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Stable Organic Monolayers on Oxide-Free Silicon/Germanium in a Supercritical Medium: A New Route to Molecular Electronics

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Ⓢ Supporting Information

ABSTRACT: Oxide-free Si and Ge surfaces have been passivated and modified with organic molecules by forming covalent bonds between the surfaces and reactive end groups of linear alkanes and aromatic species using single-step deposition in supercritical carbon dioxide ($SCCO_2$). The process is suitable for large-scale manufacturing due to short processing times, simplicity, and high resistance to oxidation. It also allows the formation of monolayers with varying reactive terminal groups, thus enabling formation of nanostructures engineered at the molecular level. Ballistic electron emission microscopy (BEEM) spectra performed on the organic monolayer on oxide-free silicon capped by a thin gold layer reveals for the first time an increase in transmission of the ballistic current through the interface of up to three times compared to a control device, in contrast to similar studies reported in the literature suggestive of oxide-free passivation in $SCCO_2$. The $SCCO_2$ process combined with the preliminary BEEM results opens up new avenues for interface engineering, leading to molecular electronic devices.

SECTION: Surfaces, Interfaces, Porous Materials, and Catalysis
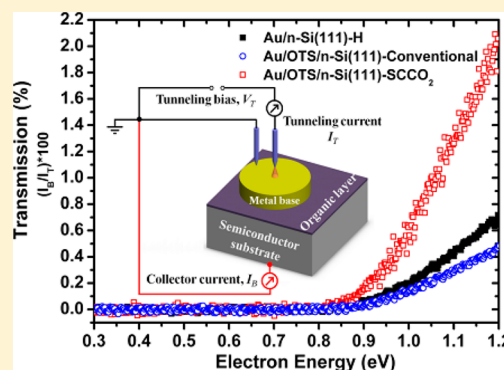
Densely packed organic layers bonded covalently to crystalline silicon (Si) surfaces, without an interfacial silicon oxide (SiO_2) layer, have received increasing interest because of the variety of applications in micro- and nano-electronics and in bio- and chemical sensors.[1−5] Likewise, Ge has gained renewed interest as a material of choice for future electronics due to its significantly higher electron and hole mobilities than Si.[6,7] Attachment of organic species on a Si/Ge substrate without intervening oxide could significantly reduce the density of defect states and traps on Si/Ge surfaces.[8,9] Furthermore, it may prevent diffusion of oxygen into the organic layer/Si interface during either growth of the insulating layer or the postannealing process, as in the formation of high-k dielectrics on Si/Ge.[10] A variety of surface passivation methods have been investigated with the aim of preserving ideal electrical and electronic properties of the H-terminated silicon surfaces at ambient conditions. Si(111), Si(100), and Ge(111) surfaces have been functionalized by a number of methods, including reaction with alkenes and alcohols and aldehydes through a radical process catalyzed by a diacyl peroxide initiator, use of ultraviolet or white light,[11,12] thermal energy,[13−15] transition-metal complexes,[16] Lewis acid catalysts,[17] electrochemical functionalization,[18] radical halogenation,[19] chemomechanical scribing,[20] diazorium salts,[9] nucleophilic addition, and a radical chain mechanism.[21,22] Fresh Si/Ge surfaces alkylated via two-step chlorination/alkylation

(Grignard reagent) with straight chain alkyl groups (C_nH_{2n+1}, n = 1−8) have shown surface passivation both chemically and electrically.[23−27]

Conventional deposition and surface derivatization methods involve use of a liquid solvent as a vehicle for the depositing species as well as for a rinse following deposition. Furthermore, conventional chemical processes often involve multiple reaction and separation steps, and the type of solvent that is optimum for a particular step may be different from the one needed in the next step. The solvent is therefore usually removed after each step and a new solvent added in preparation for the next step, significantly adding to the economic cost and environmental impact of the process. An additional issue with multiple solvent systems is the possibility of introducing adventitious impurities due to contact with different species. This cumbersome procedure can be avoided if the solvating properties of a solvent can be adjusted for successive steps, thereby enabling the same solvent to be used for several consecutive reaction or separation steps.

In the context of passivating Si/Ge surfaces by deposition of a thin film, if deposition is conducted in the vapor state or,

Scheme 1. Schematic Representation of (A) Octadecyl Trichlorosilane Deposition on Ge(100)/Si(111), (B) Octadecanol Deposition on Si(100), (C) 1-Chlorooctadecane Si(111), and (D) 4-Chloroaniline Deposition and Subsequent PMDA Deposition on 4-Chloroaniline-Modified Si(111)
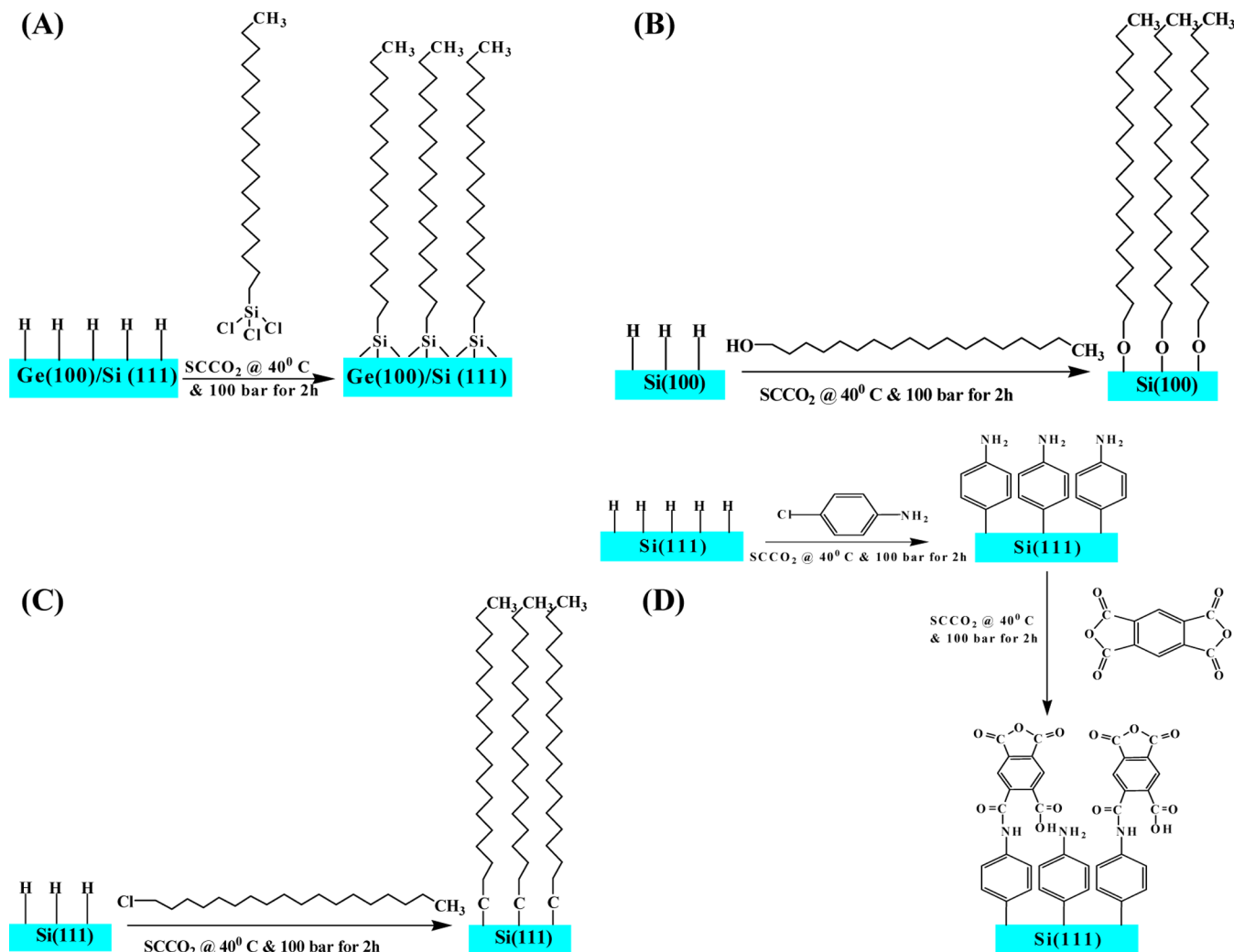
better yet, in the presence of a supercritical medium, the participation of the liquid solvent, if any, will be minimized in the fabrication process, and unused reagents, together with the residual solvent, can be displaced by the fluid phase. Supercritical fluids (SCFs) offer potential advantages over conventional solvents for fabrication of ultrathin films and synthesis of nanoparticles. The gas-like diffusivity and viscosity of supercritical carbon dioxide ($SCCO_2$) are favorable for rapid diffusion and permeation into porous substrates, and the liquid-like density allows for the dissolution of a wide range of organometallic precursors. Furthermore, residual CO_2 is negligible in the processed product because of its gaseous character at ambient conditions. $SCCO_2$ has been applied as a reaction medium for thin film fabrication on an oxidized silicon surface,[28−30] immobilization of nanoparticles in thin film systems,[31,32] and synthesis of nanoparticles such as Ag, Pt, Pd, Ir, Au, and Ag−Pd from their organometallic precursors.[33−39]

In this work, we have demonstrated the applicability of $SCCO_2$ processing for the attachment of different molecules on the semiconductor surface (see the Supporting Information for $SCCO_2$ processing (Figure S1)). In order to check the viability of the $SCCO_2$ process in forming Ge−Si−C, Si−Si−C, Si−O−

C, and Si−C bonds, methyl- terminated trichlorosilanes, alcohol, and methyl/amine-terminated chlorine molecules are deposited on hydrogen-terminated Ge(100) and Si(100)/ Si(111) surfaces.

Scheme 1A shows the schematics for the deposition of octadecyl trichlorosilane (OTS) on oxide-free Ge and Si surfaces. Deposition of OTS on Ge(100) is confirmed by the presence of the C1s peak at 285 eV due to the alkyl chain of OTS (Figure 1A). Figure 1B shows the Ge3d peak and the absence of any peaks associated with Ge oxide.[6,27] Similarly, the presence of OTS on Si(111) is confirmed by the observation of the C1s peak at 285 eV (Figure 1C) and its coverage over the Si surface by the absence of SiO_2 in the Si2p spectra (Figure 1D). Figure 1D shows the Si2p doublet spectrum (Si2p$_{3/2}$ and Si2p$_{1/2}$) with the expected 2:1 area ratio and 0.6 eV energy separation observed for OTS-terminated Si(111) surfaces.[24,26] No oxidized Si between 102.0 and 104.0 eV was observed, confirming that the absence of SiO_2 in the Si2p spectra is indicative of the protection offered by the organic layer against oxidation of silicon.[24] None of the XPS spectra of surfaces on which chloro compounds are deposited show detectable levels of chlorine, thereby attesting to the completeness of the Ge− Si−C or Si−Si−C binding.
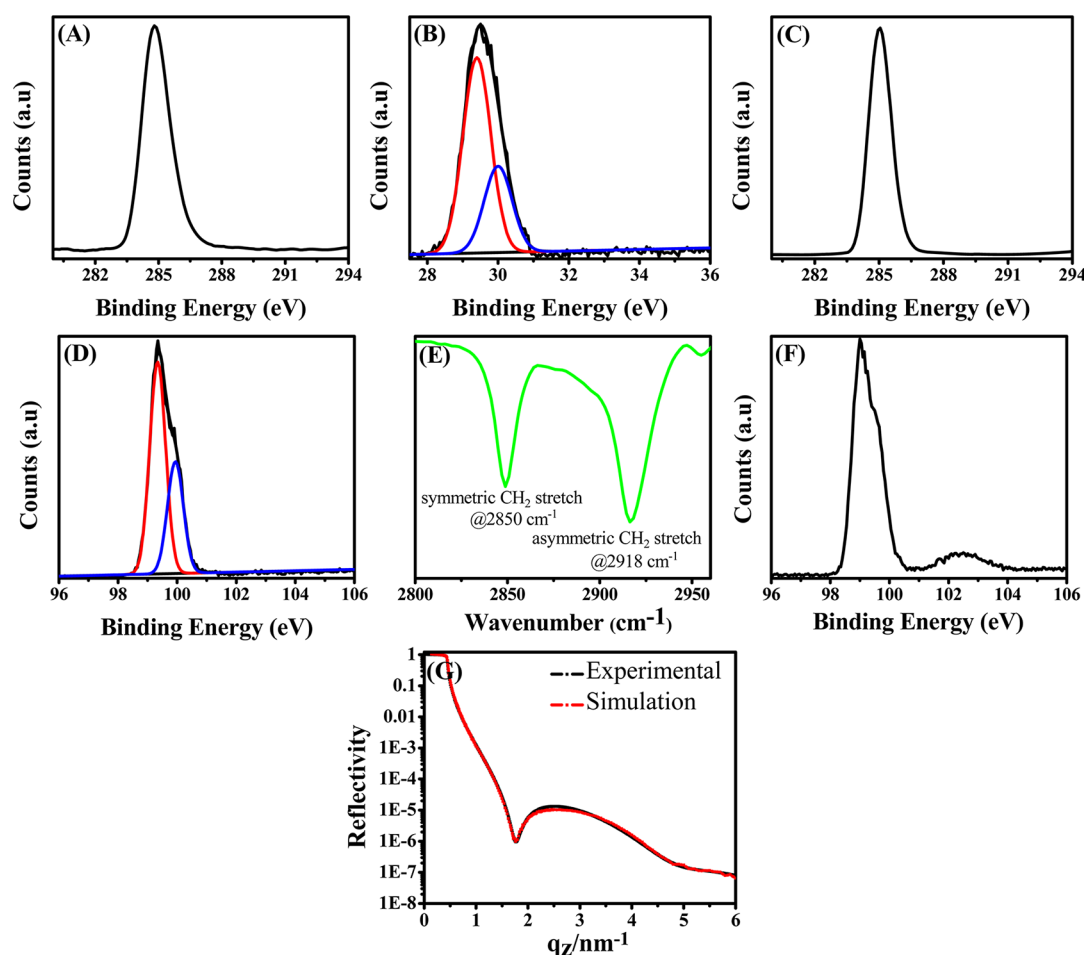
Figure 1. High-resolution XPS spectra of (A) C1s, (B) Ge3d of OTS on Ge(100), (C) C1s at 285 eV, and (D) Si2p. (E) FTIR spectra for OTS deposition on Si(111) from the SCCO$_2$ process. (F) Si2p spectra from conventional solution and (G) X-ray reflectivity profile of the OTS monolayer on the Si(111) surface from the SCCO$_2$ process.
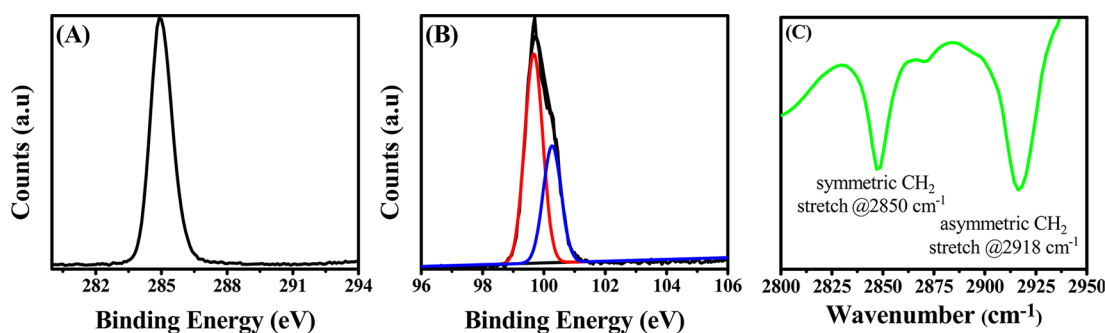

Figure 2. High-resolution XPS spectra of (A) C1s and (B) Si2p and (C) FTIR spectra of octadecanol deposition on Si(100).

We have also performed the OTS monolayer attachment on an oxide-free silicon surface by a conventional solution approach by exposing the substrate to a solution of OTS of similar concentration in an inert atmosphere (Figure 1F). XPS results showed that the presence of SiO$_2$ in Si spectra indicates that the OTS molecule is not completely covered on the silicon surface.[40] These results indicate that the OTS attachment on an oxide-free silicon surface is possible only in our SCCO$_2$ approach.

In order to check the viability of the SCCO$_2$ process in forming Si−O−C bonds, methyl-terminated alcohols were deposited on hydrogen-terminated Si(100) surfaces (Scheme

1B). XPS spectrum (Figure 2A) shows the presence of the C1s peak at 285 eV due to the alkyl chain of octadecanol deposited on the Si(100)−H surface. The effectiveness of the coverage in preventing oxidation is inferred from the absence of SiO$_2$ between 102.0 and 104.0 eV in the Si2p spectrum (Figure 2B).[22]

Formation of Si−C bonds using the SCCO$_2$ medium is demonstrated by attaching 1-chloroctadecane and 1-chloroaniline to Si(111) surfaces (Scheme 1C). The single C1s peak at 285 eV (Figure 3A) confirms the attachment of 1-chlorooctadecane onto Si(111), and the absence of the SiO$_2$ signal in the 102−104 eV Si2p region confirms chemical
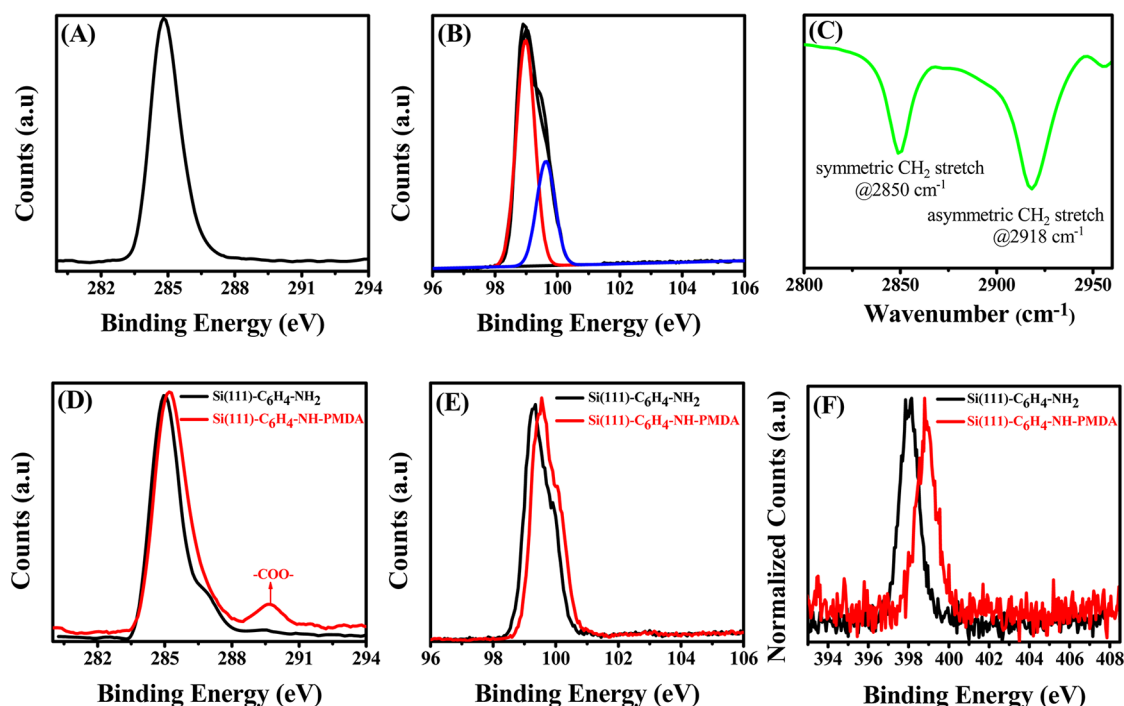
Figure 3. High-resolution XPS spectra of (A) C1s and (B) Si2p and (C) FTIR spectra of 1-chlorooctadecane on Si(111). Spectra of (D) C1s, (E) Si2p, and (F) N1s of 4-chloroaniline and subsequent functionalization of 4-chloroaniline with PMDA on Si(111).

passivation of the Si surface (Figure 3B). We have also demonstrated the formation of Si−C bonds using the SCCO$_2$ medium by attaching 4-chloroaniline on Si(111) surfaces. In addition, pyromellitic dianhydride (PMDA) is deposited from the SCCO$_2$ medium subsequent to deposition of 4-chloroaniline (Scheme 1D). The presence of the COO peak at 288.6 eV subsequent to deposition of PMDA confirms the reactivity of the amine group of 4-chloroaniline with the anhydride group of the PMDA (Figure 3D).[28] No SiO$_2$ signal in the 102−104 eV Si2p region is observed in either the Si(111)−C$_6$H$_4$−NH$_2$ or the Si(111)−C$_6$H$_4$−NH$_2$−PMDA sample (Figure 3E). The Si2p spectrum of the Si(111)−C$_6$H$_4$−NH$_2$−PMDA sample is similar to that of the Si(111)−C$_6$H$_4$−NH$_2$ sample, indicating that the Si−C bond is not affected by the secondary functionalization (Figure 3E). The N1s spectrum observed after deposition of 4-chloroaniline (Figure 3F) consists of a single peak at 398 eV assignable to primary amines, indicating that the substrate surface is comprised entirely of primary amines,[28] suggesting that Si−C bonds anchor the 4-chloroaniline to the surface. Successful reaction between amino moieties and PMDA after deposition of the latter is confirmed by a shift of the N1s peak (Figure 3F) to 399 eV, attributable to the amide group.[28,29]

Independent evidence of the covalent attachment of alkyl monolayers on silicon surfaces is obtained by FTIR spectroscopy. The presence of the C$_n$H$_{2n+1}$ chains on the Si surface are deduced from the symmetric and asymmetric stretching vibration frequencies of the methyl groups at 2918 and 2850 cm^{-1}, respectively, (Figure 1E for OTS on Si(111), Figure 2C for octadecanol deposition on Si(100), and Figure 3C for 1-choloroctadecanene deposition on Si(111)) for all of the alkyl monolayers. The observed absorption frequency for the symmetric stretch is closer to that obtained for crystalline alkane (2920 cm^{-1}) than to that expected for liquid alkane

(2928 cm^{-1}), which is suggestive of the formation of solid alkane films on the Si surface.[22]

The average contact angles observed for the methyl- and amine-terminated monolayers on Si surfaces immediately after deposition and after 30 days of exposure to air are shown in Table 1. The average contact angles for the methyl-terminated

Table 1. Contact Angles of Functionalized Ge/Si(111)/Si(100) Surfaces

sample	avg. contact angle measured immediate after deposition	avg. contact angle measured after 30 days
Si(111)−H	86 ± 1	60 ± 2
Ge(100)−OTS	113 ± 1	111 ± 1
Si(111)−OTS	110 ± 2	110 ± 1
Si(100)−octadecanol	112 ± 1	108 ± 1
Si(111)−chlorooctadecane	107 ± 1	106 ± 1
Si(111)−4-chloroaniline	56 ± 1	53 ± 1
Si (111)−4-chloroaniline + PMDA	41 ± 1	38 ± 1

monolayers are 110° ± 2, respectively which are consistent with expected values for −CH$_3$-terminated SAMs.[13] Shirahata et al. also confirmed the densely packed alkyl SAM with a contact angle around 110°, passivating the silicon from oxidation, and our results are in agreement with the related literature findings.[22,40]

In addition, we have also performed an X-ray reflectivity (XRR) study on the OTS monolayer to measure the film thickness. Figure 1G shows the XRR profile of the OTS monolayer on a Si surface. The two Kiessig fringes clearly confirm the ordering of the monolayer. The OTS film thickness is calculated to be 2.61 nm and is comparable with the literature

values of around 2.6 nm.[41] The surface and the interface roughness are 0.6 and 0.28 nm, respectively. The film density is 1.34 g/cm^3, which is comparable to the density of the OTS at ambient temperature.[42]

Characterization of monolayer-covered surfaces after long-term (2−4 weeks) exposure to the laboratory environment showed no changes in the contact angles. As an illustrative example of testing for mechanical stability, the Si(111)−OTS sample is subjected to sonication in toluene for 10 min and subsequent exposure to the ambient environment for 30 days. The Si(111)−OTS sample shows that no change in contact angle of 110° ± 1 is observed. Furthermore, XPS results (Figure 4) do not show the presence of SiO$_2$ after the exposure to the ambient air.
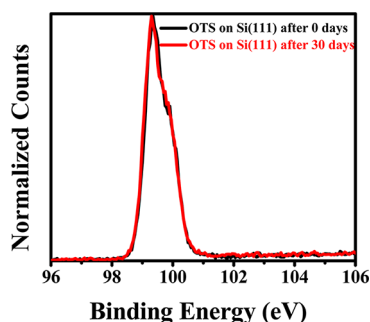

Figure 4. OTS stability on Si(111) before and after exposure to air.

The modification of the silicon surface by a SAM can be further characterized by ballistic electron emission (BEEM) with the deposition of a thin gold layer on the substrate surface. BEEM is a three-terminal technique based on scanning tunneling microscopy with an added contact at the back of the semiconductor to collect the ballistic carriers injected by the tip with enough energy to overcome the local barrier height between the metal and the semiconductor (see the inset of Figure 5 for a schematic of the setup).[43,44] Previous studies on gold/SAM/silicon show consistently a decrease in the BEEM current collected,[45] although the top metal is likely to penetrate
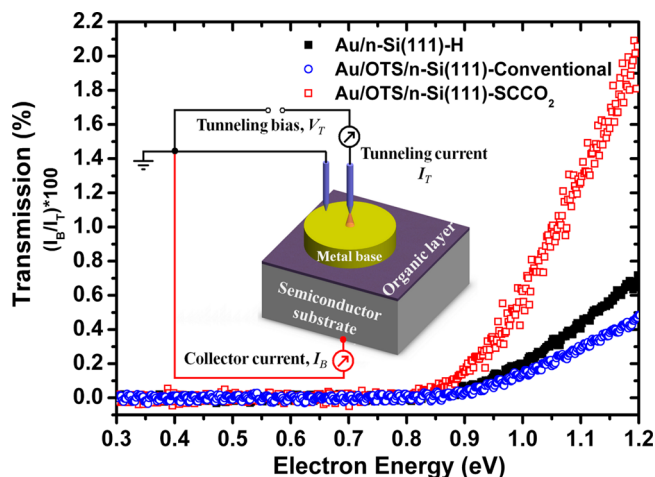

Figure 5. Representative BEES for Au/OTS/n-Si(111) diodes grown by SCCO$_2$ and conventional processes (red open square and blue open dots, respectively) and a control diode of Au/n-Si(111) with the same metal thickness (black square). (Inset) Schematic of the BEEM setup.

through the molecular layer and form shorts between the Au and the Si substrate.[46−48]

OTS deposited by SCCO$_2$ and conventional processes under conditions described above on n-Si(111) were capped by a 15 nm gold film deposited by thermal evaporation at a rate of 0.2 Å/s at a base pressure of 10^{-6} Pa. The 0.5 mm diameter diodes formed through a shadow mask were then characterized using a homemade BEEM setup.[44] A Au/n-Si(111) sample with the same metal thickness is used as a control reference.

Thousands of ballistic electron emission spectra (BEES) were acquired over a few different areas, and representative curves for the different samples are presented in Figure 5. The transmission in the BEEM current relative to the nominal current injected, that is, the tunneling current, is about 0.6% at 1.2 eV in the control Au/n-Si(111) sample, and it is 0.5% for the device with a conventionally processed OTS monolayer. Surprisingly, the device with the OTS monolayer grown by the SCCO$_2$ process shows a huge 2% at 1.2 eV. Compared to previous studies,[45−47] we observe a similar decrease in BEEM current for conventionally grown monolayer devices, but the same monolayer grown through the SCCO$_2$ process shows a much higher BEEM current than that in the control sample, although the barrier heights extracted in all of these curves are similar at about 0.80 ± 0.01 eV. To the best of our knowledge, this is the first report of such an increase in a metal/organic monolayer/semiconductor interface. Supposing the metal penetration through the monolayer,[46] the higher BEEM current seen here could be due to the oxygen-free surface provided by the effectiveness of the SCCO$_2$ process and is supported by the XPS measurements. Oxide growth is well-known to decrease significantly the current transmission in BEEM.[48,49] Another possible explanation would be a change in the surface band structure of the substrate by the anchoring of the well-packed molecular layer, which could result in an increase in the BEEM current by bettering the match in momentum pockets between the gold and the substrate.

The exact mechanism responsible for this transmission enhancement is not clear yet, but the magnitude of the effect is clearly not negligible and could be of interest in many types of existing devices, which we are currently exploring.

In summary, the single-step SCCO$_2$-based covalent mono-layer assembly process is an important and valuable addition to the repertoire of chemical methods for the formation of organic monolayers on nonoxidized silicon surfaces. A particular advantage of the current method is that it is applicable for the assembly of a variety of functional organic molecules under simple experimental conditions. Using SCCO$_2$ as the medium enables conduction of the complete assembly as a series of injections of appropriate precursors into the high-pressure environment, thereby simplifying processing. Although the SCCO$_2$ process is able to impart desired robustness to the films constructed, the idea is relatively new and has not been widely exploited in comparison to films formed by conventional methods. This technique of modifying oxide-free silicon films at close to ambient temperature in SCCO$_2$ is a clean and environmentally benign process when compared to the conventional methods using liquid solvents and enables formation of films of monolayer thickness.

The desired monolayer can be prepared in a single-step procedure. Further derivatization of the organic structures using bifunctional species containing reactive groups such as amines is facilitated by direct attachment in the same SCCO$_2$ medium; the attachment process does not require protection/activation

steps and is generally insensitive to steric factors. Organic materials with different chemical functionalities were used in this process without the need to vary the reaction conditions. In addition, a second layer could be covalently bound to the base monolayer by the same process. Furthermore, the entire process can be done in one vessel, making it easily scalable.

Preliminary results from BEEM suggest that a monolayer can play a significant role at the interface even as a simple alkane chain. The oxide-free passivated surface obtained via the $SCCO_2$ process could play a major role in the increase in BEEM current reported here. Further investigations with different end and anchoring groups and dissimilar dipoles molecule are in progress and will be reported in the near future.

The design of tailored interfaces benefits from numerous chemical strategies now available for the reaction of the Si–H surface with organic molecules. Nevertheless, a continuing challenge is in the development of robust chemistries to prevent side reactions, most notably oxidation, at the silicon/germanium surface. Although simple Si–C linked alkyl layers, with minimal traces of silicon oxides, are relatively easy to obtain, preparation of functional layers for the design of complex, chemically well-defined sensing interfaces is still a field rich in challenges and opportunities.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Detailed experimental procedure and information on characterization techniques. This material is available free of charge via the Internet at http://pubs.acs.org.

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Author Contributions

§S.R.P. and S.J. contributed equally.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

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