spincast onto an ITO (indium tin oxide)-coated quartz substrate from the heptane solution. A semitransparent aluminum electrode (thickness: 250 Å) was

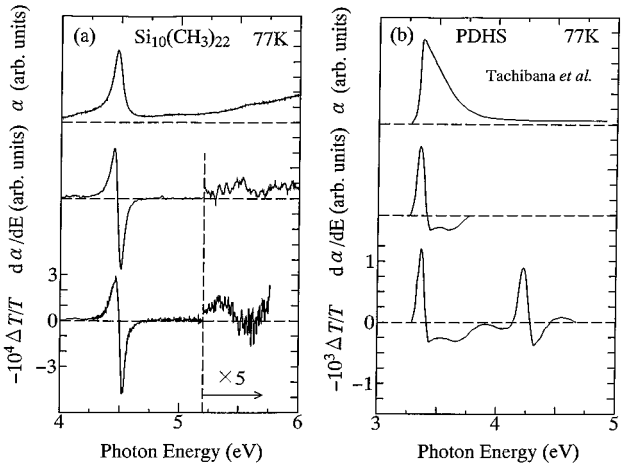

FIG. 1. (a) Electroabsorption spectrum for a spincast $Si_{10}(CH_3)_{22}$ film on a quartz substrate at 77 K (lower spectrum), compared with the absorption spectrum (α, upper), and its first energy derivative ($d\alpha/dE$, middle). (b) Electroabsorption spectrum (lower), absorption spectrum (upper), and its first energy derivative (middle) of polydihexylsilane (PDHS). The PDHS spectra are reproduced from Ref. 3.

vacuum evaporated onto the spincast film. In the EA measurements, we applied an ac electric field of 10 V between the ITO and semitransparent aluminum electrodes. The optics were the same as those used in the absorption measurements. Using a lock-in amplifier, we extracted the $2f$ component (ΔT) of the transmittance (T) under an applied electric field of frequency f (typically 1 kHz). The EA spectrum was obtained as $-\Delta T/T$.

Figure 1(a) shows the EA spectrum for a spincast film of $Si_{10}(CH_3)_{22}$ on the ITO-coated quartz substrate at 77 K. In the figure, we show the spectrum of the ordinary absorption (α) measured at the same temperature (77 K) as well as its first derivative ($d\alpha/dE$) for comparison. We also show the same set of spectra for poly(dihexylsilane) (PDHS) in Fig. 1(b), which are reproduced from Ref. 3. In the EA spectrum, a relatively large signal is observed around 4.5 eV, while a small one shows up around 5.4 eV. The EA profile around 4.5 eV is in accord with the shape of the $d\alpha/dE$ spectrum at the corresponding energy. This indicates that the oscillatory structure comes from the Stark shift induced by the applied electric field. On the other hand, the structure around 5.4 eV is different in intensity and shape from that seen in the $d\alpha/dE$ spectrum around 5.5 eV. Such a higher-lying EA band is generally seen for the one-dimensional conjugated polymers as prototypically seen for PDHS in Fig. 1(b) and can be understood in terms of higher-lying excitonic states. At a glance, however, relative magnitude of the higher-lying EA signal to that of the Stark signal is much weaker in the oligomer than in PDHS. This implies that the nonlinear optical response is much reduced in the finite chain-length system.

As described in previous papers,[3,4] the essential features of the nonlinear optical response of the one-dimensional excitons in polysilanes can be explained qualitatively by the four-level model, as shown in Fig. 2. Namely, the $\nu=0$ ground state (^1A_g type), the $\nu=1$ lowest allowed exciton (^1B_u) state, the $\nu=2$ forbidden (^1A_g) one, and the $\nu=3$ allowed (^1B_u) one are predicted. In the finite chain-length system, there may be a change of the ordering of the states.[15] According to the calculation performed by means of the Peierls-extended Hubbard model,[16] however, the one-photon forbidden state mostly contributing to the nonlinear optical process is located above the lowest one-photon allowed states irrespective of the chain length and Coulomb correlation even for short chain systems. On this background, we attempted to reproduce the experimental feature using the four-level model in which a one-photon-forbidden state is located between two one-photon allowed states.

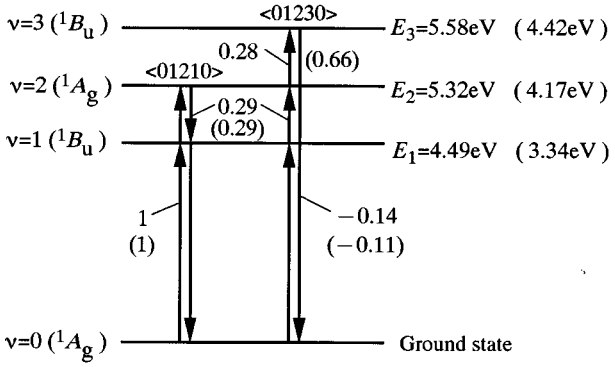

FIG. 2. The four-level model and fitting parameters used in the calculation for Fig. 3. The values of the transition dipole moments are indicated in units of $\langle 0|x|1\rangle$. For comparison, the values for the PDHS are also shown in parentheses. The value between $\nu=1$ and 2 for $Si_{10}Me_{22}$ is assumed to be the same as that of PDHS.

In Fig. 3 the experimental results are compared with the imaginary part of the $\chi^{(3)}(-\omega;0,0,\omega)$ spectrum calculated by the four-level model of Fig. 2. The calculation reproduces fairly well the EA spectrum. The $d\alpha/dE$ spectrum can only explain the structure around the $\nu=1$ main peak of the absorption spectrum, as shown in Fig. 1, whereas the four-level model can account for the whole feature. Thus, it is likely that there exist at least a one-photon-forbidden and a higher-lying one-photon-allowed state above the lowest one-photon-allowed state, the latter of which is readily observed as a

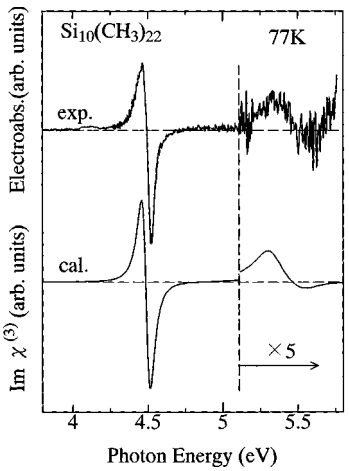

FIG. 3. Im $\chi(3)$ spectrum (lower) calculated by the four-level model and experimental electroabsorption spectrum (upper) of a spincast $Si_{10}(CH_3)_{22}$ film.

hump around 5.6 eV in the ordinary absorption spectrum shown in Fig. 1(a).

Nonlinear optical spectra are governed by superposition of the multiphoton resonant processes.[4] The two dominant processes in the four-level model are depicted in Fig. 2, i.e., the $\nu=0\rightarrow1\rightarrow2\rightarrow1\rightarrow0$ ($\langle01210\rangle$) transition and the $\nu=0\rightarrow1\rightarrow2\rightarrow3\rightarrow0$ ($\langle01230\rangle$). These processes are cooperative in the EA and EFISHG configurations, but tend to cancel each other in the THG configuration. Thus, the transition dipole moments between the higher excited states are the important factors to govern the nonlinear optical spectra including the EA one. The values of the transition dipole moments indicated in Fig. 2 and used in the following discussion are all normalized to that between the ground state and $\nu=1$, $\langle0|x|1\rangle$. The corresponding values in polysilane PDHS (Ref. 4) are also shown in parentheses for comparison.

First, from the absorption spectra, we estimate the transition dipole moment $\langle0|x|3\rangle$ between the ground state and $\nu=3$ state to be -0.14. Its absolute value is slightly larger than that of PDHS (-0.11). The peak position of the $\nu=2$ state and the ratio r of the matrix elements, $r=\langle0|x|3\rangle\langle3|x|2\rangle/\langle0|x|1\rangle\langle1|x|2\rangle$, are fitting parameters in the analysis of the EA spectrum (Fig. 3). The obtained energy positions are indicated in Fig. 2. The energy separations between the respective ($\nu=1-3$) levels for this $n=10$ oligomer nearly coincide with those for PDHS (virtually $n=\infty$), indicating a remarkably similar structure of the excited (or exciton) levels in the $n\geqslant10$ oligomers. Nevertheless, the obtained ratio for $n=10$ is $r=0.135$, which is much less than that of PDHS ($r=0.25$). By contrast, the oscillator strength of the $\nu=1$ state, i.e., $|\langle0|x|1\rangle|^2$, remains nearly unchanged for $n\geqslant10$.[14] These observations confirm that the contribution of the higher-energy-lying one-photon-allowed/forbidden states are important to the nonlinear optical spectra and that it becomes notably smaller with the decrease of the chain length.

In terms of the one-dimensional exciton picture, the squeeze of the ratio r can be interpreted as due to the confinement of the exciton wave function with higher quantum numbers. Provided that $\langle1|x|2\rangle$ of silicon oligomers is the same as that of PDHS (0.29), we can deduce that the normalized dipole moments between $\nu=2$ and 3 states is 0.28 for the oligomer, which is much less than that of PDHS (0.66). The $\langle2|x|3\rangle$ is one of the important matrix elements governing nonlinear optical spectra of the conjugated polymers. The $\nu=2$ and 3 states would have degenerated $2p$- and $2s$-like wave functions, respectively, in the one-dimensional hydrogen model, but the degeneracy is lifted due to the cutoff (finiteness) of the on-site Coulomb interaction.[17] For this reason, $\langle2|x|3\rangle$ is comparably large to the $\langle0|x|1\rangle$ in the case of polysilanes. In the oligomers, however, the confinement of the excited states further breaks the degenerate character, which reduces the moment $\langle2|x|3\rangle$ and hence the signal in the higher energy region of the EA spectra.

We may have to consider possible effects of the higher-lying states above these four levels. In fact, higher odd-numbered ($\nu\geqslant5$) states affect the EA spectrum near the $\nu=2$ state similarly to the $\nu=3$ state in terms of the one-dimensional Wannier exciton model.[2–4] Thus, the $\langle2|x|3\rangle$ can be even smaller than the value derived by the four-level model.

In summary, we investigated the electroabsorption spectrum of a thin film of the silicon oligomer $Si_{10}(CH_3)_{22}$. The EA signal arising from the one-photon-forbidden state above the lowest allowed transition is much reduced as compared with that of the virtually infinite chain system, polysilane. It turned out from the fitting procedure within the four-level model that the contribution of the dipole moment between higher excited states in the EA spectrum becomes significantly smaller than that observed for polysilanes.

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