Near-Ideal Complete Coverage of CD₃ onto Si(111) Surfaces Using One-Step Electrochemical Grafting: An IR Ellipsometry, Synchrotron XPS, and Photoluminescence Study

Florent Yang,* Katy Roodenko,† Ralf Hunger,‡ Karsten Hinrichs,‡ Klaus Rademann,⊥ and Jörg Rappich‡

†Institute for Silicon Photovoltaics, Helmholtz-Zentrum Berlin für Materialien und Energie, Kekuléstraße 5, 12489 Berlin, Germany
‡Department Berlin, ISAS - Institute for Analytical Sciences, Albert-Einstein-Straße 9, 12489 Berlin, Germany
§Department of Materials Science and Engineering, University of Texas at Dallas, Richardson, Texas 75080, United States
∥Institute of Materials Science, Technische Universität Darmstadt, Petersenstraße 23, 64287 Darmstadt, Germany
⊥Department of Chemistry, Humboldt-Universität zu Berlin, Brook-Taylor-Straße 2, 12489 Berlin, Germany

ABSTRACT: A one-step electrochemical grafting process using Grignard reagents has been performed to achieve a complete monolayer methyl-terminated Si(111) surfaces. Anodic treatment (0.5 mA/cm² for 300 s) has been applied to atomically flat H-terminated Si(111) surfaces in methylmagnesium bromide (CH₃MgBr), methylmagnesium iodide (CH₃MgI), and methyl-d₃-magnesium iodide (CD₃MgI) to obtain methylated Si(111) surfaces. Infrared spectroscopic ellipsometry (IRSE) clearly reveals a vibrational shift of the symmetric “umbrella” mode characteristic for methyl groups (CH₃ and CD₃) with a preferential z-orientation. Additionally, X-ray photoelectron spectroscopy using synchrotron radiation (SXPS) shows a well-defined splitting of the Si 2p core level spectra from the methylated Si(111) surfaces. This splitting is more pronounced for the CD₃-terminated Si(111) surfaces. Moreover, the C 1s spectra also confirm the well-defined structure of the CD₃-terminated Si(111) surfaces by the presence of C−D vibrational stretching features. Photoluminescence (PL) measurements reveal better surface passivation in the case of CD₃-terminated Si(111) surfaces. Finally, the quality of the surfaces depends strongly on the counterions. Grignard reagents containing iodine show the best performance in the formation of complete monolayer methylated Si(111) surfaces.

1. INTRODUCTION

Anodic decomposition of Grignard compounds on silicon (Si) surfaces is one of several methods to obtain organically modified Si surfaces. In the past few years the grafting of alkyl chains onto Si surfaces has received important consideration since this process can offer molecular level control which potentially leads to novel applications in semiconductor devices (microelectronics) as well as chemical and biochemical sensors.2,4 A complete monolayer coverage of the Si(111) surface by methyl groups has been achieved.5,6 Such alkylated Si surfaces are known to present excellent chemical stability and very low surface charge carrier recombination rates even after a long period of exposure time to ambient atmosphere.7 In contrast, H-terminated Si(111) surfaces possess low surface recombination rates (good passivation) but unfortunately oxidize more rapidly in ambient air, forming a large number of defects (electronically active trap sites on the surface).8 H-terminated Si(111) surfaces, which present ideal atomically flat surfaces, are very exciting since they have the potential to form well-ordered Si organic surfaces for bio-organic devices by click chemistry method or as DNA sensors, for instance.

Recently, methyl-terminated Si surfaces prepared by a two-step chlorination/alkylation process using Grignard reagents have been extensively investigated by low-temperature scanning tunneling microscopy (STM),6,13 scanning tunneling spectroscopy (STS),13,14 low-energy electron diffraction (LEED),13,15 X-ray photoemission spectroscopy (XPS),15,16 high-resolution electron energy loss spectroscopy (HREELS),13 and different IR spectroscopy techniques.5,17 These studies revealed both short-range and long-range order on these methylated Si surfaces by the formation of Si−C covalent bonds.
Until now, the one-step electrochemical process using Grignard reagents to obtain alkyl-terminated Si(111) surfaces developed by Chazalviel’ group has been left aside to the detriment of the two-step chlorination/alkylation process. In this study, the one-step electrochemical Grignard grafting method has been chosen to avoid the prestep of chlorination. The anodic process directly grafts the methyl groups onto the surface in only a few minutes. This process is stimulated by the creation of radicals near the surface, which are controlled by the charge flow.

Moreover, up to now only one report on methyl-terminated porous Si surfaces using the infrared ellipsometry spectroscopy (IRSE) technique is available. IRSE has been shown to be extremely sensitive and permits an unambiguous identification of monolayer coverage. This paper shows for the first time the vibrational shift of the “umbrella” symmetric deformation mode between CH₃ and CD₃ groups grafted onto H-terminated Si(111) surfaces using the IRSE spectroscopic method. Additionally, synchrotron X-ray photoemission spectroscopy (SXPS) data show a much more defined splitting of the signals from Si−C bonds and Si bulk contributions, respectively, as compared to the results observed for the two-step process (including chlorination). Photoluminescence (PL) and SXPS measurements reveal a better passivation and protection of the Si surface in the case of CD₃-terminated Si(111) surfaces than for CH₃-terminated Si(111) surfaces. Furthermore, the halogen in the Grignard reagent has been found to strongly influence the grafting procedure, which affects the difference of the electronic properties (passivation) as observed for these methylated Si(111) surfaces.

2. EXPERIMENTAL SECTION AND GRAFTING PROCEDURE

Float zone grown p-type Si(111) substrates with a resistivity of 0.5−2.5 Ω cm (single side polished, thickness 525 μm) were first cleaned ultrasonically in isopropanol solution and then immersed in hot boiling piranha solution (conc H₂SO₄:conc H₂O₂, 2:1 in volume). After this, the samples were etched by dipping them into a 40% ammonium fluoride (NH₄F) solution, which leads to atomically flat and H-terminated Si(111) surfaces. For each step of the procedure, the substrates were thoroughly rinsed with copious amounts of ultrapure water (18 MΩ cm) and dried under a stream of nitrogen gas. Afterward, the ideally monohydride-terminated Si surfaces were transferred in a nitrogen-purged glovebox (O₂, H₂O < 0.1 ppm) and were immersed in a U-form Teflon cell (equipped with a Pt plate as counter electrode) containing the Grignard electrolyte, where the electrochemical treatment (anodic oxidation) was performed. The electrochemical modification (anodic current of 0.5 mA/cm² for 300 s) was applied under galvanostatic conditions, and the H-terminated Si(111) surfaces were used as working electrodes. After the electrochemical reaction, the Si samples were rinsed successively in diethyl ether (DEE) and bromobutane (BrBu) solutions before removing the samples from the glovebox. They were then rinsed again in ethanol and ultrapure water and were finally dried under a stream of dry nitrogen. Afterward, the methylated Si samples obtained were immediately transferred into the infrared ellipsometer or into an ultrahigh vacuum (UHV) chamber for further measurements using IRSE and SXPS analysis, respectively. Methylmagnesium bromide (CH₃MgBr, 3.0 M in DEE), methylmagnesium iodide (CH₃MgI, 3.0 M in DEE), and methyl-d₃-magnesium iodide (CD₃MgI, 1.0 M in DEE) as Grignard reagents were purchased from Aldrich and were used as received.

3. IRSE, SXPS, AND PL MEASUREMENTS

For IRSE characterizations, a photometric ellipsometer attached to a Bruker IFS 55 Fourier transform spectrometer using a mercury−cadmium−telluride (MCT) detector with a resolution of 4 cm⁻¹ was employed. Recently, IRSE studies of thin film and interface properties on semiconductors have been shown to be a powerful tool.

SXPS measurements were performed at the BESSY II synchrotron facility on the beamline U49/2-PGM2 with a SPECS Phoibos 150 analyzer at the SoLias experimental station. X-ray photoelectron spectra were recorded in normal emission using excitation energies of 650 and 150 eV (for bulk and surface sensitive information). The measurements were performed under a pressure of 10⁻¹⁰ mbar. Before the SXPS measurements, all the modified Si samples were annealed in a preparation chamber, under UHV, and then transferred to the analysis chamber. The annealing procedure was performed to remove all adventitious organic contaminants left on the Si surface after the electrochemical deposition and/or the rinse procedure (in order to obtain clean Si surfaces). The modified Si surfaces were annealed at 390 °C (and again at 430 °C, in the case of CH₃-terminated Si(111) surfaces) for 30 min, depending on the SXPS results obtained from the annealed Si surfaces.

PL spectra were obtained with a dye laser pumped by a nitrogen laser used as an excitation light source to emit single pulses at a wavelength of 500 nm (70 μJ/pulse, 0.6 ns pulse width).

4. RESULTS

4.1. IRSE Investigation. IRSE spectra of H−Si surfaces electrochemically modified with CH₃MgBr and CD₃MgI reagents referenced to an atomically flat H-terminated Si(111) surface are shown in Figure 1. The tan ψ spectra show two peak downward pointing peaks at 980 and 2083 cm⁻¹. The IRSE spectra show a much more defined splitting of the signals from Si−C bonds and Si bulk contributions, respectively, as compared to the results observed for the two-step process (including chlorination). The anodic process directly grafts the methyl groups onto the surface in only a few minutes. This process is stimulated by the creation of radicals near the surface, which are controlled by the charge flow.

Figure 1. IRSE spectra (top: tan ψ; bottom: Δ) of methylated Si(111) surfaces after anodic treatment (i = 0.5 mA/cm² for 300 s) in CH₃MgBr (red, - - -) and CD₃MgI (blue, —) Grignard solutions referenced to the corresponding IRSE spectrum of the H-terminated Si(111) surface, respectively.
1253 cm$^{-1}$ assigned to the symmetric “umbrella” deformation (bending) mode of the methyl groups covalently bonded to Si atoms from the surface, i.e., $\delta$CD$_3$ and $\delta$CH$_3$,	extsuperscript{25} respectively. These assignments are in good agreement with FTIR results performed on a methylated porous Si surface observed by Canaria et al.\textsuperscript{25} and Dubois et al.\textsuperscript{26} The positive upward pointing peak at 2083 cm$^{-1}$ is due to the loss of the symmetric vibrational mode of Si–H surfaces species ($\nu$SiH). This behavior is an indication of the change of the Si surface from Si–H to Si–methyl. The complementary parameter $\Delta$ of IRSE spectra (Kramers–Kronig relation) confirms that the peaks observed in tan $\psi$ spectra are due to vibrational related states, since an optical change which occurs in $\Delta$ spectra is related to the respective IR absorption. Our IRSE investigation, which was the first one for these types of methylated Si(111) surfaces, reveals the high sensitivity of the IR ellipsometry technique even for an organic layer in the monolayer thickness range.

However, no absorption bands corresponding to the stretching vibration modes of methyl groups have been observed in the tan $\psi$ spectra. The stretching vibrational modes of methyl groups could not be measured since they possess a very weak transition dipole moment due to the low polarity of the C–H bond. However, the C–H stretching modes of methyl bonded to silicon have been detected, but with a very weak intensity in the case of IR techniques like infrared absorbance spectroscopy (IRAS),\textsuperscript{27} transmission infrared spectroscopy (TIRS),\textsuperscript{17,27} and Fourier transform infrared spectroscopy using attenuated total reflection (ATR-FTIR).\textsuperscript{5,25,28} Moreover, the observation of the “umbrella” vibrational mode of methyl groups on the surface is a strong indication of the presence of methyl groups bonded to the Si surfaces. The infrared dynamic dipoles of the methyl groups are essentially perpendicular to the surface since only the symmetric “umbrella” mode is visible in Figure 1. This observation confirms the preservation of the well-ordered hydrogenated Si(111) surfaces after the electrochemical treatment. Furthermore, no significant amount of silicon oxide has been observed on these modified surfaces. This finding is also supported by the high-resolution Si 2p spectra of

Figure 2. High-resolution XPS spectra of the (a) Si 2p and (b) C 1s region and (c) valence band spectra of H-, CH$_3$-, and CD$_3$-terminated Si(111) surfaces after H-termination process and electrochemical treatment in CH$_3$–MgBr and CD$_3$–Mgl solutions, respectively. The XPS spectra of the C 1s and Si 2p regions were measured with a photon energy of 650 and 150 eV, respectively, after annealing of the samples at 390 °C for 30 min and were fitted with a Voigt function (convolution of Gaussian–Lorentzian sum functions) after a Shirley background subtraction. The valence band spectra were excited under photon energy radiation of $h\nu = 150$ eV.
the methyl-terminated Si(111) surfaces as shown in the next section.

4.2. XPS Investigation. Si 2p and C 1s core level spectra of methyl-terminated Si surfaces were measured using synchrotron X-ray radiation at 150 eV (surface sensitive conditions) and 650 eV, respectively, as shown in Figures 2 and 3, respectively. The XPS spectra have been deconvoluted with a fitting procedure using spin-orbit doublets of Voigt line shapes (combination of Gaussian–Lorentzian functions) after a Shirley background subtraction. A branching intensity ratio of 0.5 and a spin-orbit splitting of 0.605 eV has been maintained for the Si envelope.

To remove all adventitious organic contaminants left on the surface after the electrochemical deposition and/or the rinse procedure (in order to obtain clean Si surfaces), the modified Si surfaces were first annealed at 390 °C for 30 min and if necessary annealed again at 430 °C for 30 min to desorb the adventitious non-methyl hydrocarbons remained on the Si surface, as observed in the C 1s spectra (see Figure 3).

The high-resolution Si 2p core level spectra of methyl-terminated Si(111) surfaces recorded at an excitation energy of 150 eV (surface sensitive, Figure 2a) reveal a Si 2p envelope with a splitting of Si 2p1/2 and Si 2p3/2 peaks. A well-separated splitting from the two main peaks expected is observed here: the bulk component Si−Si (Si°) at 99.23 ± 0.08 eV and the surface component Si−C at 99.50 ± 0.07 eV, which results from the Si atop surface atoms covalently bonded to the carbon atoms of the methyl groups for both CD3- and CH3-terminated Si(111) surfaces, respectively. The chemical shift of the doublet Si 2p peak from the methyl-terminated Si surfaces with respect to the H-terminated Si(111) surface (expected chemical shift <1 eV)30 by 0.3–1.0 eV indicates the formation of Si−C covalent bonds after the electrochemical treatment. A weak contribution located at higher binding energy by approximately +0.82 ± 0.08 eV from the bulk component Si° is certainly due to a mixture of Si bonded to bromine (iodine) Si−Br(I)31 and/or from the first state of silicon oxidation Si°+ (Si−O, Si−OH).32 Moreover, only a very minor amount of contributions related to Si oxide or suboxide species have been detected in the 101–104 eV energy range (see Figure 2a).

A more distinguishable, separate contribution from the Si 2p doublet signals (Si° and Si−C) is observed in the case of the CD3-terminated Si(111) surfaces and about 94% of this has been determined to be a Si−C contribution after the deconvolution of the Si 2p core level spectra. This behavior indicates that almost every Si atop site of the unreconstructed H:Si(111)-(1 × 1) surface has been covalently attached to a methyl-d3 group. This confirms that methyl-terminated Si surfaces are ideally and highly passivated Si surfaces.15 However, in the case of CH3-terminated Si(111) surfaces, only about 78% of the higher energy contribution is described by Si−C covalent bonds and the addition of another species is necessary to obtain a suitable fit of the Si 2p envelope. This contribution around 99.74 eV situated approximately at +0.43 ± 0.08 eV from the bulk component Si° is attributed to the formation of silicon carbide arising from the annealing process, which is in good agreement with previous XPS observations.16

C 1s core level spectra of methyl-terminated Si(111) surfaces excited with a photon energy of hν = 650 eV (see Figure 2b) show a broad emission signal around 284 eV with an asymmetry toward higher binding energies. The C 1s emission signal has been deconvoluted into four components denoted Cn with n = 0, 1, 2, 3. The C0 peak at ~284.05 eV is attributed to the adiabatic peak which corresponds to the Si bonded to C atoms of the methyl groups (Si−C bonds). The C1 and C2 peaks at higher binding energies were coupled by the relation ∆BE2 = 2 × ∆BE1 as described in ref 15, and ∆BE1 was found to be 0.28 and 0.38 eV for CD3- and CH3-terminated Si(111) surfaces, respectively. These energy values correspond to vibration frequencies of about 2258 and 3064 cm−1, respectively, and match quite well with the C−D and C−H stretching vibration energies. Moreover, these findings are in good concordance by differences of about 25 and 45 cm−1 with the theoretical values calculated by the groups of Ignatyev33 and Khabashesku,34 respectively. The difference between the experimental and theoretical values is probably due to the rotation of the molecules which has not been considered in the

Figure 3. High-resolution XPS spectra of the (a) Si 2p and (b) C 1s emission region collected after different annealing steps applied on the CH3-terminated Si(111) surfaces. The electrochemical treatment has been performed in CH3–MgBr solution by the application of an anodic current (i = 0.5 mA/cm2 for 300 s). The annealing temperatures are indicated in the figure. The XPS spectra of the C 1s and Si 2p regions were measured with a photon energy of 650 and 150 eV, respectively, and were fitted with a Voigt function (convolution of Gaussian–Lorentzian sum functions) after a Shirley background subtraction.
calculation. In the case of CH$_3$-terminated Si(111) surfaces, the value of $\Delta$BE$_i$ (0.38 eV) is in very good agreement with the methyl-terminated Si surface prepared via the two-step chlorination/alkylation process$^{15}$ but also with the other organic systems reported in ref 15. Likewise, the corresponding vibration frequency of these methyl-terminated surfaces is in good relation to the value as calculated by the Si cluster model and PBC models.$^{35}$ Therefore, these peaks have been ascribed to vibrational losses of the final state of the C$^0$ signal due to the generation of the first and second excited state of C–H stretching vibrations.$^{15}$ The C$^3$ component signal located at 285.33 ± 0.12 eV corresponds to remnant adventitious carbons remained on the Si surface after the annealing procedure. Moreover, a higher amount of non-methyl hydrocarbon atoms (about a factor 4) left on the Si surface is observed in the case of CH$_2$-terminated Si(111) surfaces in comparison to the CD$_3$-terminated Si(111) surfaces taken under the same annealing conditions (i.e., at 390 °C for 30 min, Figure 2b). The chemical shift of C$^3$ (+1.1 eV) with respect to the adiabatic peak C$^0$ corresponds well to the value observed in other studies.$^{31}$ However, in the case of CH$_3$-terminated Si(111) surfaces, another asymmetry appears toward lower binding energies. Therefore, another component (C$^4$) has been added to the fitting of the C 1s envelope to obtain an accurate fit. This component located at 283.43 ± 0.08 eV is attributed to Si carbide formation$^{16}$ as a result of the annealing step. This finding is supported by the work performed by Jaeckel et al.$^{16}$

This observation suggests that methyl-d$_3$ groups protect Si(111) surfaces more efficiently against the formation of Si carbide than in the case of CH$_3$-terminated Si(111) surfaces. Also, the halogen involved in the Grignard reaction has been shown to play a role in the electrochemical grafting process.$^{37,38}$

The kinetics of the reaction are increased by changing the halogen from Br to I.$^{39}$ The more electronegative the halogen is, the less efficient the grafting of the methyl groups becomes. This statement suggests that the concentration of surface states is a function of the increase in the halogen electronegativity. Moreover, it may also be that the CD$_3$–MgI Grignard solution is cleaner than the CH$_3$–MgX (X = halogen) Grignard solutions. Therefore, to reduce the presence of the remnant adventitious aliphatic hydrocarbons remained on the CH$_3$-terminated Si(111) surfaces, a second annealing step at 430 °C for 30 min has been performed, and the results of the second annealing step can be observed in Figure 3. After the second annealing step at 430 °C for 30 min, the C 1s emission data reveal that the contribution of the adventitious aliphatic hydrocarbons is strongly reduced by approximately a factor 3 (see Figure 3b). However, the contribution of the remnant aliphatic carbon contamination is still about 30% more than in the case of CD$_3$-terminated Si(111) surfaces. At the same time, the higher annealing temperature at 430 °C leads to an increase in the contribution due to the silicon carbide by about a factor 4 as well as a decrease in the contribution attributed to Si bonded to C by a factor 1.3, as deduced from the Si 2p emission data (Figure 3a). Thus, the higher annealing temperature leads to a less stable surface since the formation of silicon carbide increases and the Si–CH$_3$ contribution signal decreases, respectively. These observations support that a better achievement of the complete coverage is obtained in the case of CD$_3$-terminated Si(111) surfaces since a lower temperature was needed to desorb all adventitious aliphatic hydrocarbons from the surface.

The valence band spectra of methyl-terminated Si(111) surfaces presented in Figure 2c clearly indicate three main features. The intense peak around 2.62 eV corresponds to the Si 3p orbital. The intensity of this peak reflects the cleanliness of the obtained Si surface. The C 2p orbital is separated into two bands located at about 5.07 and 7.22 eV and are attributed to $\sigma_{C=C}$ and $\pi_{C=H,CD_3}$, respectively. Finally, the bands which appear at 16.22 eV for both methylated Si surfaces have been ascribed to the C 2s orbital. These results are in good agreement with the CH$_3$-terminated Si surfaces obtained from the two-step chlorination/Grignard process as described by Hunger et al.$^{15}$ which indicates that methyl-terminated Si(111) surfaces prepared with the one-step Grignard anodic process present also highly ordered modified Si surfaces.

Additionally, the presence of the $\sigma_{C=C}$ peak for both methyl-terminated Si(111) surfaces is still detected after the annealing process, even after another annealing step at 430 °C for 30 min in the case of CH$_3$-terminated Si surfaces (not shown herein). This confirms the formation of Si–C covalent bonds between the methyl groups and the Si atoms on the surface and indicates the achievement of robust methylated Si surfaces.

4.3. PL Investigations. Figure 4 shows the PL intensity ($I_{PL}$) spectra as measured for H$_3$, CH$_3$, and CD$_3$-terminated Si(111) surfaces after the grafting and rinsing procedures (see inset). The silicon native oxide (SiO$_x$) spectrum is shown for comparison. Methylated Si(111) surfaces have been achieved by application of an anodic current ($i = 0.5$ mA/cm$^2$ for 300 s) using Grignard reagents. As indicated, a dye laser pumped by a nitrogen laser was used with an excitation laser of 500 nm, 70 μJ/pulse, and 0.6 ns pulse width.

Figure 4. Maximum of the PL intensity ($I_{PL}^{max}$) as a function of the end-group molecules on the Si(111) surface. Inset: $I_{PL}$ spectra of (a) atomic and flat H-terminated, (b) CD$_3$-terminated, (c, d) CH$_3$-terminated Si(111) surfaces and (e) natively oxidized Si. Methylated Si(111) surfaces have been achieved by application of an anodic current ($i = 0.5$ mA/cm$^2$ for 300 s) using Grignard reagents. As indicated, a dye laser pumped by a nitrogen laser was used with an excitation laser of 500 nm, 70 μJ/pulse, and 0.6 ns pulse width.
Si surface recombination is only twice that of a H-terminated Si(111) (which is typically in the range of 20 cm/s) after grafting of the methyl groups. However, \( I_{\text{RE}} \) of the CD\(_3\)-terminated Si(111) surface shows about 30% higher value than the CH\(_3\)-terminated Si(111) surface, which means that CD\(_3\)-terminated Si(111) surfaces possess less recombination active defect centers than CH\(_3\)-terminated Si(111) surfaces. This conclusion is in good agreement with the SXPS data presented before, where the CD\(_3\)-terminated Si(111) surface also indicates a better splitting between the Si bulk (Si\(^{\text{+}}\)) and the Si surface components (Si–methyl). Moreover, exchanging the halogen present in the Grignard reagent from Br to I leads to a slightly better passivation of the surface states in the case of methyl groups, as shown in Figure 4. This finding supports that a better grafting is achieved when the Si–halogen bond is weaker (i.e., the halogen is less electronegative and bigger in size). The halogen radical X* which can be created during the anodic process could bind to a Si site which has a dangling bond. Then, two processes may occur: (i) Si–X bond breaking (a) via Si–X + MgX\(^{-}\) → Si\(^{\text{+}}\) + MgX\(_2\) or more probably via (b) Si–X + X\(^{\text{+}}\) → Si\(^{\text{+}}\) + X\(_2\), so that new reactive Si* sites are created which can react with *CH\(_3\) or (ii) especially in the case of bromine, the Si–Br bonds at step facets and edges are blocked for further reactions via neighbord Si–CH\(_3\) groups. Such a behavior could explain the better passivation in the case of CD\(_3\)MgI (CH\(_3\)MgI) compared to CH\(_3\)MgBr which also fits with a faster reaction of CH\(_3\)MgI with the Si surface than of CH\(_3\)MgBr.\(^{41}\) Additionally, the methylated Si surface using CD\(_3\)MgI showed the more pronounced Si envelope as observed by our SXPS measurements.

5. CONCLUSIONS

Complete coverage of covalently bonded methyl groups (CH\(_3\) and CD\(_3\)) to Si atop surface atoms has been well-achieved on H-terminated Si(111) surfaces using the one-step electrochemical Grignard grafting process. IRSE measurements have been applied to such methyl-terminated Si(111) surfaces and reveal a significant shift of the "umbrella" symmetric vibrational modes of CH\(_3\) and CD\(_3\) groups, respectively. The weak IR-absorption bands are well related to an abrupt optical change in the respective band in the \( \Delta \) spectra from the Kramers–Kronig relations, which confirm the presence of methyl groups on the modified Si surfaces. High-resolution Si 2p spectra reveal a well-defined splitting of the bulk and surface components using this anodic electrochemical Grignard process. In the case of CD\(_3\)-terminated Si(111) surfaces, this observation is more prominent and much more pronounced than using the Lewis chemical two-step chlorination/alkylation process. This suggests the well achievement and the preservation of a highly ordered structure for both types of methyl-terminated Si surfaces. Moreover, a very small amount of SiO\(_2\) (less than 1%) has been observed in Si 2p core level spectra. However, the methylated Si(111) surfaces indicate also the presence of bromine (~5–8%) on the surface. In the case of CH\(_3\)-terminated Si(111) surfaces, after a second annealing process the presence of Si–carbide contributions is indicated in both Si 2p and C 1s core level spectra, respectively. Additionally, the high-resolution C 1s core level spectra of methyl-terminated Si(111) surfaces reveal two vibrational stretching features, but also a very small amount of adventitious aliphatic carbons. PL spectroscopy has also been performed for the first time to such modified surfaces, showing a better passivated interface in the case of CD\(_3\)-terminated Si(111) surfaces and supporting the

statements drawn from the IRSE and SXPS spectra. Therefore, the CD\(_3\)-terminated Si(111) surfaces could be used to enhance electronic properties for applications in photovoltaics, biosensing, and many other potential applications and fabrications of new organic hybrid materials and devices.


