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Environmentally Friendly Polysilane Photoresists

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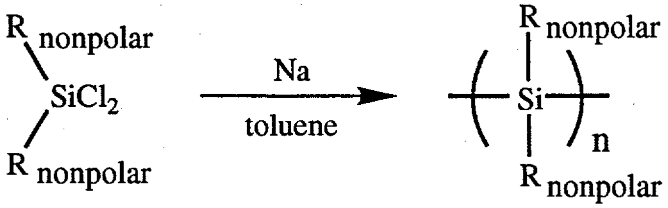
Several novel polysilanes synthesized by the free-radical hydrosilation of oligomeric polyphenylsilane or poly(*p-tert*-butylphenylsilane) were examined for lithographic behavior. This recently developed route into substituted polysilanes has allowed for the rational design of a variety of polysilanes with atypical chemical properties such as alcohol and aqueous base solubility. Many of the polysilane resists made could be developed in aqueous sodium carbonate and sodium bicarbonate solutions. These materials represent environmentally friendly polysilane resists in both their synthesis and processing.

For over a decade, polysilanes have received a great deal of attention as unusual materials with many potential applications. Polysilanes owe much of their unusual properties to the delocalization of the Si-Si sigma bonds along the polymer backbone (*1*). This delocalization allows the silicon catenates to absorb strongly in the UV region. Polysilanes have potential applications as photoconductors (*2,3,4*), semiconductors (*5*), nonlinear optical materials (*6*), LEDs (*7*) and photoresists (*8*).

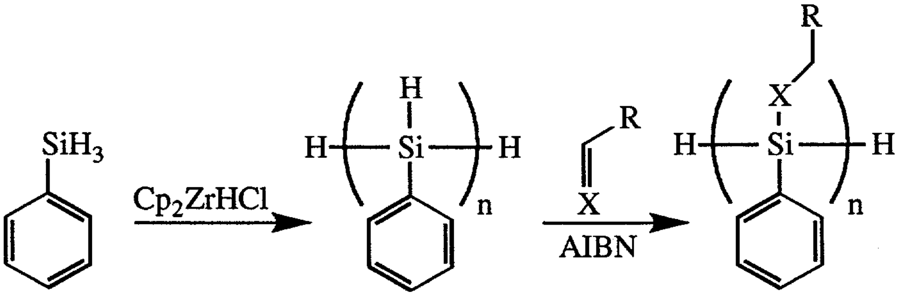
Polysilanes can perform as positive photoresists because exposure to UV light can lead to depolymerization via homolytic cleavage of the Si-Si bond (*9*). With some polysilanes, depolymerization leads cleanly to volatile products. Miller and co-workers (*10,11*) and Zeigler (*12*) demonstrated early on that some polysilanes behave as self-developing resists (a resist that does not require solvents to remove the exposed areas). Resists that self-develop would have a large competitive advantage over traditional resists because they require less processing to create an image. More importantly, dry developing does not generate the large volumes of hazardous waste associated with wet developing (increasingly restrictive EPA regulations on waste treatment have recently put a large financial burden on the electronics industry). Polysilanes also show submicron resolution and excellent oxygen-etch resistance in bilayer microlithography (*10-13*).

Despite their potential, polysilanes have yet to see industrial implementation in the United States (polysilanes are produced on an industrial scale in Japan as precursors to silicon carbide). A major factor hindering the use of polysilanes in industry is the method of their synthesis. Currently, the best synthesis of high molecular weight polysilanes is the Wurtz coupling of dichlorosilanes (Equation 1). This reaction has several drawbacks. The Wurtz couple gives low yields (5-60%) and variable molecular weights. As large quantities of molten sodium metal are used, the reaction is inherently dangerous even on a small scale. The harsh conditions exclude the incorporation of polar side groups on the monomer so only a limited number of monomers can be used. Consequently, most polysilanes synthesized by this method are soluble only in non-polar solvents. The reaction also generates large volumes of metal and solvent waste.



(1)

An alternative and less hazardous method for the preparation of polysilanes was discovered by Harrod in the mid 1980's (*14,15,16*). Titanium and zirconium metallocene complexes were found to perform dehydrogenative coupling on phenylsilane to form oligomeric polyphenylsilane. Although this reaction gives only oligomeric silane catenates, it is high-yielding, runs under very mild conditions and produces very little metal waste (*14-16,17,18*). Recently, Waymouth and Hsiao demonstrated that the Si-H bonds of polyphenylsilane undergo mild free-radical hydrosilations across a wide variety of primary olefins and carbonyl compounds (*19*). This synthesis opens the door to hundreds of novel polysilanes inaccessible by the Wurtz coupling method (Equation 2).



(2)

n = 30-40　　$X = CH_2$, O

The above synthesis represents a commercially attractive method into polysilanes. Not only is the synthesis mild and high yielding, the versatility of the reaction allows for fine-tuning of the physical and chemical properties of the polymer to meet specific applications. Because polar side groups can be attached directly to the polymer, polysilanes can be rendered soluble in environmentally benign solvents such as water or alcohols.

We have begun examining a variety of these new polysilanes for their potential as self-developing photoresists. The printed wiring board (PWB) industry is currently under governmental pressure to reduce the amount of waste water it produces. A typical shop creates about 125 gallons of waste water for every one-square-foot of board made. Use of a self-developing photoresist could reduce the amount of water needed by up to 80%. Other benefits of a self-developing resist include the reduction in the number of processing steps needed to produce a board and a significant reduction in the amount of equipment required. Any resist used in the manufacture of PWBs must show resistance to acidic plating baths and acidic/basic etching solutions. Optimally, the resist films should cast from environmentally benign solvents such as alcohols rather than nonpolar solvents like toluene or methylethyl ketone. While the resolution requirements of the resist need be no finer than 50 microns, thick films (25-50 microns) are required for plating applications. This means that, for a self developing resist, a relatively large amount of material must photovolatilize in order to create a useful image. Moreover, the resist must self develop under exposure from a common and inexpensive UV light source (Most reported self-developing resists require eximer lasers. Eximer lasers would be too expensive for use in PWB shops).

Given these demanding requirements on a self developing resist, our primary focus was on the design of a polysilane that gave clean and rapid imaging. Solubility in alcohols, however, was also desirable. The synthesis shown in Equation 2 is limited in the type of precursor polymers that can be made (low molecular weight polyarylsilanes) but virtually unlimited in the type of side group that can be attached. We explored several different types of side group (Figure 1) in an attempt to use attached functionality to engineer the desired chemical and photochemical behavior of the resist.

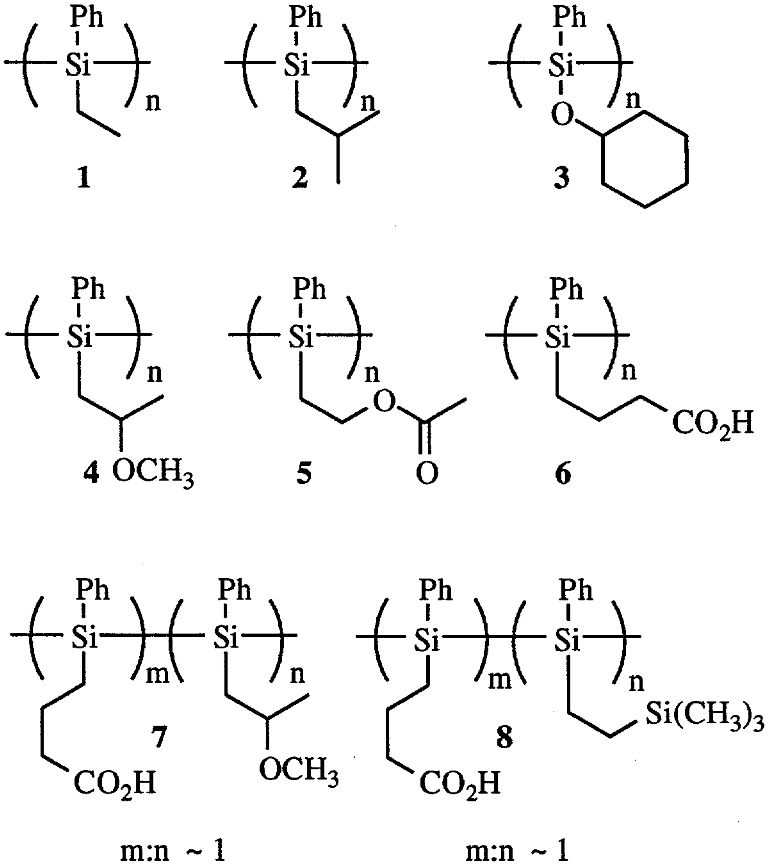


Figure 1. Structures of the polysilanes examined in this study for lithographic behavior. The polymers were all synthesized by the free radical hydrosilation of polyphenylsilane.

Experimental

<u>Substituted Polyphenylsilanes</u>

Polyphenylsilane was synthesized as described by Banovetz and Waymouth using zirconocene chloride hydride (*20*). A typical synthesis of substituted polymer involved dissolving polyphenylsilane (1.0 g) in dry THF (3.0 mL). AIBN (0.16 g, 0.98 mmole) and a slight excess of olefin (10.4 mmole) was added. The solution was degassed by three freeze pump thaw cycles and sealed under vacuum. The resulting solution was heated to 65 °C for 4 hours. The solution was concentrated and the polymer purified by precipitation from THF/MeOH. Polymer **1** was made by bubbling ethylene gas through a toluene solution of polyphenylsilane and AIBN at 65 °C. Polymer **2** was made by charging a pressure tube containing a toluene solution of polyphenylsilane and AIBN with 25 psi of isobutylene. The reaction was allowed to run at 90 °C for 4 hours. Poly(cyclohexyloxyphenylsilane) (**3**) could be made by heating a solution of polyphenylsilane and AIBN in cyclohexanone to 80 °C for 4 hours. Copolymers **7** and **8** were made from polyphenylsilane in a single reaction by adding 50 mole% vinyl acetic acid and a slight excess of 2-methoxypropene or vinyltrimethylsilane to the THF/polymer solution. The polymers were purified by precipitation from THF/benzene.

Substituted Poly(*p-tert*-butylphenylsilanes)

The *p-tert*-butylphenylsilane monomer was made in a two-step reaction. To dry diethyl ether (40 mL) was added silicon tetrachloride (16.2 g, 95.3 mmole). A 2.0 M solution (in ether) of *p-tert*-butylphenyl magnesium bromide was added dropwise over a period of 12 hours (48 mL, 96 mmole). The reaction was allowed to run for a total of 24 hours. The salts were filtered from the solution and the filtrate was added dropwise to a mixture of dry diethyl ether (50 mL) and $LiAlH_4$ (95% dispersion, 3.0 g, 79.0 mmole) at 0 °C. The reaction was allowed to warm to room temperature. After 2 hours, the mixture was cooled to 0 °C and carefully quenched with 2.5 M HCl. Caution! Phenylsilanes in the presence of $AlCl_x$ can redistribute to form silane gas (*21*). It is important that the ether is not lost during the quench to prevent redistribution. Additional diethyl ether may need to be added during the quench to replace any that boils off . The mixture was placed in a separatory funnel and the ether layer collected. The ether solution was washed with 3x50 mL of 2.5 M HCl, dried over $MgSO_4$ and concentrated. The residue was purified by distillation to yield purified product (3.2 g, 20% overall yield, unoptimized).

Poly(*p-tert*-butylphenylsilane) was made with zirconocene chloride hydride following the same procedure used to make polyphenylsilane. The polymerization reaction was allowed to run for 3 weeks and the resulting polymer could not be fractionated with toluene/pentane. No other attempt was made to separate out the low molecular weight fraction. The resulting polymer was a colorless solid with a weight-average molecular weight of 2300 (unoptimized). The free radical substitution reactions were performed as described above.

Lithography

A typical process involved dissolving 0.1 g of polymer in 2.0 mL of solvent (toluene or cyclohexanone). The solution was filtered through a 0.2 μm Nylon filter and concentrated to a volume of ~0.2 mL. The solution was spin-coated onto a silicon wafer at 2000 rpm and allowed to dry under vacuum for 1-24 hours. Exposure was performed in air using an unfiltered, uncollimated 200 watt Hg/Xe lamp through either a shadow mask or a chrome-on-glass mask. Aqueous development, if any, was performed in a beaker with 3% (by mass) aqueous $NaHCO_3$ or 15% aqueous Na_2CO_3.

Results and Discussion

Eight polysilanes were prepared with different functional groups designed to aid in imaging or alcohol solubility. Of the polymers made for this study, only polymers **1** and **2** can be made directly from a Wurtz couple. The rest of the polysilanes are novel materials. Polymer **3** is particularly interesting in that oxygen is attached directly to the silicon backbone. Full characterization of these polymers will be presented elsewhere. Though these new polysilanes are interesting materials in their own right, our immediate concern was screening these oligomers for lithographic behavior.

Table 1. Characterization of Novel Polysilane Oligomers

	% substitution[a]	UVmax	MW[b]	polydisp.
1	54%	314 nm	4322	1.88
2	51%	319 nm	---	---
3	80%	340 nm	3339	1.51
4	88 %	322 nm	3557	1.33
5	77%	315 nm	5896	1.46
6	76%	317 nm	---	---
7	~90%*	306 nm	3514	1.33
8	~90%*	313 nm	7978	1.51

[a] Determined by ^{1}H NMR. [b] Determined by GPC, polystyrene standards. *Broad overlapping peaks do not allow for accurate determination of the percent of substitution by ^{1}H NMR.

As shown in Table 1, the free radical hydrosilation of polyphenylsilane gives 50-90% substitution. The rest of the polymer units contain a Si-H linkage. Polymers **1** and **2** showed the lowest values, probably resulting from the low concentration of the olefin present during the reaction. Polymers **3**-**8** show substitution of 76-90% which are comparable to those values reported by Waymouth and Hsiao. With the exception of polymer **3**, the UV absorption maximum of the polysilane oligomers all range from 306-322 nm. High molecular weight aryl polysilanes generally show a λ_{max} ranging from 335-347 nm. The absorption wavelength maximum of polysilanes and their extinction coefficients both increase sharply with increasing degrees of polymerization (DP) but quickly approach limiting values at a DP of 40-50 (*9*). The DP of the polymers listed in Table 1 range from 30-35 so one would expect the values to be blue shifted slightly. High molecular weight alkyl polysilanes absorb at 303-325 nm. Polymer **3** shows a significant red shift in comparison to the other oligomers, presumably from the electronic effects of the oxygen substituent (*20*).

The small blue shift of our polymers relative to high molecular weight material is of little concern because all polysilane resists bleach significantly during exposure. Bleaching is an important property to photoresists since it allows the UV light to penetrate through to the bottom of the film for an even exposure. All of the oligomers listed in Table 1 show photobleaching characteristic to polysilanes. Figure 2 shows the photobleaching of a thin film of **3** spin-coated onto a quartz plate and given a blanket exposure with a 200 watt Hg/Xe lamp. A quantitative comparison of bleaching rates has not yet been done. One can see in Figure 2 that the polymer bleaches over the entire range from 250 nm to 400 nm. This bleaching, though desirable for an even exposure through a film, makes it increasingly difficult to cleave the smaller polymer chains (since the shorter chains are less photosensitive). Complete depolymerization is necessary for clean self developing. It is therefore desirable to use a UV lamp that contains a substantial emission near 250 nm so that dimers and trimers can absorb light and be cleaved (*12,22*).

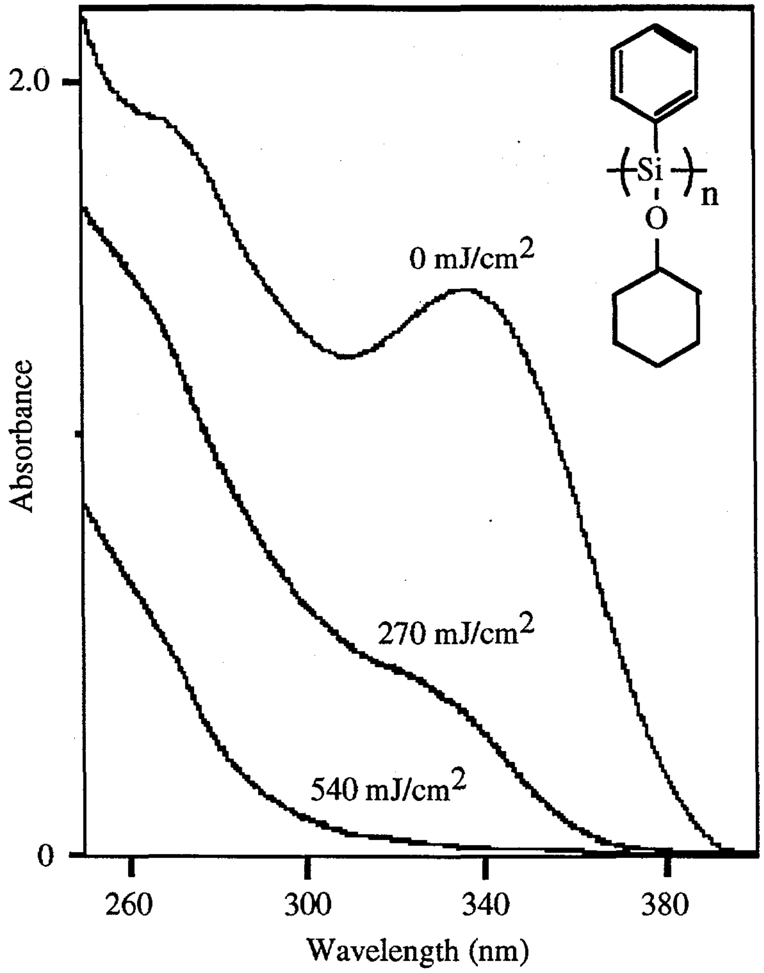


Figure 2. Photobleaching of a thin film of poly(cyclohexyloxyphenylsilane) on quartz. The UV spectra were taken after an accumulated fluence of 0, 270 and 540 mJ/cm^2.

Polysilanes **1**-**8** were examined as both self-developed and as solvent-developed systems. Thin films (5-10 μm) of the novel polysilanes were spin-coated from toluene or cyclohexanone. All polysilanes with the exception of **6** gave good quality films. Polymer **6** always gave films with a mottled surface. If any of the polymer solutions were allowed to stand in air for a period of several hours to several weeks before spin coating, films began to streak. It is assumed that the polymer solutions are slowly crosslinking by the oxidation of unsubstituted silicon units. Evidence for crosslinking has been obtained through GPC (both the molecular weight and the polydispersity of polymer solutions are observed to increase upon standing in air for several days).

High molecular weight poly(methylphenylsilane) has been reported to self-develop under eximer lasers (*23*). Polymer **1** is similar in structure to poly(methylphenylsilane) though it has a significant number of Si-H groups along the backbone. Exposure of a thin film of **1** (~1 μm) with the 200 watt lamp gave a visible image after 5 minutes but SEMs show that little material actually ablated from the film. The fluence for the 5 minute exposure was calculated to be 2700 mJ/cm^2 (measured from 300-400 nm, centered at 365 nm). Since **1** is transparent at 365 nm, this number overestimates the amount of exposure energy interacting with the film. The lack of significant ablation under these conditions is not surprising as polyarylsilanes are known to often crosslink upon exposure, presumably from attack of the silyl radical on the aromatic ring (*9,24,25,26*). Since only arylsilane monomers can be polymerized to a reasonable extent with metallocene catalysts, crosslinking is a concern with any polymer made by this method.

Polymer **2** is similar to **1** but contains a branched substituent. Zeigler has shown that branched substituents improve the photosensitivity of polysilanes, presumably by forcing the polymer chains into an all trans conformation (12). Though the substituent of **2** is slightly heavier than that of **1** (and, therefore, the fragmentation products might be less volatile), it was thought that abstraction of a hydrogen atom from the side chain could lead to the loss of isobutylene (Figure 3). Polymer **2**, however, did not give an improved image over **1**.

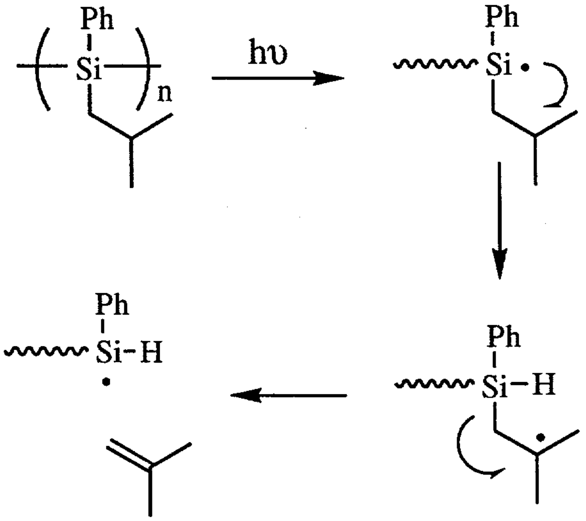


Figure 3. A mechanism for the proposed loss of isobutylene during the photodepolymerization of polymer **2**.

Polymer **3** shows the longest λ_{max} of those listed in Table 1. Since the absorbance of this polymer is red shifted at least 20 nm from the other polymers in Table 1, it was thought that this polymer might show superior lithographic performance. Unfortunately, exposure of **3** gave no discernible image even after 16.2 j/cm^2 exposure. Upon developing the exposed film with pentane, an image quickly appeared. However, as shown in Figure 4, developing left considerable residue in the exposed regions. The porous residue left behind is assumed to be crosslinked silicon oxides.

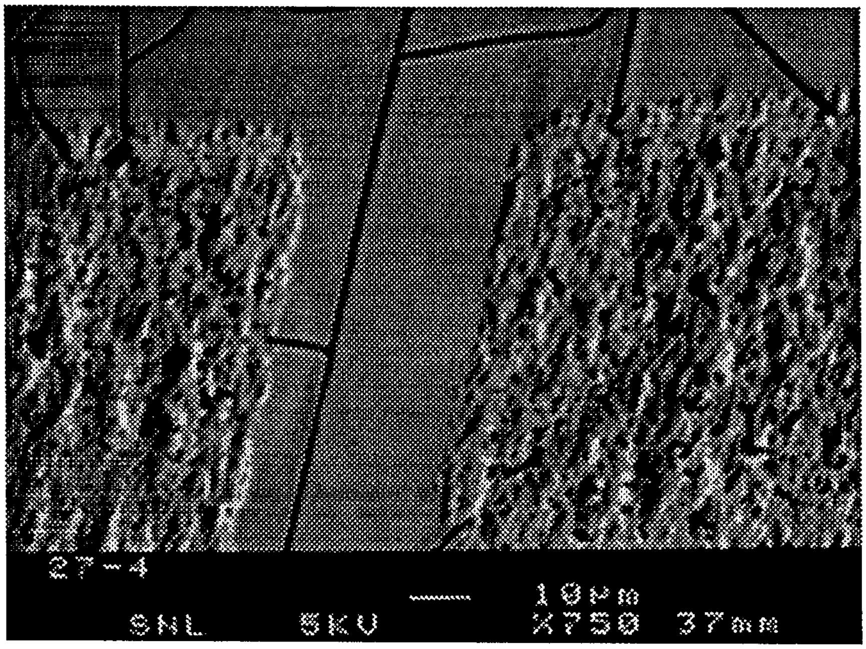
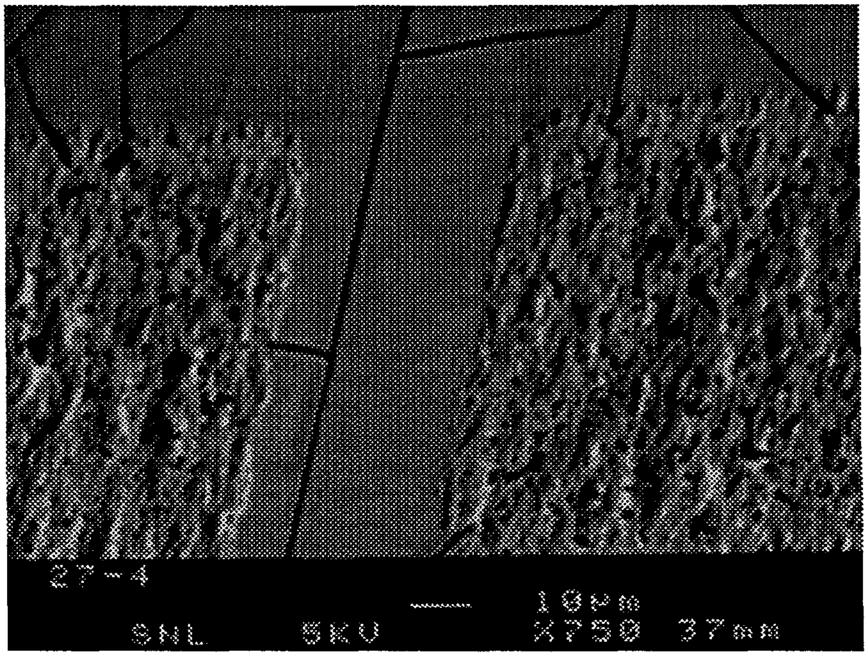


Figure 4. SEM of solvent-developed **3** after a 5 minute exposure through a chrome-on-glass mask. The unexposed areas cracked upon development. The exposed areas left behind a porous residue.

Polymer **4** has a similar branched structure to **2** but contains an ether linkage. This polymer behaves similarly to polymers **1** and **2** even though it has a greater degree a substitution. The ether linkage does not impart enough polarity to the polymer to render it soluble in alcohol. Polymer **5** incorporates a carbonyl chromophore in the side chain. The presence of a carbonyl in the side chain could have two possible interactions with the polysilane. It can aid in the absorption of UV light and it could interact with the silyl radical to help prevent crosslinking (it should be mentioned that even though polyphenylsilane can hydrosilate aldehydes and ketones under free radical conditions, it was found to be unreactive towards esters). Qualitatively, polymer **5** gave a better image than polymers **1**-**4**. Use of other chromophores may improve performance but any chromophore attached would have to be small in size as to not impede volatility.

While these polysilane oligomers were not showing immediate promise as self-developing resists, the opportunity to create an aqueous developed polysilane was apparent. It was reasoned that the attachment of carboxylic acid groups to the polysilane backbone would create a positive resist that could be developed in aqueous carbonate or bicarbonate solutions. Polymer **6** was found to be too soluble in aqueous base to give a good developed image. The number of carboxylic acid groups, therefore, was reduced in polymer **7**. Surprisingly, polymer **7** gave a dramatically improved self-developed image over any of the other polymers shown in Figure 1. Figure 5 shows that a substantial amount of material was lost upon exposure. It is not yet known why **7** performed so much better than the other polymers but it is hoped that further investigations of this polymer and the conditions of exposure will give complete self-developing. Both polymers show good solubility in isopropanol.

In addition to an improved self-developed image, Polymer **7** could be developed with a 3% solution of sodium bicarbonate to yield quality features with out



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In addition to an improved self-developed image, Polymer **7** could be developed with a 3% solution of sodium bicarbonate to yield quality features with out residue. Figure 6 shows 35 µm lines produced after aqueous development of a thin film of **7** exposed for 5 minutes through a chrome-on-glass mask (35 µm resolution is more than adequate for current printed-wiring-board manufacture). Polymer **8**, with its less polar side groups, would only partially develop in saturated sodium bicarbonate. The polymer, however, could be developed completely in 15% sodium carbonate solution. Polymers **6**, **7** and **8** demonstrate how the chemical behavior of the resist can be easily adjusted to give desired properties.

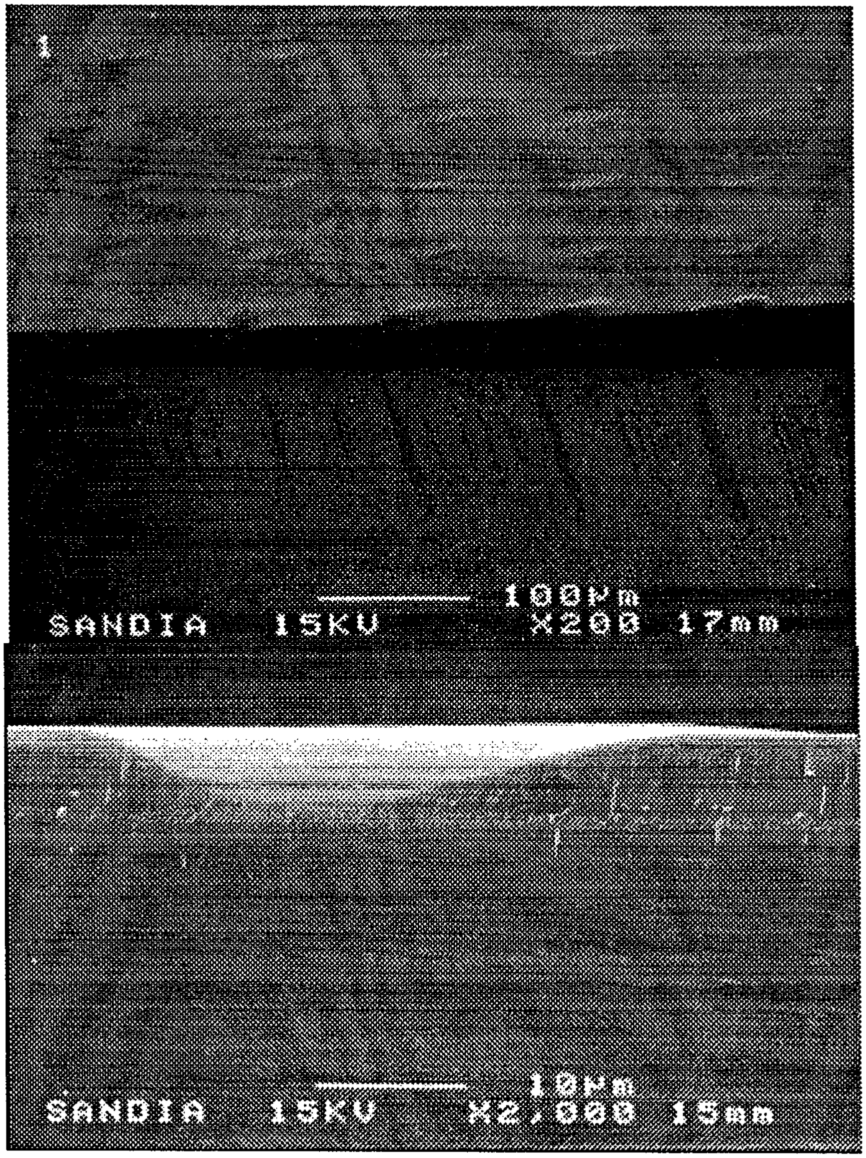

Figure 5. Self-developed image of **5**. Exposure time was 5 min. through a shadow mask.

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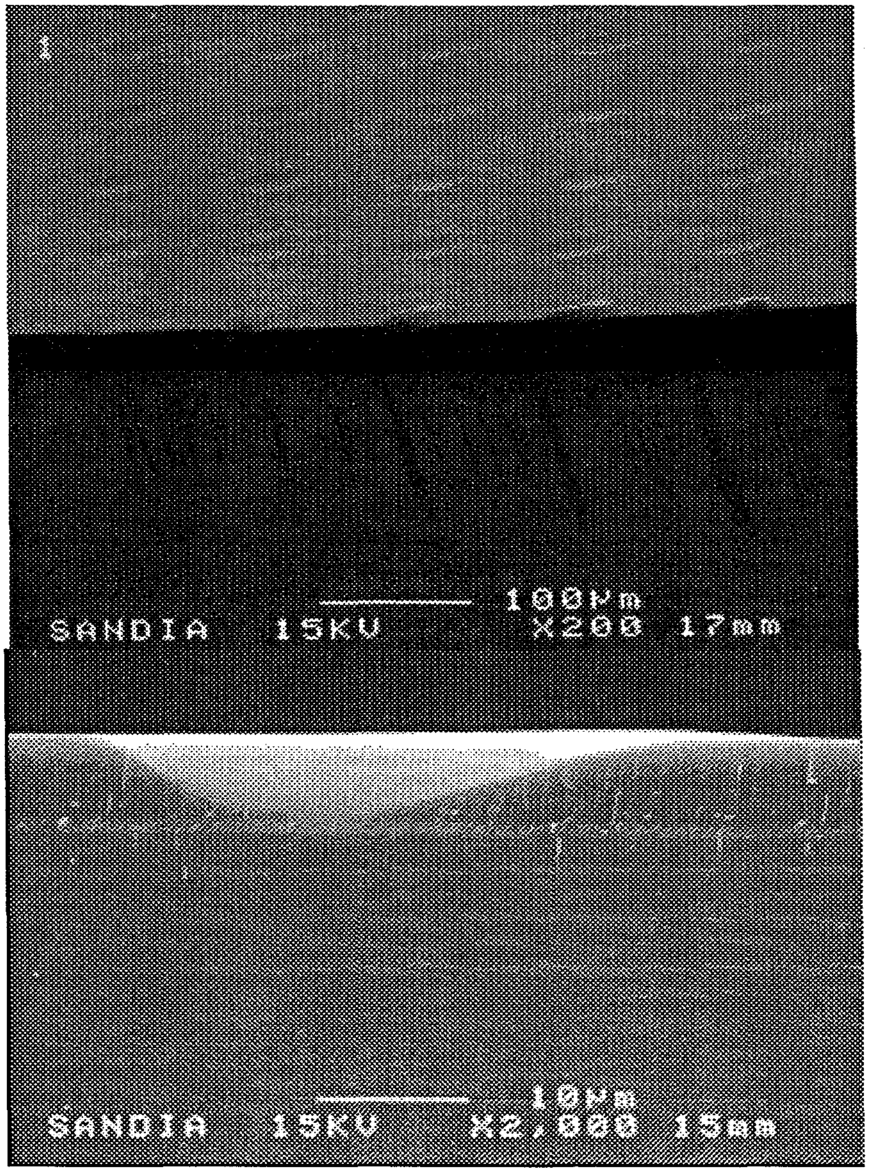


Figure 5. Self-developed image of **5**. Exposure time was 5 min. through a shadow mask.

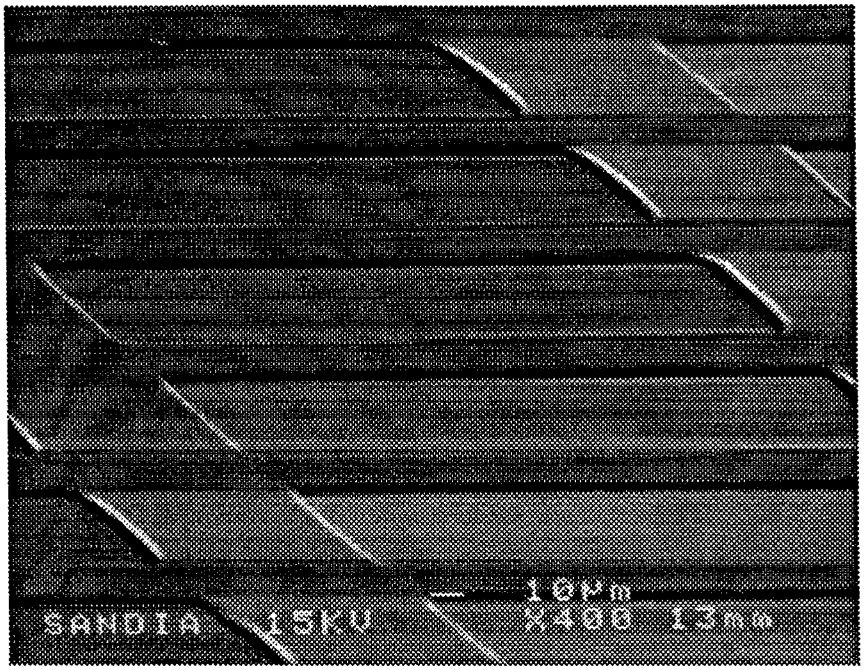
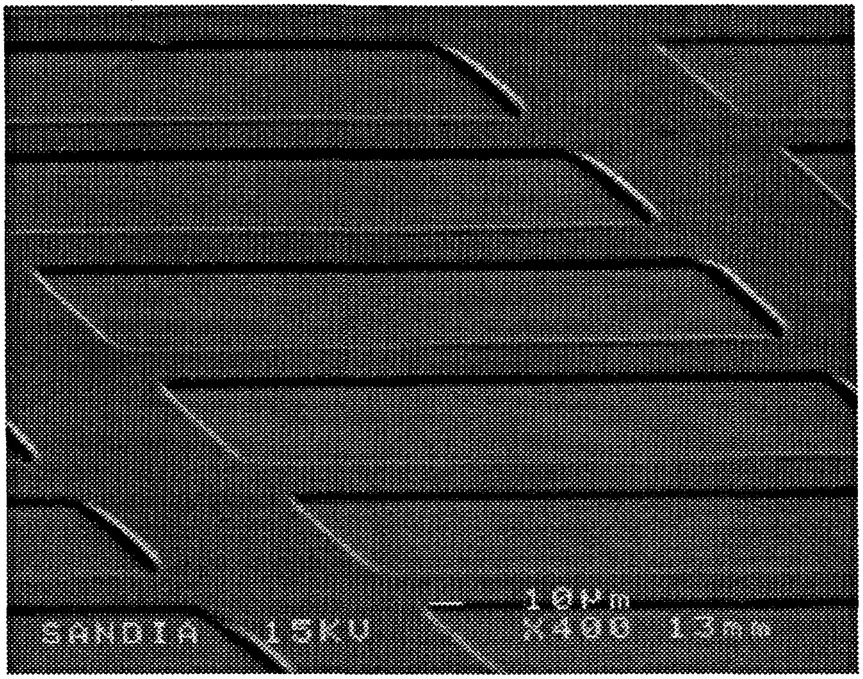


Figure 6. Aqueous-developed image of **5**. Exposure time was 5 min. through a chrome-on-glass mask.

This control is not limited to adjusting the solubility of a resist in a specific solvent. One can theoretically adjust oxygen etch behaviors of the polysilanes in bilayer microlithography. It is known that a high silicon content improves a polymer's oxygen etch resistance (*27*). One would expect, therefore, polymer **8** to have improved oxygen etch resistance over polymer **7**. By adjusting the number of silicon-containing side groups, one should see a corresponding response in etch resistance (*28*).

In an effort to further improve the lithographic performance of our materials, a poly(*p-tert*-butylphenylsilane) precursor was synthesized. It is known that poly(*p-tert*-butylphenylethylsilane) has a higher photosensitivity than poly(phenylethylsilane) (*29,30*). The increased sensitivity is presumably due to the *tert*-butyl group blocking the aryl ring from attack by the silyl radicals making it more difficult to form crosslinks. Poly(*p-tert*-butylphenylsilane) (**9**) was made in three steps from *p-tert*-butylmagnesium bromide and tetrachlorosilane (Equation 3). The polymerization reaction was noticeably slower than the polymerization of phenylsilane but conditions have not yet been optimized.



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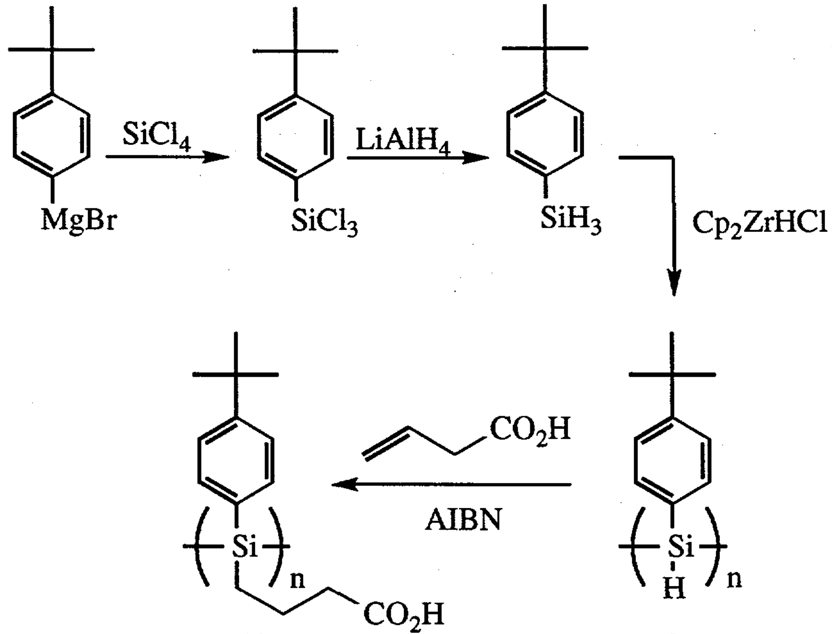

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(3)

The resulting polymer had a weight-average molecular weight of 2300 (corresponding to a DP of about 14, unoptimized) and a polydispersity of 1.18. The polymer could be easily substituted in the same manner as polyphenylsilane with a terminal olefin. Free radical hydrosilation of vinyl acetic acid gave a Polymer **10** with $> 95\%$ substitution (measured by ^{1}H NMR) and a UV absorbance maximum of 317 nm. Exposure of a 1.5 μm thick film of polymer **10** (540 mJ/cm^2) gave a poor self-developed image prior to aqueous development. However, wet developing with 15% aqueous sodium carbonate gave well defined features with 15 μm resolution (Figure 7). The resolution capabilities of this polymer will be studied later under optimal exposure and developing conditions.

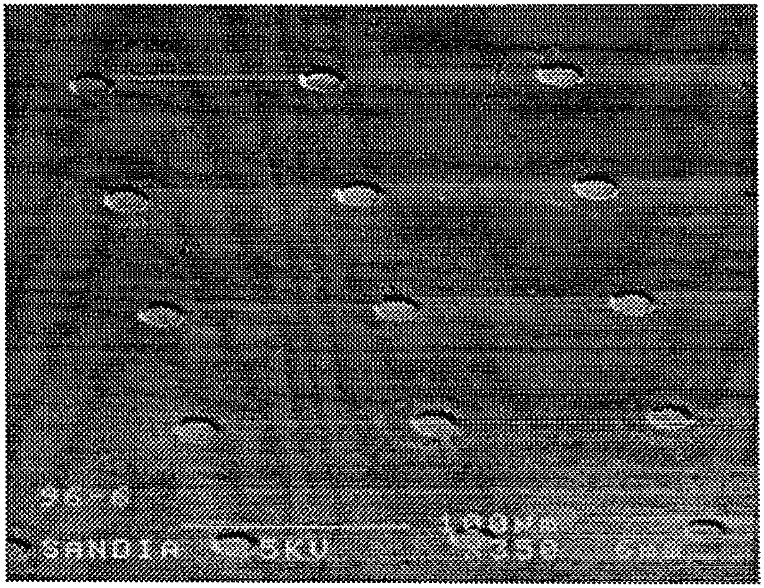

Figure 7. SEM of a 1.5 µm thick film of polymer **10** exposed for 1 minute and developed in aqueous Na_2CO_3.

Conclusions

We have synthesized several novel polysilane oligomers that show complete development in aqueous sodium bicarbonate and sodium carbonate solutions. These polymers represent a significant advancement in polysilane lithography in that the polymers were synthesized in a high yielding two-step reaction from commercially available starting materials can produce a clean image using inexpensive exposure tools (Hg/Xe lamp and a glass mask) and environmentally friendly developing solvents (aqueous $NaHCO_3$ or Na_2CO_3). Past work on polysilanes had always involved a low-yielding and dangerous synthesis, expensive eximer laser exposure tools and/or organic developing solvents. This work also demonstrates that a great deal of flexibility and control can be exercised over the chemical properties of polysilanes. We are currently investigating how different side groups influence self development of the phenylsilane polymers. It is hoped that judicial choice of the side groups can hinder crosslinking and permit clean photovolatilization. We see potential in the *p-tert*-butylphenylsilane polymers as aqueous resists for deep UV microlithography. This work is represents a quick survey of the many novel polysilanes that can be synthesized by this new method for potential lithographic application. Optimization and a detailed comparison of polymer properties is needed for better understanding of the influence complex organic side groups can have on polysilanes. This knowledge should lead to the design of new and better materials for lithography as well as other electronic applications.

Acknowledgments

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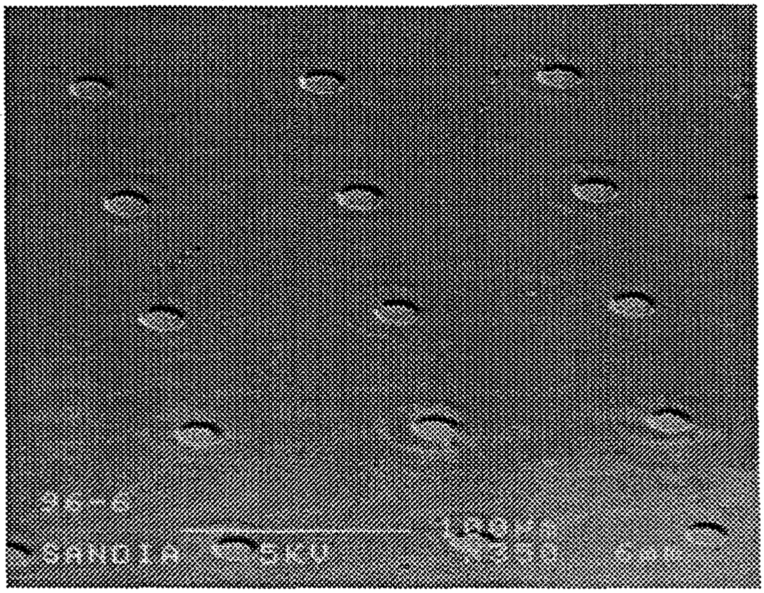

Figure 7. SEM of a 1.5 µm thick film of polymer **10** exposed for 1 minute and developed in aqueous Na_2CO_3.

Conclusions

We have synthesized several novel polysilane oligomers that show complete development in aqueous sodium bicarbonate and sodium carbonate solutions. These polymers represent a significant advancement in polysilane lithography in that the polymers were synthesized in a high yielding two-step reaction from commercially available starting materials can produce a clean image using inexpensive exposure tools (Hg/Xe lamp and a glass mask) and environmentally friendly developing solvents (aqueous $NaHCO_3$ or Na_2CO_3). Past work on polysilanes had always involved a low-yielding and dangerous synthesis, expensive eximer laser exposure tools and/or organic developing solvents. This work also demonstrates that a great deal of flexibility and control can be exercised over the chemical properties of polysilanes. We are currently investigating how different side groups influence self development of the phenylsilane polymers. It is hoped that judicial choice of the side groups can hinder crosslinking and permit clean photovolatilization. We see potential in the *p-tert*-butylphenylsilane polymers as aqueous resists for deep UV microlithography. This work is represents a quick survey of the many novel polysilanes that can be synthesized by this new method for potential lithographic application. Optimization and a detailed comparison of polymer properties is needed for better understanding of the influence complex organic side groups can have on polysilanes. This knowledge should lead to the design of new and better materials for lithography as well as other electronic applications.

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