

Vacuum-ultraviolet spectroscopy of dialkyl polysilanes

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We present here a complete experimental determination of the optical properties and electronic structure of the polymers poly(di-*n*-pentylsilane) and poly(di-*n*-hexylsilane) from 2 to 44 eV. The electronic structure revealed by these measurements is consistent with the assignment of the higher-energy transitions to the carbon-based sidechains and the lower-energy transitions to the silicon backbone. The transitions attributed to the silicon backbone correlate well with predictions by an independent band-structure calculation using the local-density approximation.

Soluble polysilanes are long, catenated polymers with carbon-based sidegroups attached to each of the atoms in the silicon backbone. These have proven useful for many technological applications, e.g., as thermal precursors to silicon carbide, ultraviolet (UV) photoresists, and photoconductors for electrophotography.¹ An unusual feature of the polysilanes is the degree of electronic conjugation along the σ -bonded silicon backbone. Associated with this conjugation are strong absorptions in the UV (typical absorption coefficients are $\alpha \approx 2 \times 10^5 \text{ cm}^{-1}$) and large optical nonlinearities.¹⁻³ The nonlinear spectroscopic studies also reveal a strong two-photon resonance for the polymer poly(di-*n*-hexylsilane), which appears to be the two-photon equivalent of the first UV absorption peak.^{3,4} Similar behavior for polysilanes with other substituent groups suggests that the two-photon transition is a common feature of the polysilanes.³ The energy of the two-photon transition, however, is $\approx 1 \text{ eV}$ larger than the first UV transition.

It is now clear that the origin of both the large oscillator strength for the linear UV absorption and the corresponding nonlinear optical properties lies in the σ -conjugated backbone. However, the exact nature of these transitions has been the subject of some debate, and it is not yet clear whether the polysilanes are best described by one-electron band theory⁵ or by correlated many-electron models.⁶

A number of band-structure calculations modeling various polysilanes have been recently published.^{5,7} The most credible of these studies are *ab initio* calculations using the local-density approximation (LDA), which model the UV transition as the direct gap of a one-dimensional semiconductor. On the other hand, recent studies of the electronic properties of polysilanes have suggested that the first UV transition is excitonic in nature.⁸⁻¹⁰ These predict that the onset of band-to-band transitions must therefore occur at higher energies, with an exciton binding energy of more than 1 eV, as is common for Frenkel excitons in molecular systems.¹⁰ In this case, the two-photon transition would also lie below the band gap, and could plausibly

arise from a two-photon exciton similar to that observed for π -bonded polydiacetylenes.¹¹

To better understand the electronic structure of the polysilanes, we present here the first measurements of the vacuum ultraviolet (VUV) spectrum of two polysilane polymers, poly(di-*n*-pentylsilane) (PDN5S) and poly(di-*n*-hexylsilane) (PDN6S). These compounds were chosen because they can be easily produced in quantity, and a large body of structural and optical data already exists for these materials. At room temperature, PDN6S is known to form a highly crystalline structure with an all-*trans* planar-zigzag backbone, while PDN5S is known to form a 7/3 helical conformation.¹ At elevated temperature, both polymers undergo a phase transition to form an extended, highly gauche backbone.¹²

The polymers used in this study were produced by a Wurtz-type coupling reaction, and were purified by reprecipitation to separate the high-molecular-weight portion. Films approximately $2.5 \mu\text{m}$ thick were prepared on quartz substrates by conventional spinning techniques using a 2% solution (by weight) of the polymer in isoctane. The films were subsequently baked in an oven at 100°C to remove the residual solvent, and cooled in a refrigerator overnight.

The spectrometer used to measure the VUV reflectivity spectrum has been described in detail elsewhere.¹³ In a large vacuum chamber, a continuum of VUV and soft-x-ray radiation from a laser plasma light source (LPLS) is focussed onto the polymer film, and the light reflected from the film dispersed by a 1-m polychromator onto an optical multichannel analyzer. The detector signals are collected and normalized for the reflectivity of the iridium reference mirror by computer. The resulting reflectivity data are then compared to transmission measurements, and adjusted to compensate for possible second surface reflections and interference fringes. Finally, the resulting reflectivity spectrum is normalized by a constant to agree with known values of refractive index at visible wavelengths (at 633 nm, $n \approx 1.58$ for PDN6S and $n \approx 1.56$ for

PDN5S).¹⁴

The reflectivity R for both polymers generated by this technique is shown in Fig. 1. The previously observed UV transitions at 3.97 eV for PDN5S and 3.32 and 3.91 eV for PDN6S are clearly present in the spectrum, along with many stronger transitions occurring at higher energies. Both measurements are within experimental error of the theoretical ω^{-4} dependence for the reflectivity at high energy, indicating that these data represent a complete measurement of the joint density of states for the valence and conduction bands. A Kramer-Kronig transform of the reflectance data therefore yields an accurate calculation of the optical properties of the film. Using numerical routines described elsewhere,¹⁵ the phase shift θ corresponding to the reflectance amplitude $r = R^{1/2}$ was generated, and the optical properties calculated.

In a solid-state material, the imaginary part of the dielectric function will be proportional to ω^{-2} times the joint density of states.¹⁶ Figure 2 shows $\epsilon_2 = \text{Im}\epsilon$ calculated from our reflectivity data for both compounds. Although the first UV transitions are significant, it is clear that a large number of interband transitions occur at energies inaccessible to conventional spectrometers, due to the air cutoff at 6.8 eV. The slightly negative values for ϵ_2 at energies below the first UV transition are an artifact of the extrapolations used in the Kramers-Kronig analysis. The extrapolation parameters chosen were those that gave

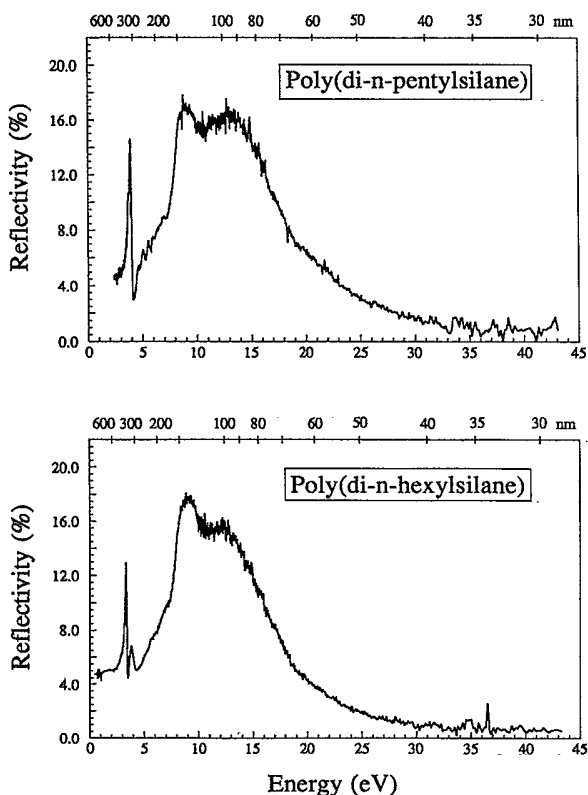


FIG. 1. Reflectivity of poly(di-*n*-pentylsilane) (PDN5S) and poly(di-*n*-hexylsilane) (PDN6S), corrected for second surface reflection at low energy and normalized to match the refractive index in the visible. The small features at ~ 5 eV in the PDN5S are uncorrected interference fringes.

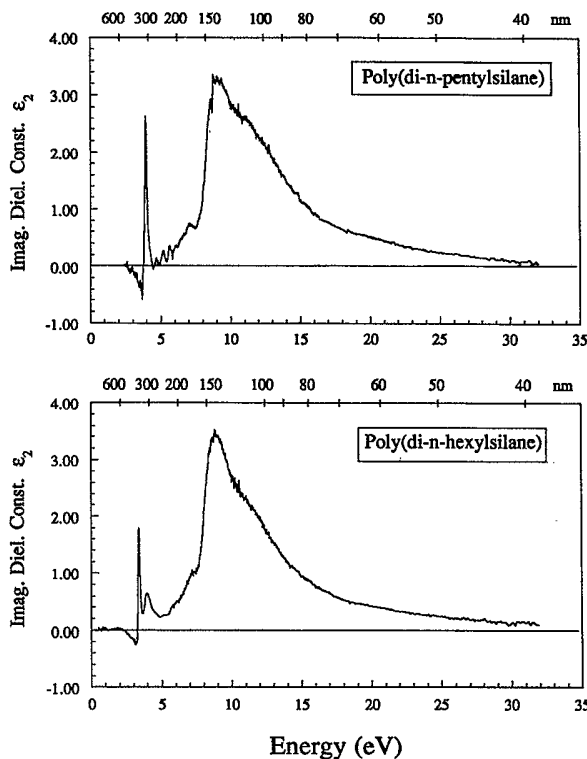


FIG. 2. Imaginary part of the dielectric function for poly(di-*n*-pentylsilane) and poly(di-*n*-hexylsilane) calculated from the reflectivity data shown in Fig. 1. The negative values of ϵ_2 just below the first UV transition are artifacts of the extrapolations used in the Kramers-Kronig analysis.

the best numerical agreement with absorption and refractive-index data measured independently in the visible and UV.

The films used for this study were isotropic, so these measurements do not discriminate between transitions in the silicon backbone and the carbon-based sidegroups. For the planar-zigzag σ -bonded carbon-based sidegroups, no conjugation is observed, so the electronic structure of the sidegroups should be quite similar to that observed for planar-zigzag carbon-based polymers. A comparison of the published absorbance for planar-zigzag polyethylene¹⁷ and the absorption coefficient derived from our reflectivity measurements, shown in Fig. 3, suggests that the sharp onset of transitions in the polysilanes at ~ 8 eV and the majority of transitions at higher energy arise from the pentyl or hexyl sidechains. Polyethylene is highly transparent in the visible and near UV, so the strong transitions observed for the polysilanes in this energy range probably correspond solely to the silicon backbone transitions. Although this is a common interpretation for the electronic structure of the polysilane polymers,^{1,5,18} polarized spectra for highly oriented samples would allow a more definitive assignment.

Theoretical predictions of the optical properties for a variety of carbon substituted polysilane backbone conformations have been recently published. From LDA band-structure calculations, Mintmire has calculated the joint density of states and determined the extinction coefficient expected for various orientations of poly(di-methylsilane)

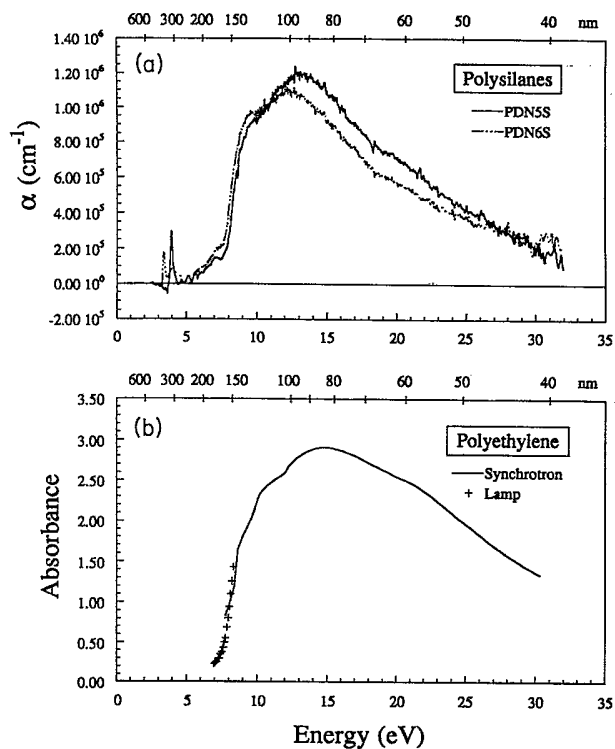


FIG. 3. (a) Optical absorption coefficient for PDN5S and PDN6S, calculated from the reflectivity measurements shown in Fig. 1, and (b) absorbance of polyethylene, measured by Hashimoto *et al.* (from Ref. 17).

in both the planar-zigzag and 4/1 helical conformations.⁵ His results for randomly oriented films are shown in Fig. 4, along with the experimental values from our reflectivity measurements. For this figure, Mintmire's calculations have been shifted to higher energy by 0.75 eV. Such a shift is common for LDA band-structure calculations, which can routinely underestimate gap energies by $\sim 30\%$.^{5,19} This shift was chosen to give the best overall correlation with the observed features in the measured spectra. The amplitude for the theoretical curves was adjusted to correspond to the experimental value at ~ 7 eV in PDN5S. This same scaling factor was also used to normalize the theoretical curve for PDN6S.

For both polymers, the width of the first UV transition is extremely narrow (≈ 0.4 eV) when compared to transitions at higher energy. In light of the excitonic properties associated with the first absorption feature, it is quite reasonable to assign this transition to be a purely excitonic transition associated with the one-dimensional (1D) silicon backbone chain. Assignment of the second peak at ~ 3.9 eV in PDN6S is more problematic. This feature remains, albeit shifted to slightly higher energy, above the phase transition associated with sidechain melting and the change of the polymer backbone from a planar-zigzag to a highly gauche conformation, while the first feature at 3.32 eV vanishes.¹² The 3.9-eV peak may therefore arise from exciton states associated with the more disordered gauche conformation. X-ray and NMR studies confirm that this phase coexists to some extent with the planar-zigzag form at room temperature.¹

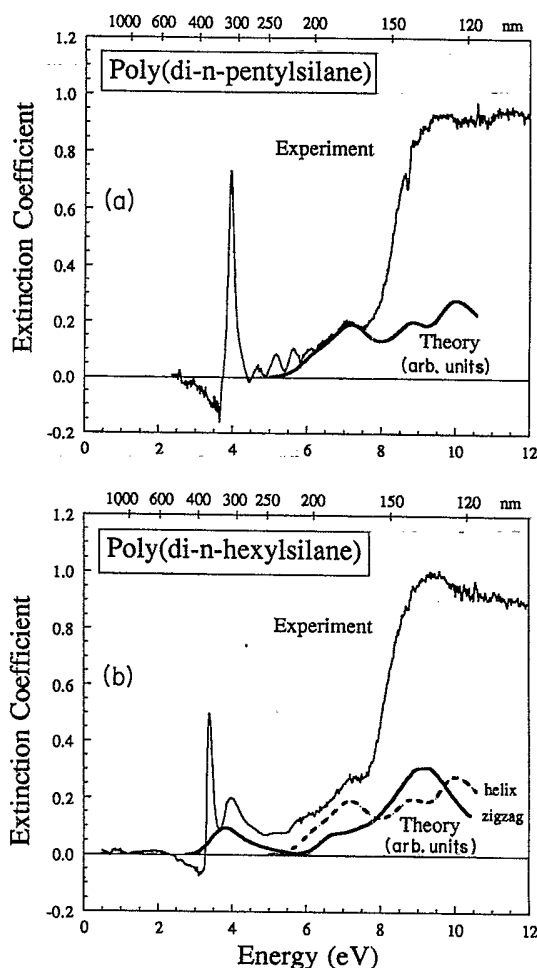


FIG. 4. Extinction coefficient for (a) PDN5S and (b) PDN6S, calculated from the reflectivity measurements shown in Fig. 1. The periodic features between 4.5 and 5.5 eV in (a) are interference fringes arising from the rear surface of the polymer film. Also shown are theoretical predictions of the extinction coefficient from the first-principles band-structure calculations of Ref. 5 for (a) helical and (b) planar-zigzag poly(dimethylsilane).

The correspondence between the experimental values and the theoretical spectra suggests that not all of the oscillator strength for PDN6S between 3 and 5 eV arises from the formation of excitons. Instead, the spectrum could correspond to a superposition of the exciton transitions for the two phases and the 1D direct gap of the planar-zigzag phase. If true, the binding energy of the exciton in the planar-zigzag conformation would therefore be a few hundred meV, corresponding to a highly delocalized excitation. This exciton could be similar to the delocalized excitons found in quantum confined semiconductor materials, or quantum wires.²⁰ On the other hand, it can be seen from Fig. 4 that the band gap for the helical conformation is more than 1 eV above the exciton transitions, suggesting a more tightly bound, localized exciton.

These assignments must be considered tentative at this time. Other band-structure calculations published for the polysilanes using the both empirical and LDA approaches have predicted gap energies of ~ 4 eV.⁷ Correcting these

calculated results with the usual LDA shift would then place the experimental gap at ~ 5.8 eV. Using this model, the onset of transitions we observe experimentally at this energy would correspond to the 1D direct gap, and all the transitions at lower energy would therefore correspond to tightly bound excitons. This would be more consistent with correlated electron descriptions of the polysilanes.⁶ These alternative band-structure calculations do not, however, present predictions of the joint density of states or optical properties, and so comparison with our experimental measurements is not possible. In addition, shifting Mintmire's predictions to correspond to this tightly bound interpretation gives very poor agreement with our measured optical properties.

In conclusion, we have measured the reflectivity spectra of solid films of poly(di-*n*-pentylsilane) and poly(di-*n*-hexylsilane) from 2 to 44 eV, and determined the optical properties of these materials. The electronic structure revealed by these measurements is consistent with the as-

ignment of the higher-energy transitions to the carbon-based sidechains and the lower-energy transitions to the silicon backbone. The experimentally determined optical properties of the polymer backbones correlate well with the predictions of first-principles band-structure calculations.⁵ The lower-energy sharp UV transitions are, however, not predicted by these calculations, supporting the previous assignment of these features to excitonic transitions.⁸⁻¹⁰ The first transition in the planar-zigzag form of poly(di-*n*-hexylsilane) would therefore correspond to a loosely bound delocalized exciton, while excitons in the helical conformations appear to be more localized.

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