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Vapor-Phase Deposition of Monofunctional Alkoxy Silanes for Sub-Nanometer-Level Biointerfacing on Silicon Oxide Surfaces

By Brian Dorvel, Bobby Reddy Jr., Ian Block, Patrick Mathias, Susan E. Clare, Brian Cunningham, Donald E. Bergstrom, and Rashid Bashir*

1. Introduction

A typical biosensor contains three components: a receptor element, which recognizes or captures the biological or chemical analyte, the transducer, which converts the stimulus to an output signal, and an output system, which translates the output signal to an interpretable format. In the construction of biosensors, a variety of chemistries have been used to link receptor elements to surfaces; however, this step remains a limiting factor in device sensitivity, reliability, and reproducibility.[1,2] The output signal relies on transduction by optical,[3–7] electrochemical,[8–10] or piezoelectric techniques,[11] or other methods, and hence sensitivity increases with proximity of the analyte to the surface. Consequently, the linkage distance from the surface to the receptor elements must be reduced in order to maximize the contributions to the signal from the bound analyte. Self-assembled monolayers (SAMs) are commonly employed for interfacing biological receptors to a transducer. Many optical and electrochemical methods contain oxides, which are effective substrates for conjugation of alkoxy- and halo-substituted organosilanes, as part of the transducer. The mechanism of their reaction with oxide surfaces has been well studied,[12] and their aqueous and thermal stabilities have been established.[1,2,13,14]

Self-assembled monolayers are commonly deposited through either liquid- or vapor-based methods. There has been some success in the formation of trialkoxysilane monolayers in solution phase[15] and by using dip pen lithography,[16,17] but there exists much room for improvement. There is a need to make the deposition processes simpler and more reliable, to reduce the generation of contaminated effluents and polymerized products, and to lower the production costs.[18] Processes which utilize vapor-phase deposition can eliminate some of the problems that are seen in liquid-based deposition and also make themselves amenable to be used in batch and microelectronics-compatible processes.[19,20] In these vapor-phase processes, the precursor chemistry is easily controlled and efficient mass transport ensures coating of high-aspect-ratio structures (such as those found in micro-electro-mechanical devices). Moreover, it has been shown that the...

Improving the performance and lowering the analyte detection limits of optical and electronic biosensors is essential for advancing wide ranging applications in diagnostics and drug discovery. Most sensing methods require direct linkage of a recognition element and a sensor, which is commonly accomplished through an organic monolayer interface. Alkoxyorganosilanes are typically used to prepare sensor surfaces on dielectric oxides. However, many silanes lead to roughened or thick interfaces that degrade device sensitivity. Here, controlled vapor phase deposition of monoalkoxysilanes is found to lead to monolayers resistant to elevated temperatures and extreme pH conditions. The formation of high density, subnanometer monolayers is demonstrated by ellipsometry, XPS, and AFM. The uniform attachment of these monofunctional silanes to such biosensing platforms as microarrays, field effect devices, and the formation of surface enhanced Raman spectroscopy substrates is demonstrated. The advantages of using this silane deposition protocol for the above technologies are also discussed.

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performance of SAM coatings that are grown in vapor phase is comparable or superior to SAMs that are grown in liquid phase,\cite{21} and the vapor phase methods can be applied at the wafer scale level.\cite{22} Indeed, vapor-phase deposition of trialkoxysilane SAMs with a variety of terminal functional groups has been achieved on oxide surfaces previously.\cite{23–28} However, these trifunctional silanes are also known to polymerize in either aqueous- or vapor-phase deposition methods over a wide range of temperatures and environmental conditions.\cite{29–33} Consequently, high-quality monolayer formation may require very stringent and specialized processing conditions, making them more challenging to integrate with very-large-scale integration (VLSI) or wafer scale microelectronic devices and processes.

Organosilanes with trifunctional reactive groups, such as octadecyltrichlorosilane and aminopropyltriethoxysilane, have been frequently conjugated to devices by vapor and liquid methods,\cite{34–37} with the latter silane of particular importance because the amino group allows simple conjugation to reactive functional groups, including active esters, aldehydes, and ketones and isocyanates.\cite{38} However, the possible difficulties with trialkoxysilanes mentioned earlier may compromise device performance by causing nonuniformities on the active areas of the sensor or by increasing the length of the interfacial region. Monofunctional silanes possess the ability to alleviate these issues, since only one functional group is available to react with the surface and since these films have been shown to successfully be deposited on oxide surfaces.\cite{39,40} Other added advantages include a higher vapor pressure than equivalent trifunctional silanes and the fact that these monofunctional silanes do not displace amine catalysts unless covalent linkage occurs. These advantages allow for extended high temperature deposition and curing times, variables known to influence the quality and robustness of the films, as well as facilitating vapor-phase deposition, which is the preferred passivation method in the semiconductor industry. However, to date only limited characterization has been performed on monofunctional silanes and little is known about their performance in solution or applicability to biosensing platforms.

In the present study, we evaluate vapor-phase deposition of two monoethoxysilanes, one amino-terminated and another glycidoxy-terminated, and demonstrate their applicability to biosensor fabrication. The kinetics of monolayer formation was measured with ellipsometry and found to follow a diffusion-limited Langmuir model. X-Ray photoelectron spectroscopy (XPS) confirmed the elemental compositions of completed monolayers. Atomic force microscopy (AFM) images of the complete monolayers suggest roughness values close to that of silicon, and the topography indicated high density coverage. A critical issue surrounding these monolayers is their aqueous stability under stressed conditions, particularly at elevated temperatures, and extreme pH values. To assess the stability, the aminooalkyl-derived surface was first allowed to react with an amine-reactive fluorophore. The fluorescent intensities were then compared for monolayers subjected to temperatures of 25 °C and 60 °C, and aqueous solution pH values ranging from 1 to 13 for time periods up to 6 hours. No measurable changes in fluorescence intensity and fluorescence uniformity were observed.

Subsequently, we applied this deposition method to optical and electrochemical biosensing platforms, including microarrays, field-effect devices, and surface enhanced Raman spectroscopy (SERS)-active substrates. We show the high deposition uniformity and decreased background noise when applied to microarrays. We also demonstrate that the conjugation technique can be applied to field-effect devices for possible applications in potentiometric sensing. Finally, we demonstrate high coverage densities of Au nanoparticles for the formation of SERS-active substrates for Raman detection capabilities. Overall, the ease of this functionalization method and its high stability show promise for increasing the performance and longevity of biosensors. As a result, this silanization can be widely applied across many biosensing platforms.

2. Results

Since monofunctional silane reaction kinetics has seldom been studied\cite{39}, we deposited silanes for various time intervals in the vapor phase using the procedure described in the Experimental Section and then removed any physisorbed material by sonication. This allows for a more accurate determination of the extent of silane reaction as compared to real-time measurements such as quartz crystal microbalance (QCM) or surface plasmon resonance (SPR), since fluidic rinses or gaseous purges may not desorb excess reagents leading to an overestimation of silane attachment.\cite{41} The ellipsometric thickness of the silane layer versus the deposition time is displayed for 3-aminopropyldimethylethoxysilane (APDMS) and (3-glycidoxy)propyldimethylethoxysilane (GPDMS) in Figure 1. Assuming that the film is uniform, the adsorbed mass can be correlated to the thickness if the molar refractivity and refractive index of the film are known.\cite{42} The molar refractivity ($A$) of molecular species may be calculated by summation of the individual atomic bond refractivities which comprise the molecule. The molar refractivities for APDMS ($A = 35.4$) and GPDMS ($A = 49.1$) were calculated using the individual bond refractivities reported by Vogel et al.\cite{43} and the adsorbed mass was calculated for each point. The right axis in Figure 1 shows the theoretical adsorbed mass for each silane. For both silanes, the thickness results indicate the deposition follows Langmuir kinetics. The first hour is dominated by rapid kinetics and as the adsorption sites become occupied, the deposition slows and finally saturates between 6–12 hours. Using trifunctional silanes with epoxy and amino functionalities, we performed the same deposition procedures, which readily gave multilayers with thicknesses in agreement with recent literature values (see Supporting Information).\cite{40} Contact-angle measurements were also taken at the same deposition times (see Supporting Information), and the values saturate at 49.5° and 58.0° for APDMS and GPDMS, respectively.

Although the early stages of monolayer adsorption are known to be described well by Langmuir kinetics,\cite{44,45} extended depositions have been known to follow second-order or diffusion-limited forms of the Langmuir model with several growth process regimes.\cite{46} In order to gain insight into the deposition mechanism, the data was fit using three Langmuir models: a first order process, a second-order process, and a diffusion limited process. By analyzing the residuals of the fit, the kinetics appear to follow a diffusion limited process which is described well by Rahn and Hallock.\cite{47} Using this model, the maximum thickness and diffusion-limited rate constant ($k_{DL}$) were calculated.
and are displayed in Table 1 for the aminosilane and epoxysilane. A purely diffusion limited process should be described by Equation 1:

$$\Gamma(t) \approx \Gamma_f \left(1 - \exp\left(-\frac{t}{\tau_D}\right)\right)^{1/2}$$

(1)

where \(\tau_D\) is the diffusion-limited time constant and \(\Gamma_f\) is the final thickness. To evaluate the validity of the model, the power exponent of 1/2 in the equation was turned into a stretched exponential creating the exponent variable \(\alpha\). By allowing \(\alpha\) to be a parameter in the fit, the optimal values of \(\alpha\) were determined for APDMS and GPDMS. The values are displayed in Table 1, and both are close to 1/2, indicating a true diffusion limited process for the vapor deposition. The theoretical adsorbed masses saturate at 101.6 ng cm\(^{-2}\) and 69.8 ng cm\(^{-2}\) for the GPDS and the APDMS, respectively. Taking the molecular weights of the compounds, this corresponds to 5.8 molecules nm\(^{-2}\) for the epoxysilane and 6.1 molecules nm\(^{-2}\) for the aminosilane. The high densities described for both silanes are not unreasonable, given the density of silanols achievable on crystalline silicon surfaces.\(^{14,49}\) By cleaning the substrates properly and depositing the silanes at 100 °C, we are able to inhibit dehydroxylation at the surface, and maximize surface silanol density.

The vapor deposition of these silanes in vacuum and at temperature above their boiling points allows for simultaneous deposition and curing, with curing known to play an important role in stabilizing the attachment of the silane to the surface.\(^{1,50}\) The ellipsometry results indicate saturated values for both monolayers by 12 hours deposition time. To confirm the compositions of the monolayers and correlate the ellipsometry thicknesses, XPS was taken for each silane after 12 hours deposition time. Figure 2 shows the C1s and N1s high-resolution spectra for a native oxide control, APDMS, and GPDMS. Within each spectrum, the curves were fitted to extract the localized bonding of each carbon or nitrogen atom. The native oxide shows very little carbon or nitrogen contamination, confirming that the signal results from the C1s and N1s of the attached silanes. The C1s spectra for each of the silanes contain binding energies for aliphatic (284.5–285.5 eV), slightly polar (286–287 eV), and highly polar (288–290 eV) carbons. The N1s spectra are split into NH\(_2\) (399 eV) and NH\(_3\)\(^+\) (401 eV) domains, which suggests that the amino groups of APDMS exist in both neutral and protonated form under the conditions of XPS analysis.

The ratios of each of the elements and the ratios of the carbon types are displayed in Table 1. The C1s:N1s ratio provides information about the elemental composition of the silanes. For APDMS, the ratio is close to the stoichiometric value of 5:1, while GPDMS, which does not contain nitrogen, has a very high C1s:N1s ratio. Similarly, the ratio of aliphatic carbons (C\(_a\)) to slightly polar carbons (C\(_p\)) can give us insight into the chemical composition of the sample. Slightly polar carbons may be regarded as O–C–O, C–O, or C–N bonded, while aliphatic carbons are assigned as C–C or C–H bonded. The C\(_a\):C\(_p\) values for GPDS and APDMS are very close to the stoichiometric values of 1:1 and 4:1, respectively. Most importantly, if the silane layer was damaged or oxidized during the long deposition time, the highly polar C1s peaks, indicating C–O or C–N, would be quite large. There is no evidence of this in the C1s spectra of either silane, indicating intact functional groups after the 12 hour deposition/curing period.

The N1s spectrum for APDMS shows greater than 97% NH\(_2\) terminations. This is an important result, since it indicates that the

Table 1. Table of values for a 12 hour deposition period of APDMS and GPDMS. The various parameters gathered from ellipsometry, XPS, AFM, and contact angle are tabulated above.

<table>
<thead>
<tr>
<th></th>
<th>Ellipsometric Thickness (Å)</th>
<th>XPS Thickness (Å)</th>
<th>(\tau_D) (min (^{-1/2}))</th>
<th>(\alpha)</th>
<th>C1s N1s</th>
<th>C–C</th>
<th>C–O/C–N</th>
<th>(R_{MAX}) (Å)</th>
<th>Contact Angle (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>APDMS</td>
<td>8.2±0.4</td>
<td>8.6±0.8</td>
<td>0.15</td>
<td>0.52</td>
<td>5.08</td>
<td>4.11</td>
<td>1.6</td>
<td>49.5</td>
<td></td>
</tr>
<tr>
<td>GPMS</td>
<td>11.1±0.5</td>
<td>11.7±1.1</td>
<td>0.11</td>
<td>0.48</td>
<td>192.12</td>
<td>1.12</td>
<td>2.1</td>
<td>58.0</td>
<td></td>
</tr>
</tbody>
</table>
silanes on the surface are covalently attached instead of absorbed in the inverted state. In an inverted state, the silane would form an \( \text{NH}_3^-\text{Si}/\text{C}_0\text{O}/\text{C}_0 \) ion pair, which commonly occurs in trifunctional silanes such as APTES. Moreover, the data also indicates that triethylamine is not absorbed on the surface, which would block binding sites. The N1s spectra of GPDMS show peaks close to the noise of the control spectrum, as would be expected. The thickness \( t \) of the monolayers was calculated by Equation 2 from the intensity of the Si2p electrons from the substrates \( I \) and the attenuation length of a hydrocarbon monolayer \( \lambda \):

\[
t = -\frac{I}{\sin \theta \ln \left( \frac{I}{I_0} \right)}
\]

where \( I_0 \) is the Si2p electron intensity from a blank sample and \( \sin \theta \) reflects the take-off angle, which is 90°, making \( \sin \theta \) equal to 1. The attenuation length for the electrons in the hydrocarbon...
layer is dependent upon the kinetic energy of the electron being ejected, which for an Si2p electron is 1.388 eV. The attenuation length as a function of kinetic energy $l(KE)$ was estimated for a hydrocarbon layer based upon the equation by Laibinis et al.,\[^{[53]}\] that is, $l(KE) = 9 + 0.022 KE$. Using this equation, the attenuation length was estimated at 39.5 Å for the monolayer. The thicknesses were then calculated using Equation 2, and are displayed in Table 1. For both silanes, the XPS appears to overestimate, but within error, the thickness of the silanes, in comparison to ellipsometry. However, both techniques complement each other and support the formation of a true, high density monolayer.

The morphologies of the formed monolayers were visualized using AFM in tapping mode after 12 hours deposition. The results of the AFM are displayed in Figure 3 for the control oxide, APDMS, and GPDMS. The morphologies look quite similar to the control image, lacking island domains which would be indicative of incomplete monolayers or solution-phase depositions. Below each image is the RMS roughness ($R_{\text{rms}}$) for that image, and the values may also be found in Table 1. The control oxide exhibits an $R_{\text{rms}}$ of 1.2 Å, which is well known to be the case for native oxides on silicon, while APDMS and GPDMS exhibit $R_{\text{rms}}$ values of 1.6 Å and 2.1 Å, respectively. The fact the $R_{\text{rms}}$ values are so close to the control and less than the heights of the molecules affirm the formation of homogeneous layers. Although the GPDMS $R_{\text{rms}}$ is larger than APDMS, this is to be expected since the overall length of the molecule is longer and has a greater tendency to aggregate.

AFM images were also taken for the same deposition times for their trifunctional analogues, showing large multilayer domains and $R_{\text{rms}}$ values larger than the lengths of the molecules (see Supporting Information).

To demonstrate applicability of this vapor-based method to the semiconductor industry, both APDMS and GPDMS were deposited on 6-inch Si wafers with $<100>$ silicon orientation. The deposition time for each silane was also 12 hours and took place in a 0.75 foot\(^3\) vacuum oven with 1 mL of silane for each deposition. The ellipsometric thickness and static contact angle was taken over 25 spots on each wafer, and the wafer maps for APDMS and GPDMS can be found in the Supporting Information as Figure S3. The values indicate a thickness of 8.3 ± 0.4 Å and a contact angle of 50.3 ± 2.1° for APDMS, while GPDMS had a thickness of 11.0 ± 0.8 Å and a contact angle of 58.9 ± 2.6°. These values over entire 6-inch Si wafers match, within the standard deviation, the values determined with 4 × 7 mm test chips. Moreover, the standard deviations are less than 10% of the mean value, indicating highly uniform depositions over large areas are achievable using this process. To gain insight into the resistance of the monolayers to hydrolysis, APDMS was subjected to various conditions over a period of 6 hours, and then allowed to react with a ROX-NHS ester. The fluorescence was then measured and is displayed over a period of 6 hours in Figure 4. Figure 4A shows the fluorescent intensity after incubation in 0.1 M HCl and 0.1 M NaOH. There is little decrease in fluorescent intensity over 6 hours for both solutions, and is within the error of each measurement. A similar experiment was performed but with the silanes incubated in pH 7.4 phosphate-buffered saline (PBS) at 60 °C and 90 °C and is shown in Figure 4B. Again, the fluorescent intensity decay is within the errors of the measurement for both solutions. Overall, Figure 4 demonstrates
the resistance of the monolayers to harsher conditions than one would encounter in the ambient. This behavior of monofunctional silanes has been observed before, and is believed to be due to increased reactivity with surface hydroxyl groups.\(^{54}\)

Next, the monolayers were applied to biosensing devices to demonstrate their versatility and application. Figure 5A shows a GPDMS-coated microscope slide spotted with streptavidin-Cy5 (SA-Cy5) in a 3 × 8 array format. The columns are boxed in white, with a zoomed-in area of an individual spot in yellow. Each pixel of the scan was 10-μm square. Three slides were spotted in the same manner and scanned to obtain the fluorescence intensity of the spots and the background. Figure 5B shows the intensity of the background and of the SA-Cy5 spots for each slide versus the column number. The intensity distribution of fluorescence and uniformity of background noise from the columns across all three slides is very uniform. The background noise of a silane-derivatized slide and an underderivatized slide were also measured, and are displayed in Figure 5C. The silane adds no background fluorescence, within error, to the measurement. Given the high gain of the photomultiplier tube at which these measurements were taken, it is likely that background noise due to substrate autofluorescence and the detection electronics will dominate over background contributions from the silane layer for any fluorescence assay. The low autofluorescence of these layers is an important advantage in ultimately maximizing the signal-to-noise ratio of fluorescence assays performed using this chemistry, and apparently leads to better background intensity than other slide formats.\(^{55}\)

The coefficient of variation across the slides is 8%, which includes effects from the variability of the spotting procedure as well as the surface chemistry.

The application of ion-selective field-effect transistors (ISFETs) and silicon nanowires to biosensing has become pronounced in recent years.\(^{56–58}\) Silicon oxide is the most common dielectric due to its ease of growth and integration. However, silicon oxide performance is known to degrade extensively over time, due to factors such as dissolution and ion diffusion.\(^{59–62}\) Organic monolayers have proven to provide resistance to this phenomena, but the effect of polymerization degrades the device sensitivity by adding to the dielectric thickness and trapping charges within the polymerized matrix. Moreover, functional group density may be affected due to groups being buried in the matrix. These variables may affect the ability of the silane chemistry to conjugate recognition agents, such as primary antibodies or DNA, close enough to the surface to regulate the devices surface potential. Here, we demonstrate the applicability and versatility of monoalkoxysilylation chemistry to biosensors. We have constructed silicon field effect devices based upon silicon-on-insulator (SOI) technology in our lab with 30-nm silicon thickness, 2-μm device width, and 20-μm device length. A bright-field top-view micrograph of a device is displayed in Figure 6 (top left). We allowed the devices to react with the monofunctional silylating reagents according to the aforementioned protocol, and then with fluorophores of varying functionalities, including an amine, an NHS ester, and an isothiocyanate. Each device was then fluorescently imaged for 5 seconds (Fig. 6). The presence of the fluorophores is demonstrated by the uniformly strongly intensity across the device. Since device response can depend on the distribution of recognition molecules on the surface,\(^{63}\) this is an important step to optimizing silicon nanowire sensitivity and repeatability.

Another important technique widely used today for biomolecule detection is SERS. Interactions of analytes with enhanced optical fields are known to increase Raman scattering by 10\(^{5}\)–10\(^{6}\). In some cases, scattering enhancements of 10\(^{12}\)–10\(^{14}\) have been encountered, which may be sensitive enough for single-molecule detections. Former SERS substrates were made out of electrochemically roughened metal surfaces, but in recent years noble metal nanoparticles have become a method of choice. Nanoparticle substrates offer the advantage of being renewable and having a high density of particles on the surface, which can lead to areas of intense field enhancement known as “hot spots”.\(^{64}\) In Figure 7, we demonstrate the formation of high-density Au nanoparticle surfaces via electrostatic adsorption with an APDMS monolayer. AFM images were taken before (Fig. 7A) and after (Fig. 7B) a 1 hour deposition of 5-nm Au particles in deionized (DI) water. Figure 7A shows a smooth monolayer over a 25-μm\(^{2}\) area. After deposition (Fig. 7B), the surface shows a high density of Au nanoparticles on the surface over the same area scale. A 1-μm\(^{2}\) image of the same area shows particles in tight clusters, with occasional gaps. A line scan across one of these small gap areas shows a height difference of 5.7 nm, indicating a homogeneous monolayer of nanoparticles.
3. Conclusions

We have developed a versatile, vapor-based method for the deposition of monofunctional silanes. By characterizing the system using ellipsometry, XPS, and AFM we were able to optimize the procedure to ensure a uniform, high density, true monolayer. The technique was shown to be successful not only on small substrates, such as ISFET’s, but also on entire 6-inch Si wafers, leaving the possibility for incorporation into VLSI semiconductor processes. Subjecting the monolayers to conditions of elevated temperatures and extreme pH showed no decay of the monolayers through fluorescent attachment. We demonstrate the applicability of this subnanometer monolayer technology to various sensing platforms. The very high uniformity of the monolayers makes them ideal for applications in sensing, whether optically or electronically based. The low background noise and coefficient of variation make it attractive for microarrays and fluorescence applications. Moreover, the chemistry indicates recognition analytes would bind in high density to field-effect sensors, enhancing the sensitivity of the devices. Finally, the high coverage of electrostatically adsorbed nanoparticles on the silane surface would make an ideal SERS substrate for detection of analytes and minimize background scattering. Overall, the deposition of monofunctional silanes is very versatile and robust, and is applicable to multiple biosensing platforms to help optimize their performance.

4. Experimental

Materials: APDMS and GPDMs were purchased from Gelest, Inc. and used without further purification. Triethylamine, toluene, and methanol were obtained from Sigma and dried with 3Å molecular sieves. The fluorescent dyes 7-amino-4-methylcoumarin, rhodamine B isothiocyanate, and 4-carboxyfluorescein NHS-ester were purchased from Sigma–Aldrich and used without further purification. pH 7.4 PBS was purchased from Gibco and degassed at 30 Torr in a desiccator for 10 minutes prior to use. All glassware prior to use was soaked in a NaOH:EtOH base bath for at least one hour and rinsed in DI water. The glassware was then dried at 150 °C in a convection oven. Four-inch Si(100) wafers from SiliconQuest Intl. were diced into 4 × 7 mm chips for AFM, XPS, and ellipsometry experiments. A 4-inch Si(100) wafer was thermally oxidized at 1050 °C for 24 hours to an SiO2 thickness of ~1 μm, which was confirmed by ellipsometry, and then diced into 4 × 7 mm chips for fluorescence-stability measurements. Low-autofluorescence Nexterion B microscope slides purchased from Schott were used for deposition uniformity experiments. Streptavidin-Cyanine-5 (SA-Cy5) for microarray spotting was purchased from Invitrogen. Silicon field-effect devices were fabricated in our lab using SOI wafers and a VLSI-compatible process [63,64]. Colloidal Au nanoparticles (Au-NPs) of 5-nm mean diameter were purchased from Sigma and used as received.

Silane Deposition: Before silane depositions, each substrate was degreased in acetone and methanol, then immersed in H3SO3:H2O2 (7:3) for 30 minutes. The substrates were then rinsed in DI water, dried under a stream of N2, and then subjected to a 300 W O2 plasma at a pressure of 500 mTorr for 10 minutes. The deposition of silanes on 4 × 7 mm chips was performed in 20 cm3 glass vials at a temperature of 100 °C and at a pressure of 30 Torr. Silanes were mixed with TEA to a 1% v/v solution, kept at 100 °C and 30 Torr, and transferred into the vials by a glass
containing 350-μL spots of 10
contact piezoelectric spotter (Perkin Elmer Piezoarray) with a pattern
spots. The native oxides for each dye ranged from 10–14 Å in thickness, as
silanes. The chips were measured before and after silanization at 5 different
The refractive indices utilized were 1.46 for the native oxide and 1.43 for the
8
8
was purged with N2 and then vacuumed out 3 times. The
t-junction was then opened to allow the silane to flow into the vacuum
oven, PTFE tubing, and the silane were all preheated
heated on a hot plate. A copper heating tape was put around the PTFE
tube and a 

t-junction for carrying the silane vapor from outside the oven. The
silane was purged with N2 and then vacuumed out 3 times. The
The 6-inch Si wafers were silanized using the same vacuum oven setup
and same conditions, except the N2 inlet port was modified with a
10-uL drop of ultrapure water (18.2 MΩcm) was allowed to
to a pass energy of 120 eV and high-resolution spectra at a pass
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Silane Characterization: The ellipsometry measurements were taken on
a Rudolph FE-III ellipsometer at an angle of 70° and a wavelength of 6328 Å.
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silanes. The chips were measured before and after silanization at 5 different
spots. The native oxides for each dye ranged from 10–14 Å in thickness, as
determined by ellipsometry and XPS. Contact-angle measurements were taken on a
KSV CAM200 system in static mode using the sessile drop technique. A 10-μL drop of ultrapure water (18.2 MΩcm) was allowed to
stabilize for 10 minutes before the measurement was taken. Error for each
measurement is approximately ±0.5 degrees. TOF-SIMS XPS analysis was
done on a KRATOS AXIS ULTRA at a take-off angle of 90°. Monochromatic\n\[\text{Al} \ x\text{-rays were used as the source. The control sample was carefully cleaned to remove carbonaceous material according to Seah and Spencer}[67]. Silanized samples were subjected to a similar treatment, but without
the use of O2 plasma to keep the monolayer intact. Survey spectra were taken at a pass energy of 120 eV and high-resolution spectra at a pass
energy of 40 eV. Each dye was mounted using a conductive copper tape and the
CdTs, N1Ts, and Si2p spectra recorded at a dwell time of 200 ms and 10 passes. All spectra were processed using CASA XPS software. The spectra were fitted with a modiﬁed Gaussian–Lorentzian algorithm using a Shirley background.
Atomic force microscopy (AFM) images were taken on an Asylum Research MFP-3D AFM with a silicon tip at 300 kHz in AC Mode. The amplitude and phase images were both recorded and image sizes ranged from 1 x 1 μm to 5 x 5 μm. Microarray spotting was done using a non-contact piezoelectric spotter (Perkin Elmer Piezoarray) with a pattern containing 350-μL spots of 10 μg mL⁻¹ \[\text{SA-Cy5 in PBS at pH 7.4 with 0.05%}

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