ADVANCED MATERIALS

Polysilanes—A New Look at Some Old Materials

Radiation Sensitivity
Ceramic Precursors
Photoinitiators
Microlithography
Nonlinear Optics

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In spite of the fact that the first polysilane derivatives were probably prepared in the mid 1920's, there was little scientific interest until recently. The synthesis of the first soluble homo and copolymers about 10 years ago has stimulated an explosive development of this class of materials. This brief review traces the historical development of the polysilanes and focuses on recent studies of polymer structure, electronic properties, photochemical reactions and mechanisms and finally on new applications.

1. Introduction

Substituted silane polymers, i.e. materials which contain only silicon atoms in the polymer backbone, represent a new class of radiation sensitive materials with very unusual electronic properties.[1, 2] The unique combination of physical, mechanical and electronic properties has recently stimulated a flurry of theoretical and experimental studies and has resulted in the discovery of potential applications. In this regard, the polysilanes have been investigated as (i) new thermal precursors to β-silicon carbide,[3, 4] (ii) a new class of photo and charge conducting materials,[5, 6] (iii) radiation sensitive materials for microlithography,[7–9] (iv) broad spectrum photoinitiators for free radical vinyl polymerizations[10] and recently (v) as materials with interesting nonlinear optical properties.[11, 12]

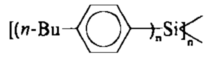
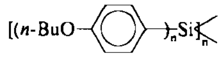
Historically these materials are quite old and the first aryl substituted materials were probably prepared in the 1920's by *Kipping*.[13] However, these early materials attracted little scientific attention, since they were highly crystalline, insoluble and intractable. In 1949, *Burkhard*[14] reported the preparation of the first alkyl derivative poly(dimethylsilane), (PDMS) by a similar synthetic route, i.e., the condensation of dichlorodimethylsilane with sodium metal. This material, like the earlier derivatives, also proved to be insoluble and intractable. The poor polymer properties of the early materials led workers to believe that these characteristics were generic to the class and as a result they attracted little interest until the middle 1970's when *Yajima* and coworkers[3] showed that PDMS could be converted to β-silicon carbide in a series of thermal steps which involved soluble and processable intermediates. This work rekindled the interest in polysilanes and subsequent studies produced the first soluble high molecular weight homo[15, 16] and copolymers.[17, 18] The preparation of the first soluble materials about 10 years ago initiated the modern era in the study of polysilane chemistry which continues today.

It is interesting that in spite of considerable efforts, the original Wurtz-type coupling shown below in Equation 1, with some experimental modifications, is still the most viable general procedure for the preparation of high molecular weight, linear polysilane derivatives. Usually the metal of choice for the condensation is sodium. Lithium tends to produce cyclic oligomers while potassium, particularly in polar solvents at elevated temperatures, often results in substantial degradation of the linear polymers to produce oligomers. In spite of the drawbacks of the Wurtz-type coupling procedure, i.e. low yields of high polymer and limited functional group tolerance, a large number of soluble, high molecular weight polysilanes have been prepared[1, 2] and a representative sample is shown in Table 1.

$$RR'SiCl_2 + 2\,Na \rightarrow \left(RR'Si \right)_n + 2\,NaCl \qquad (1)$$

When purified, most polysilanes are both thermally and oxidatively stable. Those with aromatic substituents attached to the backbone can often be melted and recast without significant decomposition. In general, the thermal stability of these materials is high and samples heated in nitrogen show little weight loss below 250 °C. The mechanical proper-

Table 1. Representative substituted silane polymers prepared by Wurtz-type coupling.

Entry	Polymer Structure	Yield (%)	$\bar{M}_w \times 10^{-3}$	R [a]
1.	$(n\text{-PrSiMe})_n$	32	64.4, 13.3	0.4
2.	$(n\text{-HexSiMe})_n$	11	524, 20.5	2.4
3.	$(n\text{-DodecylSiMe})_n$	8	1345, 9.4	2.7
4.	$(n\text{-Bu}_2\text{Si})_n$	34	110, 5.9	1.5
5.	$(n\text{-Hex}_2\text{Si})_n$	6	1982, 1.2	3.1
6.	$(n\text{-Tetradecyl}_2\text{Si})_n$	60	3071, 27.8	1.9
7.	$(\text{PhSiMe})_n$	55	193.5, 5.6	0.7
8.	$(p\text{-}t\text{-ButylPhMe})_n$	14	153	–
9.	$(p\text{-MeOPhSiMe})_n$	12	13	–
10.	$(p\text{-Me}_2\text{NPhSiMe})_n$	13	3.3	–
11.	$(\text{PhSiMe}_2\text{SiMe})_n$	9	13.2	–
12.	$(\beta\text{-NaphthylSiMe})_n$	20	30	
13.		6.2	231.6, 2.1	0.8
14.		8.5	1248, 2.6	0.8

[a] Ratio of high/low molecular weight fractions

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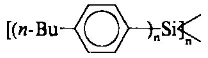
ties depend on the nature of the substituents and the polymer microstructure, and measured glass transition temperatures range from −75 °C to above 120 °C. In general, polymers with aromatic substituents tend to be more crystalline and higher melting.

Depending on the type of substituents and the reaction conditions employed, the Wurtz-type coupling procedure results in polymeric materials with a broad range of molecular weights varying from a few thousand to several million. The polymer molecular weights and dispersities can be controlled to some extent by judicious choice of the solvent and the polymerization conditions.[2, 7] The material properties can also be altered by the preparation of copolymers of structure $\leftarrow R^1R^2Si)_n(SiR^3R^4 \rightarrow_m$, permitting further fine tuning of the mechanical and electronic characteristics. For this reason, a large number of structural and compositional copolymer variants have been described.[1, 2]

2. Spectral and Electronic Properties

It was the curious electronic properties of catenated silane oligomers which first attracted the attention of both theorists and experimentalists.[19] The spectral properties were consistent with significant delocalization of the sigma electrons in the sigma backbone. All soluble, high molecular weight polysilane derivatives absorb strongly in the UV and the absorption characteristics of a number of typical polysilane derivatives are shown in Table 2. Solution UV spectroscopic studies suggest that alkyl substituted polysilanes absorb in the region 300–325 nm, and the position of the absorption maximum depends on the steric bulk of the substituents.[20] Aryl substituents directly bonded to the backbone cause a red shift of 20–30 nm due to the electronic interaction of the substituent π orbitals with those of the silicon backbone. The absorption characteristics of linear substituted silane polymers also depend on the extent of catenation.[20] In this regard, both the position of the long wavelength absorption maxima and the molar absorptivities per silicon-silicon bond increase rapidly at first with increasing molecular weight, but approach limiting values beyond a degree of polymerization (chain length) of 40–50 as shown in Figure 1. The gross spectral characteristics of linear silicon catenates have been adequately rationalized computationally by simple linear

Table II. UV spectral characteristics of some polysilane derivatives. Data is listed for the longest wavelength transition only.

Entry	Polymer Structure	λ_{max} (nm)	ε/SiSi
1.	$(n\text{-PrSiMe})_n$	306	5600
2.	$(n\text{-DodecylSiMe})_n$	309	5000
3.	$(c\text{-HexylSiMe})_n$	320	7390
4.	$[(n\text{-Hexyl})_2Si]_n$	317	9700
5.	$[(n\text{-Tetradecyl})_2Si]_n$	322	8400
6.	$(PhSiMe)_n$	341	9300
7.	$(p\text{-MeOPhSiMe})_n$	346	8180
8.	$(\beta\text{-NaphthylSiMe})_n$	350	2800
9.	$(p\text{-BiphenylSiMe})$	352	4000
10.		395	26600

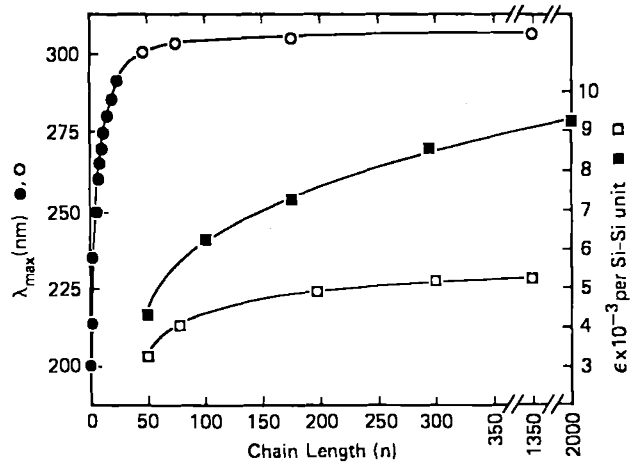


Fig. 1. Absorption wavelength maxima (λ_{max}, ●○) and extinction coefficients (ε_{SiSi} ■□) as a function of oligomer/polymer chain length of n-units $\leftarrow SiRR' \rightarrow_n$. (●) $Me(Me_2Si)_nMe$, (○) $[(n\text{-dodecyl})(Me)Si]_n$, (■) $(PhSiMe)_n$, (□) $[(n\text{-dodecyl})(Me)Si]_n$.

Robert D. Miller received his Ph.D. in organic chemistry from Cornell University in 1968 working with Professor A. T. Blomquist. After post-doctoral work at Union Carbide Research Institute on low temperature spectral characterization of reactive intermediates generated by flash vacuum pyrolytic techniques, he joined IBM Research in Yorktown Heights, New York as a member of a multidisciplinary "basic studies" group. In 1971, he moved to the San Jose Research Laboratory. His current research interests include: basic photochemical processes, radiation sensitive polymers, synthetic methods involving multifunctional synthons, spectroscopy and chemistry of reactive intermediates, the synthesis and characterization of highly strained and/or theoretically interesting molecules, and novel rearrangements promoted by structural strain. He is a member of the American Chemical Society and is presently on the editorial board for Chemical Reviews.

combination of atomic orbitals (LCAO) or Sandorfy-type theoretical treatments.[19] However, the absorption spectra of the polysilanes also depend strongly on the backbone conformation,[21, 22] a fact which was not predicted from the simple molecular orbital treatments. More sophisticated semiempirical and ab initio studies are required to adequately describe the electronic ground state and the nature of the electronic transitions.[2] INDO/S calculations rationalize the conformational dependence of the absorption spectra in terms of long range 1,4-orbital interactions and predict furthermore that *trans* sequences should absorb at longer wavelengths than *gauche*. Moreover, these studies also suggest that the electronic excitation energy tends to localize in the *trans* segments even when they are quite short.[23, 24] A solution model for the dialkyl polysilanes, which has emerged from wavelength dependent fluorescence polarization studies, is one of a polymer chain composed of discrete chromophoric segments (presumably *trans* or nearly *trans* units of varying lengths). The individual spectral characteristics depend on the segment length and are partially electronically decoupled by conformational twists or kinks. These segments apparently communicate by rapid energy transfer.[24, 25] Such a model is also supported by the INDO/S calculations. Consistently, the experimental absorption and emission characteristics of polysilanes in solution may be adequately modeled[26] using rotational isomeric state theory (RIMS) assuming both a statistical distribution of chromophoric segments of varying lengths, and conformational defects which mediate the electronic interaction between the chromophores. As expected from such a model, the polysilanes are predicted to be thermochromic as is often the case, although the detailed conformational interpretation of the solution thermochromism[26, 27] is complicated by possible aggregation effects.

The fluorescence emission from most polysilane derivatives in solution is short-lived (75–200 ps)[24, 29] and the band width is much narrower than the corresponding absorption bands.[24, 26, 28] The short radiative lifetimes, narrow spectral band width, and lack of fine structure of the fluorescence is suggestive of a highly delocalized excited state. Comparison of the absorption and emission spectra of poly(di-*n*-hexylsilane) in solution suggests that emission is occurring from segments containing 20–36 silicon atoms, assuming that the oscillator strength is independent of the chromophore length.[24, 29] In contrast to the intense, narrow fluorescence reported for poly(di-*n*-alkylsilanes), a weak, broad, long-lived emission is often observed at longer wavelengths in rigid media.This has tenatively been attributed to phosphorescence.[25, 26, 28, 41] On the basis of band structure and width, *Zeigler* et al.[26, 41] have suggested that the triplet excitation is more localized and hence, may be responsible for the polymer photolability. While the apparent localized nature of the triplet excitation is more consistent with the observed photolability (vide infra), this connection has been unambiguously established only for poly(methyl-*n*-propylsilane).[28]

Many polysilane derivatives are strongly thermochromic in the solid state. This effect was first reported for poly(di-*n*-hexylsilane) (PDHS) (see Fig. 2)[22] and this material has been the object of many structural studies.[21, 30] In this case, crystallization of the *n*-alkyl side chains enforces an all-*trans* planar backbone conformation which is responsible for the ~ 60 nm spectral red-shift. Above the transition temperature, which for PDHS is around 42 °C, the backbone conformationally disorders. It appears that for polysilane derivatives with sterically demanding substituents some type of intermolecular interaction in the solid state is necessary to enforce a stable planar all-*trans* conformation. This characteristic leads to a series of very subtle substituent effects which can dramatically effect the spectral properties. For example, poly(di-*n*-pentylsilane) (PDPS), in which side chain crystallization does not occur to a significant extent, adopts a 7/3 helical backbone conformation in the solid state at room temperature.[21] In this case, a deviation in the polymer backbone of only ~ 30° from *trans* planar results in a spectral blue-shift of almost 60 nm.

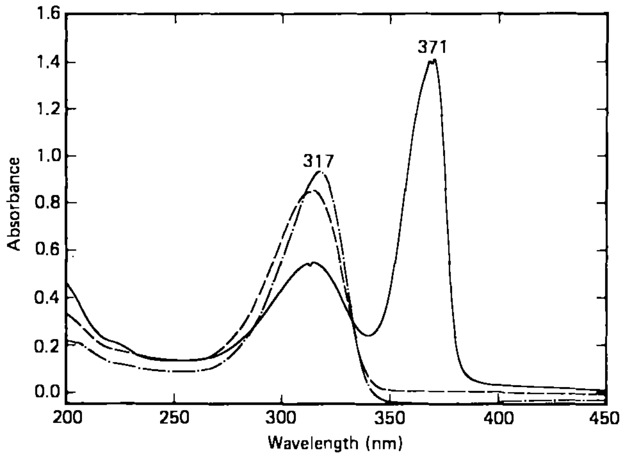


Fig. 2. UV absorption spectra of poly(di-*n*-hexylsilane): (●—●) solution in hexane; (—–) thin film run immediately after baking at 100 °C, (—) thin film after standing at 20 °C for 3 h.

Recent studies suggest, however, that side chain crystallization does not always assure the formation of a stable, planar all-*trans* conformation for polysilanes with sterically demanding alkyl substituents. For example, poly(di-*n*-tetradecylsilane) (PDTDS) adopts a non-planar TGTG′ backbone conformation in spite of spectral evidence of side chain crystallization.[31] Apparently, the backbone retains sufficient flexibility for derivatives with long chain *n*-alkyl substituents, even in the presence of strong intermolecular interactions to allow alternative non-planar conformations. It is also interesting that PDTDS is still thermochromic, suggesting that the observation of a spectral red-shift need not necessarily be uniquely associated with the formation of planar all-*trans* backbone segments. We have also observed that the introduction of sterically unsymmetrical substituents such as aryl groups, which can minimize intrachain steric interactions by rotation around the silicon-carbon substituent bond, can also produce dramatic spectral effects. For example, the poly(bis-alkylphenylsilanes) are among the most red-shifted of all polysilanes ($\lambda_{max} \sim 400$ nm) and the spectral data supports the presence of long *trans* sequences which persist even in solution.[32]

3. Radiation Sensitivity

Polysilane derivatives are sensitive to light and ionizing radiation both in solution and in the solid state. Irradiation causes a rapid bleaching of the long wavelength absorption, and the formation of lower molecular weight fragments.[20] This spectral bleaching, which is key to a number of applications (vide infra) is unusual and occurs because the absorption characteristics are a function of the polymer's molecular weight. The measured quantum yields for polymer scission in solution are high (0.25–1.0) although competitive cross-linking is often observed particularly when pendant unsaturated substituents are directly attached to the polymer backbone.[8, 20] The efficiency of both processes decreases markedly (50–100 fold) in the solid state. However, in every case that we have examined, photoscissioning predominates and this behavior can be considered to be characteristic of the linear polysilanes.

Exhaustive irradiation of soluble polysilanes at 254 nm in solution in the presence of trapping reagents such as trialkylsilanes or alcohols suggests that both silylenes and silyl radicals are intermediates (Equations 2a and 2b). Thermodynamic considerations and experimental studies[34] suggest that the silylene-forming reaction and the pathway to the silyl radicals are uncoupled and competing processes. In many respects, the photochemical decomposition of substituted silane high polymers resembles that previously reported for shorter chain oligosilanes.[33]

$$-\mathrm{SiRR'SiRR'SiRR'}- \xrightarrow{h\nu} \begin{cases} \mathrm{\ddot{S}iRR'} + -\mathrm{SiRR'SiRR'}- & \text{(2a)} \\ -\mathrm{RR'Si}\cdot + \cdot\,\mathrm{SiRR'SiRR'}- & \text{(2b)} \end{cases}$$

However, recent mechanistic studies in solution suggest that the polymer photochemistry is more complex than first imagined. There is an unusual wavelength dependency and the quantum yield for the extrusion of silylenes decreases markedly with increasing irradiation wavelength, becoming very small above 300 nm.[34] On the other hand, the photodegradation proceeds at all wavelengths absorbed by the polymer as evidenced by the continuous spectral bleaching and decrease in molecular weight. Studies on isotopically labeled polymers show that silyl radicals produced by polymer chain scission disproportionate in addition to recombining. In addition, a new photochemical chain-cleavage reaction, i.e., 1,1-reductive elimination (see Equations 3a and 3b)[35] has been identified. The wavelength dependent photochemistry has been rationalized in terms of the proposed solution model for the polysilanes consisting of a statistical collection of chain segments of varying lengths with differing absorption characteristics which are only weakly electronically coupled due to conformational defects.[23, 24, 25, 26, 28]

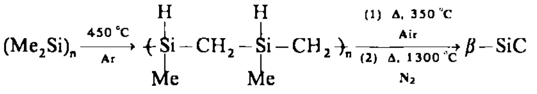
$$-\mathrm{SiRR'SiRR'SiRR'}- \xrightarrow{h\nu} \begin{cases} -\mathrm{SiR_2R'} + \mathrm{\ddot{S}iR'SiRR'}- & \text{(3a)} \\ -\mathrm{SiRR'_2} + \mathrm{\ddot{S}iRSiRR'}- & \text{(3b)} \end{cases}$$

In summary, mechanistic studies in solution suggest that there are at least three photochemical pathways leading to polysilane molecular weight reduction: (i) substituted silylene extrusion and chain abridgement; (ii) silicon-silicon bond homolysis to produce chain-cleaved silyl radicals and (iii) 1,1-reductive elimination to produce chain silylenes. Current evidence indicates that these pathways are uncoupled and competing.

4. Potential Applications

4.1. Preceramic Precursors

The excellent thermal and mechanical properties, unusual electronic characteristics and photolability of the polysilanes have led to a number of potential applications, as enumerated in the introduction. The earliest uses for these materials were as preceramic precursors to β-silicon carbide. In the middle 1970's, *Yajima* and coworkers[3, 36] discovered that poly(dimethylsilane) (PDMS) could be converted, in the series of steps shown in Equation 4, to silicon carbide fibers of exceptional strength. Fibers of this type are now marketed under the trade-name of Nicalon. The intermediate carbosilanes are crucial intermediates, as they are soluble and can be either cast or spun. The initial thermolysis step can be bypassed by using soluble silane homo and copolymers and materials of this type can be employed either as impregnating reinforcing materials for porous ceramics such as silicon nitride or directly for the formation of β-silicon carbide.[4] Dimensional stability of fibers can be introduced either by surface oxidation, as in the *Yajima* process, or by the photocrosslinking of unsaturated polysilanes, prior to firing to 1200 °C.



$$(\mathrm{Me_2Si})_n \xrightarrow[\mathrm{Ar}]{450\,^{\circ}\mathrm{C}} \left(\underset{\mathrm{Me}}{\overset{\mathrm{H}}{\mathrm{Si}}} - \mathrm{CH_2} - \underset{\mathrm{Me}}{\overset{\mathrm{H}}{\mathrm{Si}}} - \mathrm{CH_2} \right)_n \xrightarrow[\substack{(2)\ \Delta,\ 1300\,^{\circ}\mathrm{C} \\ \mathrm{N_2}}]{\substack{(1)\ \Delta,\ 350\,^{\circ}\mathrm{C} \\ \mathrm{Air}}} \beta-\mathrm{SiC} \quad (4)$$

4.2. Photoinitiators for Vinyl Polymerizations

Recently *West* and *Wolff* have utilized the broad spectrum photolability of polysilane derivatives for the photoinitiation of a variety of vinyl polymerization reactions.[10] The polydispersities obtained for poly(ethyl acrylate) and poly-

(styrene) produced in this manner were very similar to those observed in standard free radical initiated polymerizations suggesting that silyl radicals generated by chain scission may be responsible for initiation. Although the initiation efficiency is relatively low, this is partially compensated by the broad, active spectral range of the initiators and their very high extinction coefficients. In addition, vinyl polymerizations initiated by polysilane derivatives are curiously insensitive to the presence of oxygen. This sensitivity can be further decreased by the addition of certain antioxidants such as *tert*-amines and phosphines. The authors speculate that the in-situ generation of certain oxygen scavengers such as silenes, which are expected products from radical disproportionation, may be responsible for the reduced oxygen sensitivity.

4.3. Photo and Charge Conduction

The reduced spectral band gap of most polysilane derivatives relative to that of polymers with saturated carbon skeletons (~ 4 eV versus 8 eV) suggests that these material may comprise a new class of charge conducting and/or photoconducting media. In this regard, conducting films of a number of polysilane derivatives have been prepared either by doping with arsenic pentafluoride[18] or by casting from sulfuric acid solutions.[37] Similarly, the photo and charge conducting characteristics of a number of polysilane derivatives have been studied in some detail.[5,6] Drift mobilities of $\sim 10^{-4}$ cm^2/Vs have been measured both for the direct photogeneration of carriers[5] and for hole injection[6] from a variety of light absorbing substrates. For the polysilanes, charge conduction is by holes only. The measured charge drift mobilities are among the highest reported for amorphous polymers and are approximately four orders of magnitude greater than those described for poly(*N*-vinylcarbazole). Similarly, the measured activation energies (0.25–0.28 eV) which are associated with hole hopping, are also very low for an amorphous organic polymer. In photoconductivity studies on poly(methylphenylsilane), *Kepler* et al.[5] have estimated that the hole generation quantum efficiency approaches 1% at high electric fields and that the carrier lifetimes are in excess of several milliseconds.

The high discharge efficiencies, coupled with the large drift mobilities and nondispersive transport characteristics of the polysilanes are promising for potential Xerographic applications.

4.4. Microlithography

The polysilanes have a number of unique material characteristics for certain lithographic applications, particularly those utilizing multilayer techniques. They are (i) thermally and oxidatively stable yet photochemically labile; (ii) strongly absorbing over a broad spectral range, yet bleachable; (iii) good film formers which are incompatible with most common organic carbon polymers; (iv) high in silicon content and hence, very resistant to etching under oxygen plasma conditions and (v) sensitive not only to light but also to various types of ionizing radiation (γ-ray, X-ray, e-beam, etc.). This combination of characteristics is ideally suited for a variety of multilayer lithographic processes. Accordingly they have been used as soluble, oxygen reactive ion etch (O_2-RIE) resistant barrier layers in trilevel schemes,[7] as new resists for ionizing radiation imaging,[21,38] as combined imaging and etch barrier layers in bilayer processes utilizing both wet[7–9,21,39] and dry development techniques[8,9,38–43] and as short wavelength contrast enhancing materials.[8,9,42,44] Space limitations prevent the detailed discussion of each application and the interested reader is referred to the reference list. The important concepts of bilayer imaging and contrast enhancement are discussed in more detail below.

Multilayer resist imaging schemes for the production of high resolution images offer certain advantages, particularly where troublesome chip topography causes difficulties for single layer schemes. In a bilayer process (see Fig. 3) the substrate with its topographic features is initially coated with a thick (1–5 μm) layer of a planarizing polymer which is usually not photosensitive. A thin imaging layer (0.15–0.5 μm) is then coated on top of the planarizing layer. Upon exposure, the top layer can be imaged and developed with high resolution because the imaging layer is very thin, flat and of uniform thickness. In principle, the initial develop-

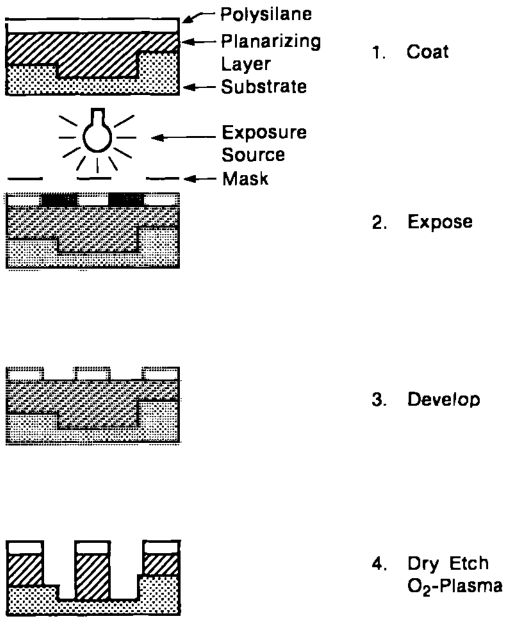


Fig. 3. Bilayer lithographic scheme utilizing a polysilane as the combination imaging and O_2-RIE resistant barrier layer. For ablative self-development in an all-dry process, the image is produced and developed directly during the exposure step.

ment could be either by a classical wet process or by dry, photoablative development. Transfer of these high resolution images through the planarizing polymer layer is usually accomplished by O_2-RIE plasma techniques, since highly anisotropic etching conditions can be employed to assure that the transfer of the initial photoimages maintains near-vertical side wall profiles. The successful utilization of such a scheme requires a photosensitive imaging layer which is also significantly more resistant to etching in the oxygen plasma than the planarizing polymer. The polysilanes are ideally suited for such procedures, since they are strongly absorbing in thin films and permit efficient light absorption, photosensitive over a broad spectral range, and resistant to O_2-RIE conditions due to the formation of a thin skin (50–100 Å) of etch-resistant SiO_x on the polymer surface. Accordingly, they have been utilized in a bilayer configuration for the production and transfer of high resolution images generated by exposure in either the near UV (350–400 nm)[8] or in the mid UV (300–340 nm) spectral regions.[7–9, 39] The use of shorter wavelength exposure sources (e.g., KrF excimer laser, 248 nm) in a 10X projection printing tool leads to significantly improved resolution and allows the delineation of sub 0.5 µm features in a bilayer configuration (see Fig. 4).[45]

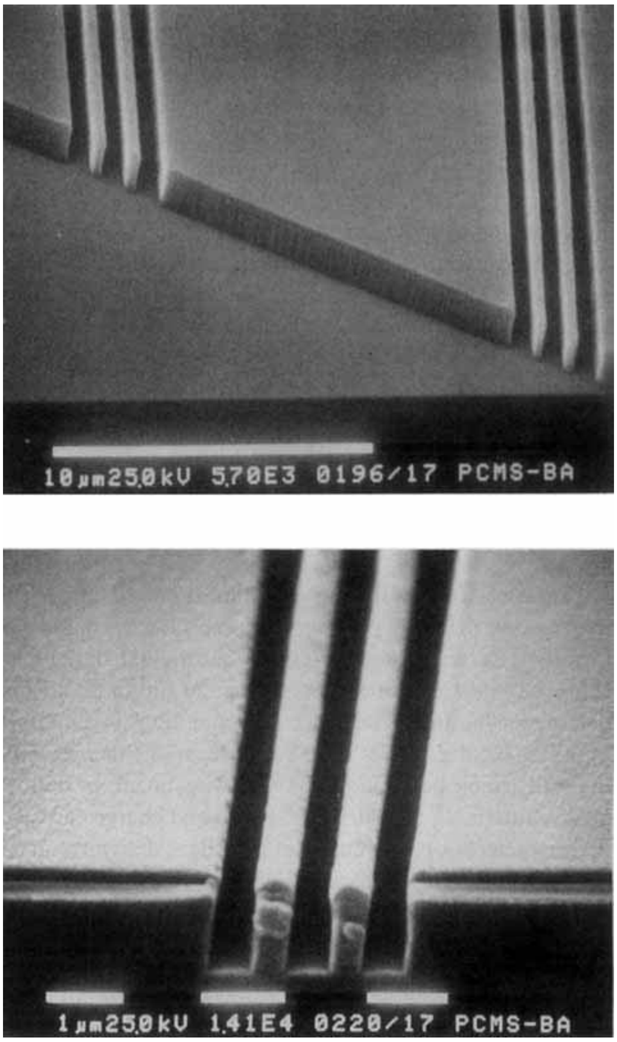


Fig. 4. Images produced in a polysilane bilayer configuration using a deep UV, KrF excimer laser exposure source (248 nm). Bilayer: 170 nm poly(cyclohexylmethylsilane) over 1.0 µm of hard baked AZ-type photoresist; 248 nm. 150 mJ/cm^2, developed 80/20 butyl acetate-isopropanol, O_2-RIE image transfer; (Top) 0.45 and 0.5 µm features, (Bottom) 0.4 µm features.

The bilayer processes described above used classical wet development steps for the production of images in the irradiated polysilane layer. However, high resolution images can also be produced directly in a thin polysilane layer by photoablative imaging. In this process, the polysilane is exposed to a high intensity radiation source (e.g., an excimer laser) during which the polymer spontaneously degrades and volatilizes. Since the image thus produced is subsequently transferred by gas phase O_2-RIE techniques, the procedure constitutes an all-dry, solventless lithographic process requiring no wet development step. The production and transfer of submicron images in such an all-dry process utilizing certain polysilane derivatives for imaging and an UV excimer laser exposure source have been successfully demonstrated.[8, 9]

The generation of images by projection printing in cases where the photomask features are of comparable size to the exposure wavelength is complicated by diffraction distortion of the mask features at the photoresist surface. Contrast enhanced lithography[46] is a technique which employs a thin layer of an appropriate contrast enhancing layer coated on top of a conventional photoresist to improve the diffraction distorted mask image incident on the photoresist. Although a discussion of the concepts involved in the contrast enhancement of images is beyond the scope of this article, the reader is referred to the background information contained in the literature.[46] However, consideration of the process suggests that a workable contrast enhancing material should possess a number of characteristics: (i) it should be thermally and oxidatively stable; (ii) the material should be very strongly absorbing at the exposure wavelength and bleach rapidly upon irradiation and (iii) it should be incompatible with the underlying photoresist so that the material boundaries are clearly delineated. Initially it was also felt that the contrast enhancing layer should be removable prior to the development of the exposed photoresist, but recent studies indicate that this characteristic is not essential.

Certain of the polysilane derivatives not only satisfy the above criteria but also absorb and bleach at shorter wavelengths than commercial materials thus providing the possibility of realizing the enhanced resolution intrinsic to short wavelength exposure sources.[8, 9, 42, 44] A system composed of a conventional diazoquinone-novolac type photoresist overcoated with a thin layer of poly(cyclohexylmethylsilane) has been studied in detail and significant improvements in the image quality relative to the same photoresist without the contrast enhancing layer have been demonstrated.[8, 9, 44] Similar image enhancement for mid UV exposure using other polysilane derivatives[42] has been reported recently.

4.5. Nonlinear Optical Properties

Finally, there is currently increased interest in the nonlinear optical properties of the materials due to their potential utility in optoelectronic or opto-optic devices for telecommunications and optical computing. In this regard, organic materials are of considerable interest because of their intrinsically large nonlinear susceptibilities, rapid response times and high threshold radiation damage values.[47] Furthermore, the utilization of third order effects eliminates the stringent requirements for an acentric molecular environment thus expanding the range of useful materials to polymeric systems.

Studies of the third order susceptibilities ($\chi^{(3)}$) of polymers to date have focused on highly polarizable materials containing conjugated π electron systems such as the polyacetylenes and diacetylenes, rigid rod aromatic polymers, ladder polymers, etc. While these materials have high intrinsic susceptibilities, many have other drawbacks such as limited processability, thermal and/or oxidative liability, nonideal spectral matching, etc.

The polysilanes represent a new class of potentially interesting nonlinear optical (NLO) materials. They are: (i) thermally and oxidatively stable, (ii) the σ-conjugated backbone is highly delocalized and absorbs very strongly in the UV region, (iii) electronic substituent effects can be transmitted over large distances and (iv) the polarizability is large, anisotropic and dependent on backbone conformation. In fact, many of the electronic properties of the polysilanes more closely resemble conjugated π systems than saturated σ bonded carbon-based polymers. In addition, the polysilanes are imagable to high resolution using standard lithographic techniques, an attribute potentially useful for guided wave applications.

Initial NLO measurements on polysilane derivatives have revealed some interesting properties. Relatively large $\chi^{(3)}$ values ranging from 10^{-11} to 10^{-12} esu[11,12,48,49] have been measured and the variation in these numbers with the film thickness suggests possible polymer orientational effects.[12] The resonant $\chi^{(3)}$ value measured for thin films of poly(di-*n*-hexylsilane) ($\sim 10^{-11}$ esu) is the largest reported for a polymeric system which is transparent in the visible and is comparable to values reported for rigid aromatic polymers such as poly(*p*-phenylenevinylene) and poly(*p*-phenylenebenzobisthiazole). Thermal effects on the third harmonic generation efficiency have been correlated with the known thermochromic characteristics of the polymers[12] and the picosecond time response[48] of the nonlinearity reported for poly(methylphenylsilane) is consistent with an electronic mechanism. In addition, biphotonic nonablative, nonlinear photochemical processes have been observed upon exposure to high intensity visible laser light. This photochemistry is anisotropic, and refractive index changes of greater than 2.5×10^{-2} (at 632.8 nm) have been induced due to selective polymer chain degradation in a direction parallel to the electric field of the laser light.[50] Birefringence changes of this magnitude are adequate for the fabrication of channel waveguides and birefringent grating structures.

Although the study of the NLO properties of polysilane derivatives is in its infancy, the unusual spectral properties, the substantial nonlinearities, the capacity for polymer orientation and the anisotropic photolability suggest that these materials are worthy of future investigation.

In summary, the polysilanes represent a new class of radiation sensitive polymers whose unusual electronic structure and properties, and thermochromic behavior are attracting considerable attention. Although most of the work to date has been science-oriented, the modern era of investigation is less than 10 years old. In spite of this, a number of potential applications for these interesting materials have been discovered and described.

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