



Water Dispersible Silanes for Wettability Modification of Polysilicon

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The objective of this research has been to develop the chemistry and techniques for the application of hydrophobic coatings on polysilicon substrates from aqueous media with the ultimate goal of applying these techniques for preventing or reducing release as well as in use stiction in microelectromechanical structure devices. In this paper, the results obtained from a chemical system consisting of a water dispersible silane and a cationic surfactant are presented. Key experimental variables that have been investigated are the concentration of reactive silane and cationic surfactant, type of oxidation pretreatment, pH of the silane dispersion, and curing temperature.

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Surface micromachining using deposited polysilicon films is a technology that is now widely used for the fabrication of microelectromechanical structures (MEMS). One of the biggest yield and reliability problems in the fabrication of such structures is stiction or adhesion to the substrate and to adjacent microstructures. This may occur during the drying step that is required after wet processing and/or during use of a device.

In a conventional drying process liquid is removed by evaporation, and capillary forces that arise as a result of the surface tension of the liquid-vapor interface cause stiction. A number of methods have been investigated to reduce or prevent stiction, and they are based on reduction of surface tension or increase of contact angle. One technique is to carry out the drying at elevated temperatures to exploit the fact that surface tension decreases on increasing the temperature.¹ Another method uses a supercritical drying process,^{2,3} where the liquid is transferred to vapor via the supercritical phase and hence there are no capillary forces to contend with. Carbon dioxide has been the material of choice for supercritical drying because of its low critical temperature and pressure ($T_c = 31.1^\circ\text{C}$, $P_c = 72.8$ atm).

Deposition of self-assembled monolayer (SAM) coatings is one of the most successful approaches to wettability modification of silicon surfaces in order to reduce adhesion in microstructures. This approach involves making the surfaces of the polysilicon hydrophobic, through the formation of a SAM film.⁴⁻⁶ As a result, microstructures come out of the final water rinse extremely dry. Coatings of different alkylchlorosilanes (RSiCl_3), alkylsiloxanes [$\text{RSiO}_x(\text{OH})_y$], and alkylaminosilanes have been deposited onto oxidized silicon surfaces.⁷ High quality SAMs of alkyltrichlorosilane derivatives are not easy to form, mainly because of the difficulty in controlling the amount of water in the liquid medium used for deposition. While loosely packed monolayers are formed in the absence of water, excess water results in polymerization of silanes and eventual deposition of polysiloxane on the surface.⁸ As a result, the solvents used for SAM coating with RSiCl_3 precursors must be as anhydrous as possible. Typically, for an octadecyltrichlorosilane (OTS) coating, an alkane is used with 30 vol % of a cosolvent such as carbon tetrachloride (CCl_4) or chloroform (CHCl_3).⁹ The overall coating procedure also requires the use of isopropyl alcohol (IPA) in a number of intermediate rinsing steps.

Increasing concerns regarding the use of organic solvents in the work place and the generation of organic wastes have sparked interest in the feasibility of applying highly hydrophobic coatings from aqueous media. The objective of this research has been to develop

the chemistry and techniques for the application of hydrophobic coatings on polysilicon substrates from aqueous media. Specifically, a water dispersible silane has been used to render polysilicon hydrophobic, and the hydrophobicity of the silane coatings has been characterized.

Experimental

Materials.—The polysilicon samples used for experimental work were 2 μm thick low pressure chemical vapor deposition (LPCVD) films deposited on top of Si wafers and were donated by Motorola, Inc., in Phoenix. Phosphorous doping of the samples was achieved by depositing 2 μm phosphosilicate glass (PSG) (6.5 wt % P) followed by annealing at 1015°C for 5 h. The films had an rms roughness of 43 nm.

A commercially available, proprietary, water dispersible octadecylsilane based compound (Siliclad®) was used to form the hydrophobic coatings on polysilicon. This compound, purchased from Gelest, Inc., is reported to contain the reactive silane at a concentration of 20% in a mixture of tertiary alcohols and diacetone alcohol. According to the manufacturer, this silane can be used for coating glass from a 0.1-1% reactive silane solution in water at a pH of 4 to 5. The chemical was diluted in controlled amounts of deionized (DI) water (resistivity of 18 M $\Omega\text{-cm}$) before use.

Water dispersible silanes typically have a general structure of (PB)-(PL)-spacer-(O-X)₃, where PB is the hydrophobic alkyl group, PL is the hydrophilic head group, X is a proprietary end blocker, and the spacer is a short $(\text{CH}_2)_n$ group that gives flexibility to help alignment and assembly. In alcoholic solutions the -O-X groups are stable, but in aqueous solutions they undergo hydrolysis and condensation at a rate dependent on the pH. Depending on the chain length of the alkyl group in R, the silane may form micelles in an aqueous solution with the core containing R-(CH₂)_n- (Fig. 1).

An alkyl dimethyl benzyl ammonium chloride cationic surfactant [Empigen BAC 50, $\text{RN}(\text{CH}_3)_2\text{CH}_2\text{C}_6\text{H}_5\text{Cl}$ where R is predominantly C₁₂-C₁₄, Mw = 354] was used to improve the stability of aqueous silane dispersions. This surfactant was obtained from Albright & Wilson as a 50% aqueous solution. The critical micelle concentration (CMC) of this surfactant was determined to be ~70 ppm. The organosilane and surfactant were used as received.

Procedure.—Polysilicon samples (1.5 × 1.5 × 0.37 cm) were subjected to different surface pretreatments that included an HF etch followed by immersion in SCl , H_2O_2 , or $\text{H}_2\text{SO}_4/\text{H}_2\text{O}_2$ solution (see Table I for experimental conditions).

Organosilane coatings were prepared by controlled immersion of the polysilicon substrates at a rate of 140 $\mu\text{m/s}$ in dilute dispersions of reactive silane in water with and without the surfactant. At this immersion speed the coating time was ~2.5 min. The coated substrates were cleaned by rinsing with DI water. Hydrophobicity of the

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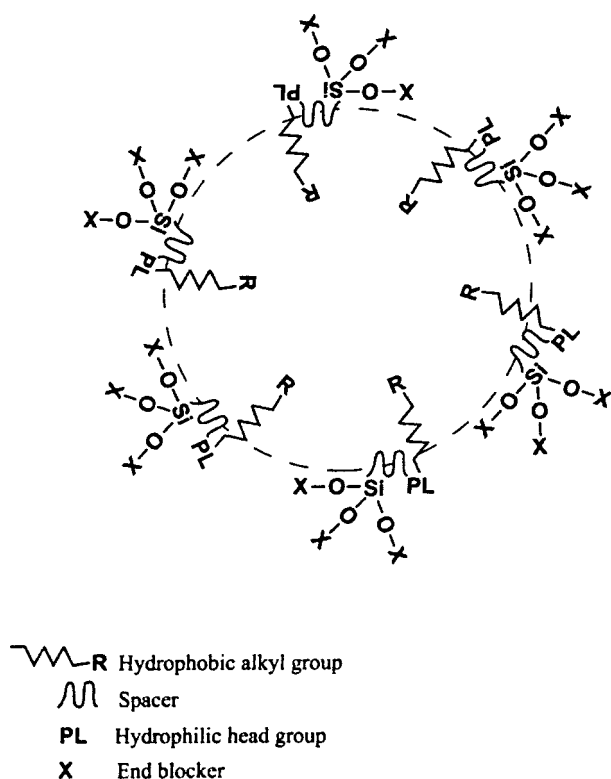


Figure 1. Aggregates of water dispersible silanes.

coatings was characterized by measuring the contact angle of deionized water immediately after film deposition using a dynamic contact angle analyzer (Cahn DCA-312). Curing of the coatings was done in a convection oven (VWR model 1330 FD) for 5 min at a constant, predetermined, temperature. Thermal stability experiments were carried out at atmospheric pressure by heating the samples in a tube furnace for 5 min in air and nitrogen environments.

The stability of silane dispersions was determined by viscosity measurements using a vertical Ostwald viscosimeter at 30°C.

In situ attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR) was used to follow the formation of silane coatings as a function of time. These measurements were carried out using a Perkin-Elmer spectrum 2000 FTIR spectrometer equipped with a midinfrared deuterated triglycerine sulfate (TGS) detector. Undoped single-crystal silicon parallelogram plates (50 × 15 × 0.5 mm), polished on both faces and beveled at 45°, were used as internal reflection elements (IRE). Samples were positioned into a liquid flow cell made from polytetrafluoroethylene (PTFE) (Harrick Scientific model MEC-1T0). The cell was installed in a twin parallel mirror reflection attachment (Harrick Scientific model TMP-F-PO5

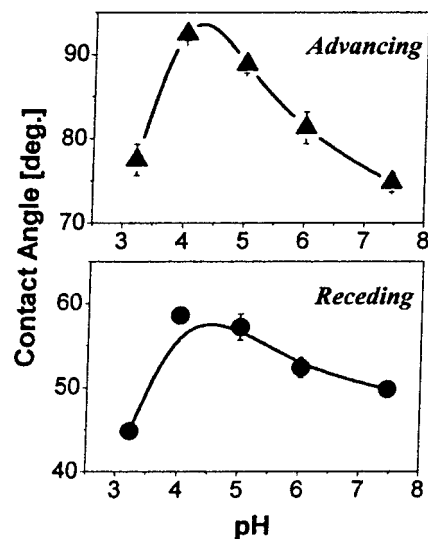


Figure 2. DI water contact angles on coatings deposited from an aqueous medium containing 3% reactive silane at different pH.

45°). Up to 60 solution sensing internal reflections of an IR beam incident normal to the beveled faces of the IRE were achieved. Interference from atmospheric H₂O and CO₂ was minimized by flushing the spectrometer optics and sample compartment with ultrapure nitrogen gas.

The silicon crystal was first subjected to an oxidation treatment with NH₄OH/H₂O₂/H₂O (SC1) and then mounted in the ATR flow cell. The cell was flushed with DI water, and a background spectrum of the Si-water interface was taken. A dilute solution of water dispersible silane was then injected rapidly (~0.3 mL/s) into the cell, followed by continuous pumping of the solution at a slower rate (0.2 mL/min). Spectra were recorded every minute during the first 15 min and then less frequently for a total time of 3 h. The IR spectra were collected at 4 cm⁻¹ resolution and averaged over 5 to 15 individual spectra scans.

Results and Discussion

Since the kinetics of hydrolysis and condensation of alkoxy-silanes in water has been reported¹⁰ to be strongly dependent on pH, initial experiments were focused on applying the coatings from an aqueous dispersion containing 5% reactive silane at different pH values. The pH was adjusted with hydrochloric acid and potassium hydroxide. It may be seen in Fig. 2 that the hydrophobicity of the coatings exhibited a maximum at a pH of 4. It should be mentioned that at pH 6 the dispersion was hazy, and at pH values above 7 the dispersion separated into two phases. In the pH range of 3 and 6 the silane dispersion was clear for almost 1 day. For optimal dispersion stability it is desirable to have fast hydrolysis and low condensation,

Table I. DI water dynamic contact angles on coatings deposited onto chemical oxides formed on polysilicon by different treatments.

Oxide	Without coating		With coating			
	Advancing	Receding	Before curing		Cured at 125°C, 5 min	
			Advancing	Receding	Advancing	Receding
1:1:25 NH ₄ OH:H ₂ O ₂ :H ₂ O (10 min, 70°C)	15 ± 3	14 ± 1	91 ± 4	52 ± 8	108 ± 6	68 ± 1
1:4 H ₂ O ₂ :H ₂ SO ₄ (15 min, 80°C)	18 ± 2	17 ± 1	88 ± 2	50 ± 2	111 ± 5	64 ± 1
30% H ₂ O ₂ (15 min, 20°C)	13 ± 5	17 ± 1	87 ± 1	55 ± 1	108 ± 5	67 ± 2
50:1 HF (1 min)	90 ± 4	46 ± 3	93 ± 4	50 ± 1	110 ± 2	63 ± 1

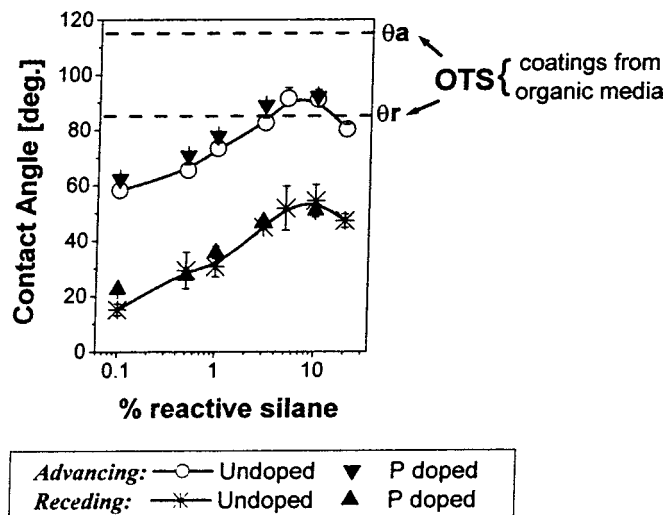


Figure 3. DI water contact angles on coatings deposited from aqueous silane dispersions containing different amounts of reactive silane onto undoped and P-doped polysilicon.

which for Siliclad appears to be around pH 4 and is similar to what has been reported in the literature¹¹ for other alkyltrialkoxysilanes.

Water contact angles on undoped and phosphorous-doped polysilicon samples coated by immersion in silane dispersions at pH 4 are displayed in Fig. 3 as a function of reactive silane concentration. As may be seen from this figure, highly hydrophobic coatings, as determined by the value of the advancing (θ_{adv}) and receding (θ_{rec}) contact angles, are formed when the reactive silane concentration is higher than 3%. Phosphorous doping of the samples did not affect the hydrophobic character of the coatings. The contact angle values for coatings prepared from a dispersion containing 3% or more reactive silane are lower by $\sim 30^\circ$ than those for coatings formed from an organic solvent containing octadecyltrichlorosilane (OTS) ($\theta_{adv} = 115^\circ$ and $\theta_{rec} = 85^\circ$).¹²

The next step in this research was to check whether drying/curing at elevated temperatures could improve the coating hydrophobicity. The effect of curing temperature in air on the hydrophobic character of the coatings applied on a peroxide conditioned surface from an aqueous medium containing 5% reactive silane is shown in Fig. 4. Both the advancing and receding contact angles increase with an increase in the curing temperature. For example, curing of the coatings at 250°C increased the advancing contact angle from 90° to 120° and the receding angle from 60° to 85° . The same behavior was observed for coatings formed on polysilicon surfaces subjected to other types of oxidation pretreatments. This increase could be as a result of improved packing of the film due to cross-linking of Si-OH groups in the silane molecules deposited on the surface. It has been reported that covalent attachment of hydrolyzed organosilanes with surface silanols can be facilitated by heating the silane solution at 70°C .¹³ Interestingly, the contact angles obtained by curing the silane coatings at 250°C are equal to or slightly higher than the reported values for OTS coatings with and without curing.^{4,5,12}

One of the drawbacks of the aqueous-phase deposition process is that water can be trapped in the coatings and decrease their hydrophobic nature. The ATR-FTIR spectrum of an uncured coating in a nitrogen environment was taken (Fig. 5) to determine whether water was contained in these coatings. It was found that moisture, which can be identified as a strong and broad peak in the $3600\text{--}3200$ and $1640\text{--}1615\text{ cm}^{-1}$ region was not present in the coating. This indicates that cross-linking most likely occurs during curing of the coating.

A preliminary study of the effect of surface roughness on the coating hydrophobicity was also investigated. For this purpose, coatings were also applied to single-crystal silicon samples pretreated in

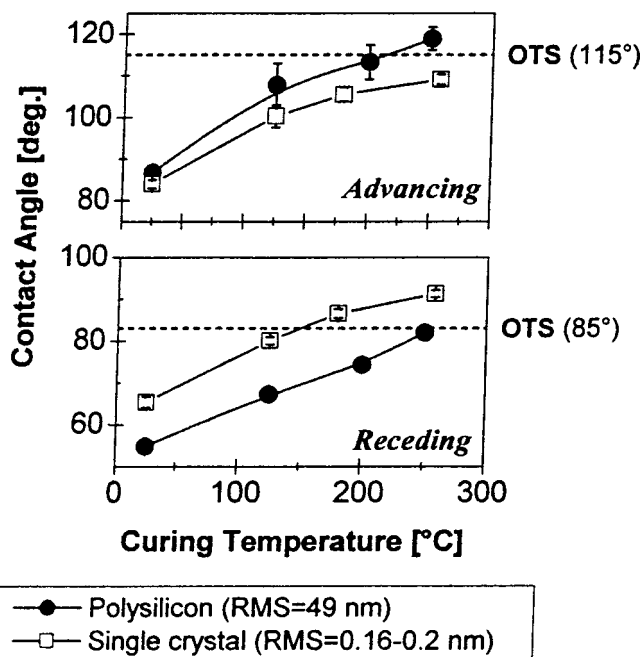


Figure 4. Effect of temperature and substrate roughness hydrophobicity of coatings (coatings deposited from 5% reactive silane dispersions).

a 30% H_2O_2 solution. A comparison of advancing and receding water contact angle values obtained on a smooth single-crystal surface and a rough polysilicon surface is also shown in Fig. 4. The advancing angles of water on polysilicon are higher than those on single-crystal silicon, while the reverse is true for receding angles. This can be explained using Wenzel's theory,¹⁴ which relates the contact angle on a rough surface to that on a smooth surface through the roughness factor ($r > 1$)

$$r = \frac{\cos \theta_{\text{rough}}}{\cos \theta_{\text{smooth}}} \quad [1]$$

Contact angles of less than 90° are decreased by roughness, while angles greater than 90° are increased by surface roughness.

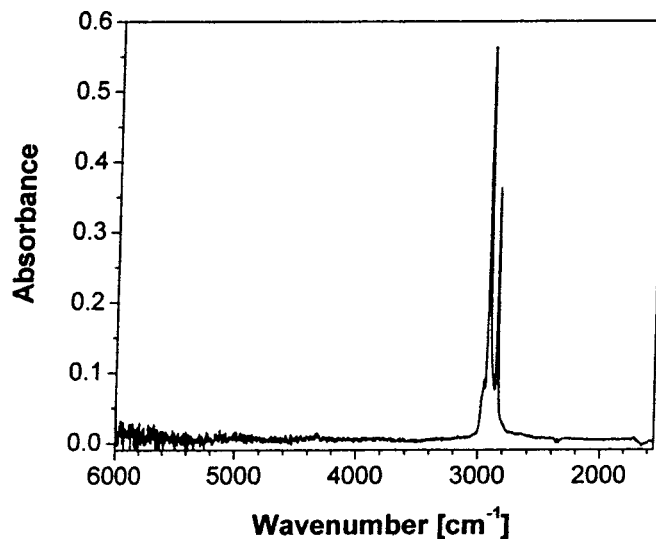


Figure 5. ATR-FTIR spectrum of Siliclad coating onto single crystal under a nitrogen environment.

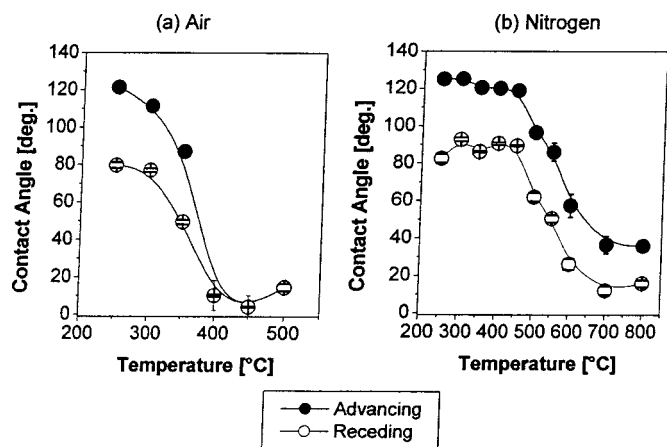


Figure 6. Thermal stability of Siliclad coatings deposited on polysilicon in air and nitrogen environments.

Figure 6 shows the DI water contact angles on polysilicon samples coated from 3% reactive silane dispersion at pH value of 4 as a function of annealing temperature. These samples were annealed in a nitrogen or room air environment. For the samples annealed in nitrogen, the contact angles remained constant up to 450°C. However, the film hydrophobicity is severely degraded when heated in air above 250°C. Considering the literature information^{4,5} that OTS coatings degrade when heated in air above 150°C and in nitrogen at 400°C, the aqueous silane system may offer some advantages in high temperature environments.

In order to immobilize the organic silane molecules on the substrate, a covalent bond between the silane molecules and Si-OH groups on the substrate surface is necessary. Since the nature and reactivity of Si-OH groups may depend on the oxidation treatment, investigations were carried out to determine the effect, if any, of the type of chemical oxidation treatment on the hydrophobicity of coatings. Table I shows that the quality of the coating is independent of the type of oxidation pretreatment. Interestingly, it was found that hydrophobic coatings could also be applied to freshly prepared hydrogen-terminated surfaces. It is not clear at this point whether this is due to oxidation that may have occurred during the water rinsing step, physical adsorption of the silane onto bare polysilicon, or chemisorption of the hydrolyzed silane on the hydrogen-terminated surface. Even though the reaction of alcohols with

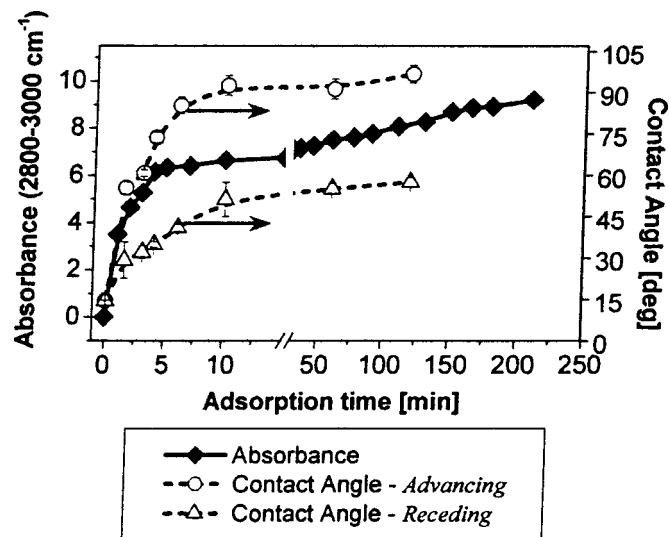


Figure 7. Effect of immersion time in a 0.5% reactive silane dispersion.

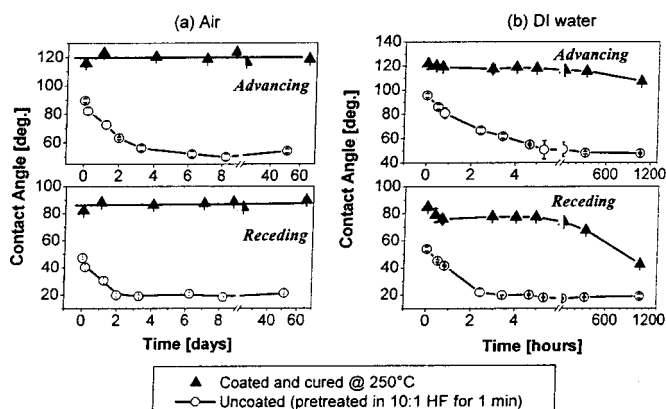


Figure 8. Stability of coated and uncoated samples in (a) air and (b) DI water.

hydrogen-terminated silicon surfaces has been reported to occur in dry environments,¹⁵⁻¹⁸ no literature data suggest interaction in an aqueous environment. If Siliclad has a cationic group in its structure, then the negatively charged Si-H surface¹⁹ could induce the adsorption of the silane molecule to the substrate through electrostatic interactions. As shown later (Fig. 8), the hydrogen-terminated surface requires many hours of immersion in water to be transformed to a hydrophilic state.

Decreasing the reactive silane concentration in the coating solution is likely to enhance the bath life due to reduced bath cross-linking of hydrolyzed end groups of silane. Hence, the feasibility of applying the coatings from solutions containing 0.5% reactive silane was investigated as a function of immersion time. In these tests the coating formation was followed by measuring the absorbance due to the asymmetric -CH₂, symmetric -CH₂, and -CH₃ stretching vibrations in the 2800-3000 cm⁻¹ region of the ATR-FTIR spectra. As shown in Fig. 7, coating coverage increased rapidly during the first 10 min and slowed down perhaps due to silane adsorption onto empty spaces and/or reorientation of the molecules. In the same

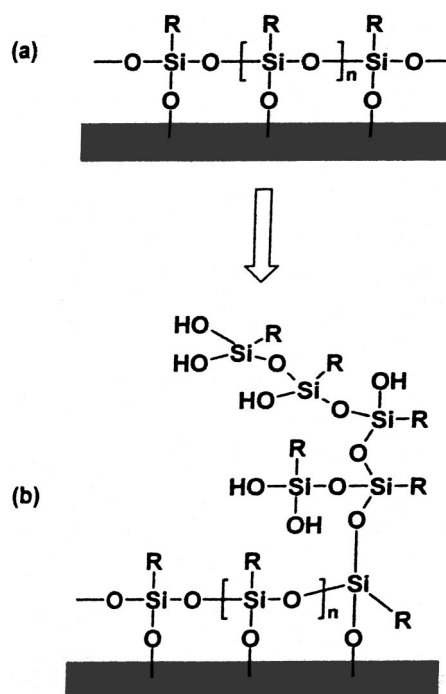


Figure 9. Monolayer vs. built-up organic film.

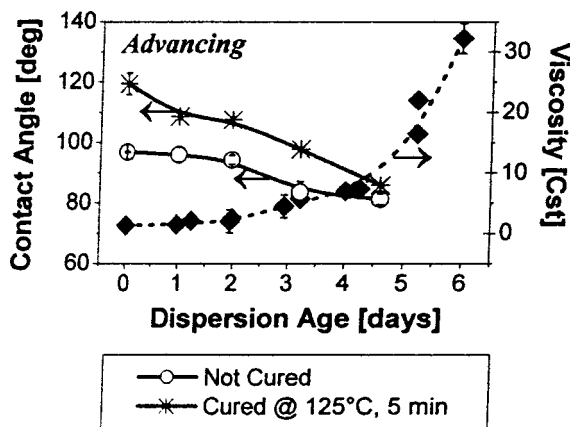


Figure 10. Viscosity of silane dispersions and water contact angles on coated surfaces as a function of dispersion age.

figure, contact angles on coatings deposited at different immersion times are shown. It may be seen that a 10 min immersion time in a silane dispersion containing 0.5% reactive silane yields coatings which are comparable to coatings deposited from a 3% reactive silane by the immersion/emersion technique done in ~2.5 min (Fig. 3). This indicates that high coverage can be achieved by exposing the substrate to reactive silane dispersions of low concentration for long periods of time.

The effect of the presence of oxygen in air and in water on the hydrophobicity of the coatings was studied by placing coated and uncoated samples in laboratory air and by immersing samples in DI water. Bare polysilicon samples pretreated in HF were used as a baseline. It may be seen in Fig. 8b, that the advancing and receding water contact angles on hydrogen-passivated polysilicon decreased rapidly, in a couple of hours, on exposure to water as a result of native oxide growth. The coated samples did not show any degradation for almost a month. This indicates that the coatings are stable for long periods of time under high humidity conditions. When exposed to laboratory air, a bare polysilicon sample showed significant oxidation after a couple of days, but the coated sample did not show any decrease in its hydrophobic nature.

The attachment of aqueous silane to oxidized silicon surface is shown in Fig. 9a. For efficient attachment to surfaces, water dispersible silanes need to be hydrolyzed but at the same time cross-linking between silane molecules in the bulk needs to be minimized. The attachment of bulk cross-linked silane oligomers would result in the buildup of silane films, as shown in Fig. 9b. Aqueous silane dispersions containing 3% reactive silane at a pH value of 4, were not very

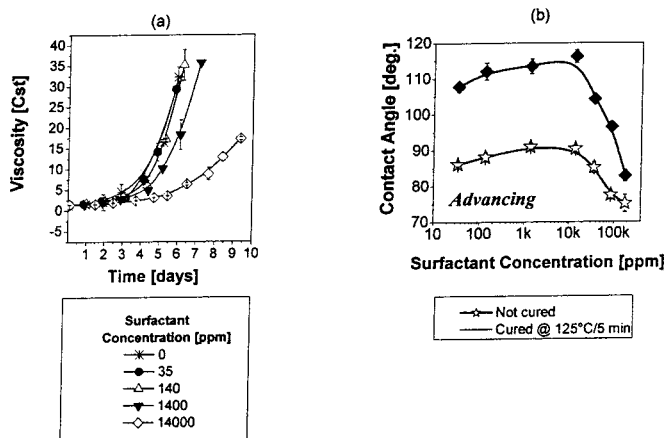


Figure 11. (a) Stability of silane dispersions and (b) coating hydrophobicity as a function of surfactant concentration.

stable and turned cloudy and precipitated after standing for several days. The stability of silane dispersions was evaluated by measuring the viscosity at 30°C as a function of aging time (Fig. 10). The viscosity increased slowly during the first few days and then increased rapidly. The stability limit was taken at the time when rapid change in viscosity started to occur. This pattern of rapid increase in viscosity at the gel point is typical for thermosetting systems. It may be seen from Fig. 10 that the hydrophobicity of the coatings decreased with the onset of the rise in viscosity of the silane dispersion. After aging the dispersion for 4 days, curing at 125°C did not improve the hydrophobic character of the coatings.

Experiments were conducted to check whether the addition of a cationic surfactant can increase the stability of the silane dispersions and thereby improve coating bath life. A cationic surfactant was chosen because changing the pH can control its adsorption onto preoxidized polysilicon. As may be seen from Fig. 11a, the addition of a cationic surfactant, at a suitable concentration, can delay the onset of the rise in viscosity. The surfactant addition had no deleterious effect on the contact angle when the surfactant concentration was below 10,000 ppm (Fig. 11b), but at higher concentrations the surfactant molecules prevented the silane molecules from adsorbing onto the surface, which is reflected by the decrease of contact angles.

Based on the results presented it should be evident that water-dispersible silanes can be useful in the application of hydrophobic coatings while at the same time provide a significant reduction in solvent use. A comparison of steps that are involved in the applica-

Table II. Comparison of steps involved in applying silane coatings using a conventional SAM technique and the method reported in this paper.

	Organic media (Ref. 4, 5)	Aqueous media
A. Sacrificial layer etch	1. Dilute HF	1. Dilute HF
B. Surface oxidation	2. H ₂ O rinse	2. H ₂ O rinse
	3. Dilute HF	3. H ₂ O ₂ soak
C. SAM formation	4. H ₂ O rinse	4. H ₂ O rinse
	5. IPA rinse	5. Modified octadecylsilane dispersed in water containing a surfactant
	6. Iso-octane rinse	
D. Rinse and dry	7. OTS solution in 4:1 hexadecane:CCl ₄ or hexadecane:CHCl ₃	
	8. Iso-octane rinse	
	9. IPA rinse	
	10. H ₂ O rinse	6. H ₂ O rinse
	11. Pull structures directly from water	7. Cure at 250°C

tion of hydrophobic coatings from traditional organic media and from the predominantly aqueous media is shown in Table II. The aqueous-based coating process is capable of eliminating many solvent rinses required in the conventional organic-based process.

Conclusions

This study has shown that a chemical system containing a water-dispersible organosilane and a cationic surfactant can be used to render oxidized polysilicon highly hydrophobic. The developed methodology can reduce the use of undesirable organic solvents and processing time. The hydrophobicity of the coating can be improved through a heat-treatment step.

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