Photoelectron spectra of polysilanes

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Some organopolysilanes (high-molecular-weight polymers which only contain silicon atoms in their backbone) can be used as highly sensitive, self-developing uv photoresists. To understand the electronic structure of polysilanes and help rationalize their solid-state uv photosensitivity, we have recorded the photoelectron spectra of several polysilanes: poly(β-naphthylmethylsilane), poly(phenylmethylsilane, poly(n-dodecylmethylsilane, and poly(n-propylmethylsilane). We find that if the polymer photoemission spectra can be described in terms of backbone Si-Si and side-chain Si-C levels which do not hybridize (as in the alkyl polysilanes), then the solid-state uv sensitivity of the polymer is high. An explanation of this correlation in terms of the degree of hybridization of the low-lying bonding and antibonding Si-Si levels with the levels of the carbon side-group molecule will be presented.

INTRODUCTION

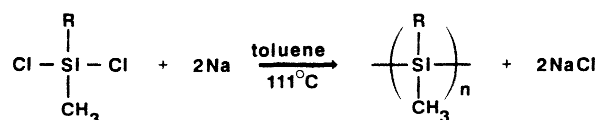
Organopolysilanes (polysilanes) are high-molecular-weight polymers whose backbone consists entirely of silicon atoms. In these polymers, each monomer unit is composed of a central Si bonded to a methyl group (CH_3) and a larger "side group." The monomers (all identical in the cases considered herein) are σ bonded to each other through the silicon atoms to form the polymer chain. This type of bonding results in Si-Si σ-electron delocalization.[1] Although polysilanes were first studied decades ago,[2,3] they did not elicit interest due to the intractability of the materials first prepared. Recently, the development of new soluble polysilanes has led to widespread interest in their application as precursors for SiC fibers,[4] ceramics precursors,[5] polymerization catalysts,[6] uv resists,[7] and self-developing deep uv resists.[8] Their use as self-developing resists is based on their high-quantum-yield, deep-uv-initiated (248 nm, 5.0 eV) photochemical volatilization process. In particular, it is believed that less than six monomers can be expelled per photon absorbed in air.[8]

This paper will present a model for the electronic structure of polysilanes, which will be supported by their He II (40.8 eV) —excited, angle-integrated photoemission spectra. The model will also be used to rationalize general trends in the deep uv solid-state photosensitivity of the polysilanes. We conclude that a major factor in chain scission is the degree of interaction of "Si-Si" levels with those of the side-group molecules. The weaker the hybridization, the stronger the spatial localization of the Si-Si levels to the silicon backbone. When photon absorption excites a Si-Si bonding electron to a Si-Si antibonding level, a greater degree of localization to the Si-Si backbone makes the rupture of the Si—Si bond more likely.

EXPERIMENTAL

The polysilane homopolymers of this study were synthesized by a Wurtz-type reductive coupling with sodium dispersion of the corresponding dichlorosilanes (Fig. 1). By careful control of reaction parameters, polymers with modal molecular weights $>5\times10^5$ and narrow[9] molecular-weight distributions were obtained.[10] All of the polymers utilized in this study were purified by at least four precipitations from three different solvent systems and show no observable contamination by the cyclic oligomer by-product formed in the coupling reaction. The polymers were characterized by infrared, ^{1}H NMR, and uv spectroscopy and gel-permeation chromatography. All polymers had acceptable elemental analyses ($\pm0.3\%$ relative to the calculated composition for C,H,Si). A large difference in the uv-absorption position and solid-state uv sensitivity is observed for the alkyl polysilanes (in this paper, those whose side groups are n-propyl or n-dodecyl) versus the aryl polysilanes (i.e., with phenyl or naphthyl side groups). The alkyl polysilanes show uv-absorption spectra dominated by excitations involving the silicon levels and high solid-state uv sensitivity, while the aryl polysilanes are much less prone to chain cleavage by uv and their threshold uv absorption probably involves both the carbon side rings and the silicon-silicon backbone.[8]

The polysilanes were spin-cast on tantalum foil to give essentially amorphous films. These films were mounted in a sample-introduction vacuum chamber and pumped down within 3 h after the spin casting. Several sample treatments were employed to test for sample contamination. These involved deep-uv irradiation, heating, and ion bombardment. The first two treatments caused little or



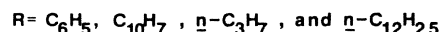


FIG. 1. Schematic of the Wurtz-type reductive condensation reaction.

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no effect on photoemission peaks, while the latter resulted in a broadening of the spectra. The Auger spectra associated with the samples shown here show only carbon and silicon and negligible oxygen signal (O-to-C intensity ratio ≤ 0.05). For other samples, especially if the polysilane had been prepared months in advance, a large oxygen signal was observed. This result implies, as in previous photoemission studies of polymers,[11] that there is negligible sample contamination by either bonded or absorbed oxygen. The photoemission spectra were recorded using a double-pass cylindrical mirror analyzer (CMA) in the nonretarding mode and with $\Delta E/E = 0.016$. The helium resonance lamp produced unpolarized light incident at 75° from the axis of the CMA, and as will be seen, caused some charging of the samples.

The polysilanes, as discussed above, are excellent uv photoresists at photon energies of ~ 4 eV. We were concerned with possible degradation under uv light of 40.8 eV energy and examined 40.8-eV radiation-induced changes in the sample visually and with Auger spectroscopy. For the low photon fluxes used here, there was no apparent damage. We believe this is due to the specificity of the transitions caused by the 4-eV light (σ to σ^* transitions) which are not caused by 40.8-eV radiation.

RESULTS AND DISCUSSION

The model of the electronic structure of the polysilanes which we present assumes that an infinite initial chain of $Si(CH_3)$ monomers is bound to an infinite number of noninteracting side groups (R) to form $(R\text{-Si-}(CH_3))_n$. We will assume that the binding energy of the center of the Si-Si band in the infinite initial silicon chain is approximately the same as in $Si_4(CH_3)_{10}$ and that since the side groups R do not bond directly to each other the electronic levels of the side-group molecules are those of the individual molecules RH. The degree of hybridization of the Si-Si levels with the carbon levels of the side-group molecule is largely determined by their relative energies. A greater difference in the binding energies of the levels results in lesser hybridization of Si-Si and carbon levels and greater spatial localization of the Si-Si levels to the silicon backbone atoms.

To make qualitative estimates of the hybridization, we review the results of Bock and co-workers[12] on the small-chain polysilanes: Si_nH_{2n+2}, where $n = 1,2,3,4,5$, and $Si_n(CH_3)_{2n+2}$, where $n = 1,2,3,4$. The photoemission spectra of these molecules in the gas-phase show (1) levels which are mostly Si—Si bonding at low ionization potential (8.0—9.3 eV in the methylsilanes and 9.4—10.9 eV in the silanes); (2) a broad Si—H (12.3 eV) or Si—C bonding peak (10.5 eV); and (3) the C—H bonding peak (14 eV) in the methylsilane. Their results also show that the lowest unoccupied levels have Si—Si antibonding character and thus the first peak in the uv absorption in these molecules corresponds to transitions between Si—Si bonding to Si—Si antibonding levels. Furthermore, it is crucial to our results to note that for the methylsilanes no admixture of Si-C or C-H into the Si-Si levels was found, in contrast to the hydrogen series where Si-H character does mix into the Si-Si levels. Thus, the initial methylpolysilane $[Si(CH_3)]_n$ should have Si—Si bonding and antibonding levels which show little carbon admixture and hence are confined to the silicon-silicon backbone. To understand if the bonding of the side group R changes this picture, we compare the gas-phase spectra of the individual molecule RH (naphthalene, benzene, dodecane, and propane) to that of $Si_4(CH_3)_{10}$. A similar analysis of the uv photoelectron spectra of small-chain polysilanes has been carried out by Pitt.[13,14]

Figure 2 shows the uv-excited photoemission spectra of propane,[15] butane,[16] nonane [Ref. 17, x-ray photoemission spectroscopy (XPS)], benzene,[18] naphthalene,[19] and $Si_4(CH_3)_{10}$ (Ref. 12) as bar graphs, where the height of the bar represents their relative peak intensity. The peaks which occur at about 20 eV binding energy are assigned to the C 2s levels. These peaks are uninteresting with respect to any bonding of the molecule since they will not shift or hybridize, although they will be used to calibrate the degree of charging of the polymers. The peaks with binding energy lower than ~ 18 eV are mostly C 2p in character and are expected to change energy position upon bonding. Note that the energy difference between the highest occupied orbital of the side group relative to the Si-Si levels of $Si_4(CH_3)_{10}$ is reduced as we go from propane to butane to nonane to benzene and, finally, naphthalene. Quantitatively, the centroid of the Si-Si band in the methyl silane (8.7 eV binding energy) is higher in energy than the highest occupied levels of the side-group molecule RH as shown: propane, 3.3 eV; butane,

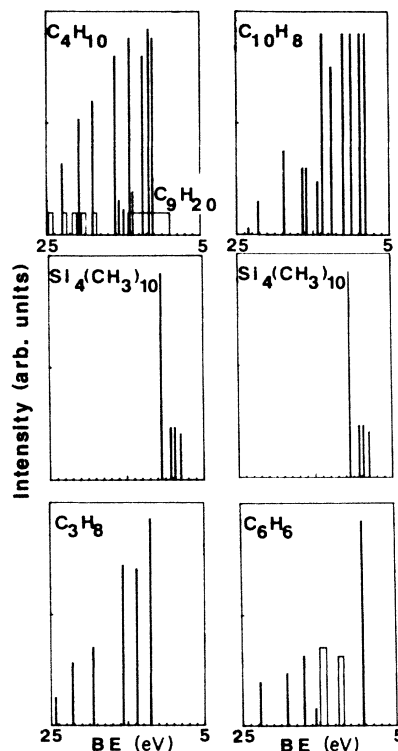

FIG. 2. Gas-phase uv photoelectron spectra of side-group molecules RH in bar-graph form. Included is the XPS spectra of nonane, where we have marked the C 2s peak positions and the total width of the valence band.

2.5 eV; nonane, ~1.8 eV; benzene, 0.6 eV; and naphthalene, −0.6 eV. A similar trend is observed when we compare the energy of the bottom of the Si-Si band (9.3 eV binding energy) with the highest occupied level of *R*H: propane, 2.7 eV; butane, 1.9 eV; nonane, ~1.2 eV; benzene, 0.0 eV; and naphthalene, −1.2 eV.

The photoemission spectra of the polysilanes are shown in Fig. 3 together with the bar graphs previously shown in Fig. 2. Charging of two of the samples forces us to shift the binding-energy scale to achieve good alignment of the C 2*s* peaks, although the spectra of the *β*-naphthyl and dodecyl samples only required a shift of 0.7 eV (which was not necessarily due to charging). The only spectra where charging could have caused any ambiguity in the assignment is the phenyl-methyl polysilane spectra (see Fig. 4). We believe that the assignment shown is correct. The only other possible alignment of the peaks would result in even a larger discrepancy between the gas-phase and polysilane data, thus strengthening the following points discussed.

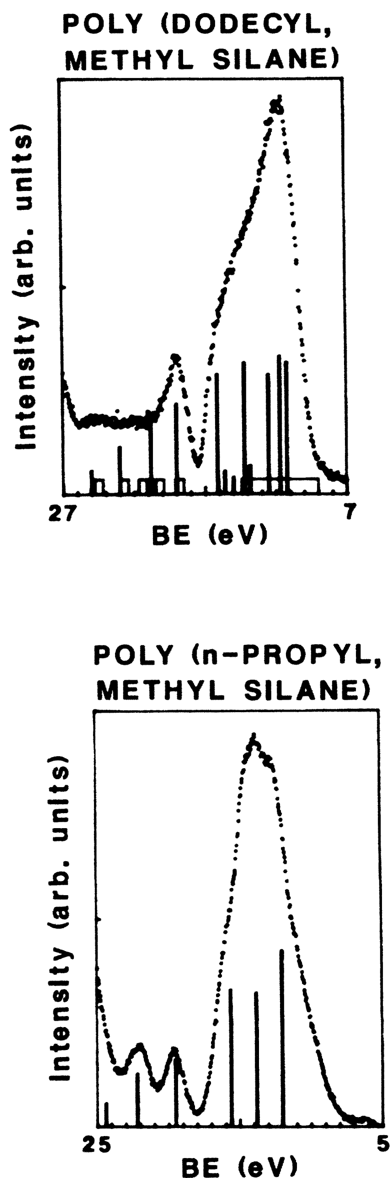

FIG. 3. He II photoemission spectra of the alkyl polysilanes superimposed on the bar-graph representation of the uv spectra of the alkanes *R*H corresponding to their side groups *R*. The spectra are plotted in terms of the binding energy relative to vacuum by alignment of the C 2*s* region of the polysilane with those of the gas-phase molecule. This results in a shift of 5.7 and 1.7 eV toward higher binding energy for the propyl and dodecyl silanes, respectively.

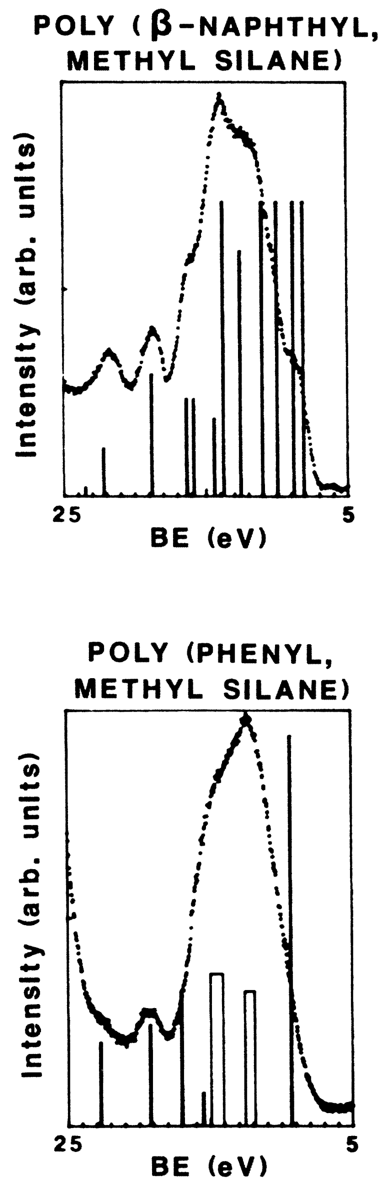

FIG. 4. He II photoemission spectra of the aryl polysilanes superimposed on the bar-graph representation of the uv spectra of the arenes *R*H corresponding to their side groups *R*. The spectra are plotted in terms of the binding energy relative to vacuum by alignment of the *C* 2*s* region of the polysilane with those of the gas-phase molecule. This results in a shift of 5.7 and −0.2 eV toward higher binding energy for the phenyl and *β*-napthyl silanes, respectively.

The photoemission spectra of the polysilanes show the expected trend in the admixture; the alkyl polysilanes have less mixing and the aryl polysilanes more, with the propylsilane showing the least perturbation and the naphthyl showing the largest. The best correlation can be seen for the propyl polysilane, whose spectrum is almost identical to that of propane. This spectrum also shows a weak shoulder whose binding energy is about 10 eV relative to the vacuum level and may be associated with the Si-Si band. The silicon band is not expected to be intense since the photoemission cross section of the Si $3p$ is much less than that of the C $2p$ (ratio of 0.22) (Ref. 20) and the greater total number of C $2p$ over Si $3p$ electrons. The worst correlation between the photoemission spectrum of the side-group molecule and the corresponding polysilane occurs for naphthalene. In our model this mismatch is due to the hybridization of the low-binding-energy C $2p$ levels of naphthalene and the Si-Si level of the initial silicon chain. When this happens we expect the C $2p$ levels to shift in energy and to assume some Si $3p$ character. Due to the lower cross section of the Si $3p$, this effect results in a diminution of the photoemission intensity of the peaks which hybridize upon bonding. The latter is clearly observed at the low-binding-energy region of the naphthalene spectrum when compared to the β-naphthyl polysilane.

The trends in hybridization, and admixture of C $2p$ character into the Si—Si bonding band, can be used to explain the nature of the threshold uv absorption and rationalize the general trends in solid-state photosensitivity observed in the deep-uv-initiated depolymerization of the polysilanes. First, uv excitation for the alkyl polysilanes is largely confined to the silicon backbone while that of the aryl polysilanes involves the side rings as well, because the highest occupied levels of the alkyl polysilanes are mostly Si—Si bonding (and presumably, the lowest unoccupied levels are Si—Si antibonding), while in the aryl polysilanes the highest occupied levels show an admixture of the wave functions of the side-group and silicon-backbone levels. Second, due to the predominantly main-chain character of the excitation in alkyl polysilanes, promotion of electrons from the bonding to the antibonding levels is more likely to rupture backbone bonds than if the excitation energy resided partially in the side group (as in the aryl polysilanes).

The above discussion has not included several factors that further influence the uv sensitivity of the polysilanes. First, the uv energy that ruptures the chain is only about 5.0 eV, which may only be sufficient to break one or two Si—Si bonds.[21] The removal of six monomers requires added energy from interaction of the served chain with oxygen and/or physical strain[8] in the molecule. Second, the mechanism of chain scission we envision merely localizes Si—Si antibonding energy to the chain and a more detailed picture of the localization of this energy to a specific bond is required. Finally, photosensitivity trends for polysilanes in solution are not the same as those observed in the solid state, e.g., poly(phenylmethylsilane) is quite photoliable in solution but very insensitive in the solid state, suggesting that other photochemical and photophysical factors play an important role in determining the ultimate efficiency of main-chain scission.

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