Vibrational and Electronic Characterization of Ethynyl Derivatives Grafted onto Hydrogenated Si(111) Surfaces

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Covalent grafting of ethynyl derivatives (–C≡C–H, –C≡C–CH3, –C≡C–aryl) onto H-terminated Si(111) surfaces was performed by a one-step anodic treatment in Grignard electrolytes. The electrochemical grafting of such ethynyl derivatives, which tends to form ultrathin polymeric layers, can be controlled by the current and charge flow passing through the Si electrode. The prepared ultrathin layers cover the Si surface and had a thickness up to 20 nm, as investigated by the scanning electron microscopy (SEM) technique. Exchanging Cl for Br in the ethynyl Grignard reagent leads to very thin layers, even under the same electrochemical conditions. However, for all ethynyl derivatives, high-resolution synchrotron X-ray photoelectron spectroscopy (SXPS) investigations reveal the incorporation of halogen atoms in the organic layers obtained. Moreover, it was observed that the larger the end group of the ethynyl derivative, the thinner the thickness of the ultrathin polymeric layers as measured by both SXPS and SEM techniques after low and high current flow respectively. For the first time, these new types of ultrathin organic layers on Si surfaces were investigated using infrared spectroscopic ellipsometry (IRSE). The different possible reaction pathways are discussed.

1. Introduction

Organic modification of the silicon (Si) surface has become an attractive subject, because of a wide range of potential applications in molecular electronics, biosensors, microelectronics and organic hybrid devices. Therefore, it is important to functionalize and investigate Si/organic heterointerfaces. Achievement of covalently attached organic monolayers onto H-terminated Si(111) surfaces without the interfaceal native silicon oxide layer provides surfaces that exhibit superior properties, such as electronic passivation (low concentration of electron states in the band gap) and chemical stability toward oxidation. Many studies concerning such anchoring on hydrogenated Si surfaces have already revealed the formation of well-ordered monolayers covalently bonded to Si among those are alkyl chains, alkenes, alkynes, aryl and phenyl compounds. Several techniques have been performed to obtain the formation of organic monolayers on Si surfaces via Si–C covalent bonds applying chemical processes, e.g. by alkyl-Grignard (alkyllithium reagents), chemical and photochemical and...
thermochemical reactions, electrochemical grafting or reaction in ultrahigh vacuum.

Methyl groups are small enough to fit atop every Si(111) surface site, and a complete coverage of the Si(111) surface can be achieved, because the atomic distance between adjacent Si surface sites on an unreconstructed 1 × 1 H–Si(111) surface is 3.8 Å. However, such methylated Si(111) surfaces that strongly protect the surface against chemical attack are not convenient for further functionalization. In the case of other molecules, such as long alkyl chains or phenyl groups, a complete coverage of the Si(111) surface could not be realized, because of steric constraints, and only a partial coverage of ~50% has been reached. Further candidates for complete coverage on the Si(111) surface are unsaturated organic species such as ethynyl or propynyl moieties (−C≡C−R, with R = H, CH3), because of the linearity of these molecules. Moreover, the functionalization of Si surfaces by C≡C groups opens new reaction pathways for further organic modification of these surfaces to introduce functional groups by click chemistry (for reaction in ultrahigh vacuum).

Electrochemical methods, which are especially attractive and are efficient with regard to providing a straightforward and very fast way of generating radicals near the surface, have been chosen for the grafting of these ethynyl derivatives onto Si(111) surfaces. The anodic decomposition of Grignard compounds process used here is a one-step reaction, where radicals R• are created (arising from Grignard compounds) when an anodic current is applied to the Si surface. The radicals R• formed react with the H-terminated Si(111) surface to create a Si dangling bond, and, subsequently, another R• is able to react with this dangling bond to form a covalent Si–C bond. Grignard reagents are always anhydrous solutions and avoid oxide formation on Si surfaces. However, the radicals formed seem to attack the first monolayer grafted onto Si surfaces (e.g., C≡C bonds) and lead to the formation of C≡C and C≡C bonds. The results obtained here indicate the formation of ultrathin polymeric layers (10−20 nm), which interestingly decrease when the end group of the ethynyl derivatives is larger. This electrochemical method is different from the two-step method (prestep: chlorination of the Si:H surface) which has been extensively used by Lewis’ group and for which a longer deposition time is required. In this paper, we investigate the grafting of ethynyl, propynyl, and phenylethynyl (as a molecule, which will show a steric hindrance on the Si(111) surface) from ethynyl magnesium chloride, propynyl magnesium bromide, and phenylethynyl magnesium bromide on H-terminated Si(111) surfaces. These surfaces have been characterized using infrared spectroscopic ellipsometry (IRSE), scanning electron microscopy (SEM) and high-resolution synchrotron X-ray photoelectron spectroscopy (SXPS). The first-time study by IRSE reveals the presence of typical vibrations arising from ethynyl derivatives while the detailed analysis of binding energy shifts of the XP emissions from Si 2p and C 1s signals allows us to determine different interface species after the grafting process. Moreover, SEM imaging confirms the formation of ultrathin polymeric layers on Si surfaces. Possible chemical reaction pathways are discussed.

2. Experimental Section

2.1. Preparation of the H-terminated Si. Si samples were cut from p-type Si(111) wafers (float zone, single-side polished, 525 μm thick) with a resistivity of 0.5–2.5 Ω cm. Atomically flat and hydrogenated Si substrates were obtained from the following typical procedure: first, Si samples were cleaned ultrasonically in 2-isopropanol, then immersed in hot piranha solution (H2SO4:H2O2 = 2:1) to remove organic contaminants, and finally etched in 40% NH4F solution to obtain atomically flat and hydrogenated Si surfaces. The Si samples were rinsed in ultrapure water (18 MΩ cm) before and after each step. These hydrogenated Si surfaces were transferred in a nitrogen-purged glovebox (O2, H2O < 0.1 ppm) and used for the electrochemical modification. All chemicals were of VLSI grade.

2.2. Grafting Procedure. The electrochemical modification was performed under galvanostatic conditions in a two-electrode cell equipped with a platinum plate as a counter-electrode. Anodic currents of 0.5 or 0.02 mA cm−2 were applied to the Si samples for each Grignard electrolyte for 15 or 20 min, to vary the charge flow from 450 μC cm−2 to 24 mC cm−2, respectively. Afterward, the modified Si samples were rinsed successively in anhydrous tetrahydrofuran (THF) and bromobutane (BrBu) solutions. Furthermore, Si samples were removed from the glovebox and exposed again in ethanol and ultrapure water and then were finally dried under a stream of nitrogen gas. The modified Si samples were then directly transferred into the infrared ellipsometer for IRSE measurements (samples with higher charge flow) or into an ultrahigh vacuum (UHV) chamber for the SXPS analysis (samples with lower charge flow). All Grignard reagents: ethynyl magnesium chloride (H−C≡C−MgCl, 0.5 M in THF), ethynyl magnesium bromide (H−C≡C−MgBr, 0.5 M in THF), propynyl magnesium bromide (CH2−C≡C−MgBr, 0.5 M in THF) and phenylethynyl magnesium bromide (C6H5−C≡C−MgBr, 1 M in THF) were purchased from Aldrich and used as supplied without any further purification. In addition, D3-terminated Si(111) surface has been also prepared under a galvanostatic condition by applying a charge flow of 0.5 mA cm−2 for 5 min in methyl-d3-magnesium iodide (CD3−MgI, 3 M in diethylther) solution.

2.3. IRSE Measurement. IRSE measurements were performed in a photometric ellipsometer attached to a Bruker IFS 55 Fourier transform spectrometer, which is equipped with a mercury–cadmium–telluride (MCT) detector with a resolution of 4 cm−1.
Figure 1. Tan Ψ spectra (left) and SEM micrographs (right) after anodic treatment (i = 0.5 mA/cm² for 900 s) in (a) H—C≡C—MgCl, (b) CH₃—C≡C—MgBr, and (c) C₆H₅—C≡C—MgBr normalized to the tan Ψ spectrum of the H-terminated Si(111) surface. For each ethynyl derivative, tan Ψ spectra and SEM micrographs indicate al the formation of polymeric layers 10–20 nm thick. Please note: curve a’, which represents anodic treatment in H—C≡C—MgBr (using a Kolmar detector, 6 cm⁻¹), has been added to the figure.

2.4. SXPS Measurement. Synchrotron X-ray photoelectron spectroscopy (SXPS) experiments were performed at the beamline U49/2-PGM2 of the BESSY II Synchrotron facility.Photoelectron spectra were recorded in normal emission (model KV104-1, Kolmar Technologies Inc., Conyers, GA). IRSE recently has been shown to be a powerful tool for structural studies of thin-film and interface properties. 35–38

3. Results

3.1. IRSE and SEM Investigations. IRSE has been used to inspect the vibrational fingerprint of the surface species after the electrochemical grafting of ethynyl derivatives onto Si surfaces, and SEM measurements have been performed to determine the thickness and morphology of the organically modified Si surfaces. Figure 1 shows the IRSE spectra and SEM micrographs of H-terminated Si(111) surfaces after electrochemical modification by applying a high charge flow (450 mC/cm²) in H—C≡C—MgCl, CH₃—C≡C—MgBr, and C₆H₅—C≡C—MgBr solutions, respectively. The spectra were normalized to the H-terminated Si(111) surface to highlight the changes after electrochemical grafting. The upward pointing band at ~2083 cm⁻¹ in all spectra indicates the loss of Si—H surfaces species after the grafting process and suggests that the organically modified Si surfaces are no longer well-hydrogenated. After electrochemical treatment in H—C≡C—MgCl solution, the formation of a polymeric layer ~20 nm thick has been determined by SEM measurement. This finding is supported by the presence of strong and broad IR-absorption bands, from contaminations and the layer itself, ascribed to symmetric and asymmetric stretching vibrational modes of CH₃(s) bands at ~2870 and ~2958 cm⁻¹, respectively. 20,22 The presence of the absorption peak at ~3300 cm⁻¹ appears only for the Si(111) surface modified in H—C≡C—MgCl. This weak and broad IR band is assigned to the acetylenic C—H stretching modes in the C—C≡C—H unit, which is a strong indication of the presence of C=C bonds in the modified surface. Moreover, the stretching vibration of the ethynyl groups (νC≡C) at ~2046 cm⁻¹ is more distinguishable for the Si(111) modified by H—C≡C—MgCl. 20 A weak band also appears at 1725 cm⁻¹ after grafting of H—C≡C—, which can be attributed to C=O stretching vibrational mode and obviously arises from THF, which is the Grignard solvent, as proposed in previous work. 20 Two other peaks appear at 1450 and 1630 cm⁻¹ in this IR spectrum, which are ascribed to the symmetric bending and stretching vibrational modes of C—C≡CH and C=C groups, respectively. 17,20,60,62,64 All these features indicate the formation of a polymeric layer for ethynyl-modified Si surfaces in H—C≡C—MgCl solution. Furthermore, an attack of intermediate radicals on the C≡C—H species, which are grafted onto the Si surface, has been recently proposed, 20 leading to C=C, C≡C, and C≡C bonds in a polymeric layer, as reflected by IR absorption, because of C=C, C≡C, and C≡C—H in the spectra of Figure 1. However, exchanging the halogen Cl atoms in the Grignard compound by Br atoms leads to a very thin layer, even under the same experimental conditions. 22

In addition, no IR absorption in the C—C≡C—H or CH₂ region has been observed with H—C≡C—MgBr as a reagent, probably because of the formation of a very thin layer (confirmed by SXPS). Therefore, the halogen atoms present in the Grignard reagents play an important role in the grafting process, as proposed in the Discussion section.

The grafting of propynyl onto Si(111) surfaces (Figure 1b) leads to a very small IR absorption, at ~1100 cm⁻¹, that can be assigned to the C≡C—C stretching vibrational mode. 60,65 This is due to the formation of a 12 nm ultrathin polymeric layer (see SEM micrograph in Figure 1). As shown in Rosu et al., 66 the amplitudes of the CH₂ and CH₃ stretching bands in the tan Ψ spectra are strongly dependent on the average angle of the related transition dipole moments. For oriented hexadecanethiol monolayers, for example, band amplitudes of ~15×10⁻⁵ were determined for a band related to the CH₃ stretching vibrations of the headgroup. Because the average tilt angle, the coverage, and the high-frequency refractive index of CH₃ monolayers are not well-known, it is very difficult to make an estimation for theoretically expected band amplitudes. For the presented data, no CH₃ bands related to stretching modes could be identified above the limiting noise level (depending on the actual experimental setup) of ~5×10⁻⁵ in the referenced tan Ψ spectra. This very weak transition dipole moment of CH₃ groups made the detection of their stretching vibrational modes by IRSE impossible with the actual setup.


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The IR spectrum of the Si surface modified in C$_6$H$_5$-C≡C-MgBr solution reveals the presence of an IR absorption of aromatic C–H bonds in the 3000–3200 cm$^{-1}$ region and the ring stretching mode at 1405 cm$^{-1}$, which indicates the presence of phenyl groups (C$_6$H$_3$) on the Si surface (see Figure 1c). The SEM micrographs also show the presence of ultrathin polymeric layers that have formed on the Si surfaces. Interestingly, the larger the end group of the ethynyl derivatives, the thinner the thickness of the layer determined.

To summarize, IRSE spectra in Figure 1 confirm that especially the –C≡C–H species grafted onto the Si surfaces have been attacked by intermediate radicals, leading to C–C, C≡C, and C≡C bonds, which are in agreement with the C 1s spectra from SXPS measurements, as presented in the next subsection. This attack leads to the formation of ultrathin polymeric layers for these ethynyl derivatives. However, the chemical mechanism will be discussed in the following part.

3.2. XPS Investigation. Synchrotron X-ray photoemission spectroscopy (SXPS) was performed to inspect the chemical environment of modified Si surfaces obtained with ethynyl derivatives. For the “thick” organic layers used for IRSE measurements, no signal from the Si 2p core level spectra could be observed at 650 eV. Thus, the thicknesses of the organic layer were larger than the information depth of the X-ray energy at 650 eV, which is equivalent to an inelastic mean free path (IMFP) of ~18 Å. SEM measurements (see Figure 1) have shown a typical thickness of ~20–10 nm for the “thick” organic layers modified with ethynyl–MgCl, propynyl–MgBr, and phenylethynyl–MgBr. Therefore, the charge flow was strongly reduced (from 450 mC/cm$^2$ to 24 mC/cm$^2$) to suppress the polymerization effect observed at higher charge flow, especially for H–C≡C–MgCl. Thus, high-resolution SXPS spectra were measured for Si(111) surfaces modified by H–C≡C–MgCl, CH$_3$–C≡C–MgBr, and C$_6$H$_5$–C≡C–MgBr by applying an anodic current of 0.02 mA/cm$^2$ for 1200 s. The SXPS measurements have been performed at 150 eV (under surface sensitive conditions for Si 2p) and 650 eV for C 1s core level spectra, respectively.

Figures 2a–c show high-resolution SXPS spectra in the C 1s and Si 2p region after organic modification in (a) H–C≡C–MgCl, (b) CH$_3$–C≡C–MgBr, and (c) C$_6$H$_5$–C≡C–MgBr solutions, recorded with an X-ray energy of 650 and 150 eV, respectively. Moreover, SXPS spectra from the methylated Si(111) surface (Figure 2d) are shown for comparison. The methyl-terminated Si surface represents a highly ordered Si(111) surface. For this reason, the C 1s emission signal of this methylated Si(111) surface has been determined to correspond to one monolayer (ML). The spectra have been analyzed by deconvolution with a fitting procedure using split-orbit doublets of Voigt line shapes composed of Gaussian–Lorentzian functions after subtraction of a Shirley background. The Si 2p core level spectra (Figure 2, right) have been deconvoluted into a doublet consisting of similarly shaped components (ΔE$_{\text{BE}}$ = 0.605; 1:2 peak area ratio) from 2p$_{3/2}$ and 2p$_{1/2}$ Si peaks.

2p$_{3/2}$ Si peaks. Different contributions are required for a quantitative study. The C$_6$D$_{14}$-terminated Si(111) surface (Figure 2d) shows a doublet of Si 2p signals from the bulk Si (Si$^{0}$), which are well seen at ~99.26 and 99.84 eV with a shift of the doublet assigned to Si–C signatures from the methyl groups at ~99.9 and 100.08 eV, respectively. This small chemical shift, which is as low as 0.2–0.3 eV, has been expected for alkyl-terminated Si surfaces. The chemical shift by 0.3–1.0 eV of the doublet Si 2p peak of the Si surfaces modified by ethynyl derivatives, with respect to the Si(111)–H surface (not shown here), present clear evidence of the organic grafting onto Si surfaces where Si–C covalent bonds were formed (with an expected chemical shift of ~1 eV). Moreover, the chemical shift of the Si atoms bonded to ethynyl groups observed in the higher binding energies indicates that the Si surface is positively charged, as expected by the difference in Pauling’s electronegativity of Si (1.90) and C (2.55). Furthermore, the SXPS spectra of Si 2p from these modified Si surfaces show a weak peak located at ~100.66–100.75 eV, which may be responsible for the Si–OH (Si–O–H) and/or Si–Br(CI) bonds.

This contribution has an intensity that is ~5 times higher in the case of CH$_3$–C≡C– and C$_6$H$_5$–C≡C– modified Si(111) surfaces, compared to the H–C≡C–Si(111) surface. This result leads to the assumption that a higher contamination level of OH and/or halogen atoms appeared after the grafting of CH$_3$–C≡C– and C$_6$H$_5$–C≡C– onto Si(111) surfaces, in comparison to the

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H–C≡C–Si(111) surface. However, no or weak pronounced contributions related to Si oxide or suboxide species have been detected in the 101–104 eV energy range, even under these surface-sensitive conditions.

In addition, the C 1s peaks (Figure 2, left) from the modified Si surfaces have been deconvoluted into three principal contributions. The C 1s peak of the methyl-terminated Si(111) surface (Figure 2d) shows only one contribution, at 284.1 eV, which is attributed to Si–C bonds, as previously observed for methylated Si(111) surfaces prepared with other grafting methods.63,67 This statement leads to the conclusion that this methylated Si(111) surface has no other contaminations. Moreover, such low-energy position of C 1s peak is very specific and unequivocally considered as an indication of the Si–C bond.66,77 In the case of the Si surfaces modified by ethynyl derivatives, the component peak corresponding to Si–C bonds is slightly shifted to a lower binding energy of ~283.7 eV.21,69,70 The two other contributions at higher binding energies at ~284.6 and 286.1(286.3) eV are assigned to aliphatic and adventitious contamination carbons C–C(C=H, C≡H),21,64 and carbon bonded to oxygen/halogen (C–O or C–Br(Cl)).21,68 The C 1s contribution related to Si oxide or suboxide species has been detected only in a very low quantity,63,67 with the exception of the Si surfaces modified with bromine species via reaction schemes 3a, 3b, and 3c (or via reaction scheme 3d). Therefore, the amount of Si–Br species formed via oxidation of the Br(Cl)MgX–C bond (ideal case, reaction scheme 1 and 2), but also via the breaking of the C≡C bond (reaction schemes 3a–e) and via the reaction of halogen atoms with the Si surface (reaction scheme 3d). The Si dangling bonds (reaction scheme 1) formed, which are positively charged (δ+), can easily react with the halogen atoms (strongly negatively charged, (δ–)) contained in the Grignard compounds (reaction scheme 3d). This reaction then is in competition with the main reaction (ideal case, scheme 2) and also with the oxidation of the C≡C bond. Typically, the Si–X surface species will react with the Grignard compound (reaction scheme 3e). However, reaction via reaction schemes 3a, 3b, and 3c (or via reaction schemes 3a, 3b, and 3c′) will lead to a steric hindrance of further reaction of neighboring Si–X species formed via reaction scheme 3d. Therefore, the amount of Si–Br at the interface is increased, compared to Si–Cl for grafting of the smaller ethynyl group by the MgCl compound.

(1) Initial reactions by formation of Si dangling bonds on the surface.

(a) $R–C \equiv C–MgX + h^+ \rightarrow R–C \equiv C + MgX^+$

(b) $Si + H\cdot\cdot\cdot C \equiv C – R \rightarrow H\cdot\cdot\cdot C \equiv C – R$

(2) Main reaction by bonding of an organic radical (anodically formed via reaction scheme 1a) with a Si dangling bond.

(a) $Si\cdot\cdot\cdot h^+ + R–C \equiv C–MgX \rightarrow Si\cdot\cdot\cdot C \equiv C – R + MgX^+$

(3) Side reactions with Grignard compound, which lead to halogen incorporation in the layer.

Figure 3. (a) Atomic concentration (expressed as a percentage) of O, C, Cl, SiOx, and Br on the modified Si surfaces and (b) the layer thickness in monolayer (ML) and angstroms (Å), respectively, as obtained from the SXPS measurements (see Figure 2). One monolayer corresponds to an atom areal density of $N_{Si(111)} = 7.8 \times 10^{14}$ cm$^{-2}$, which is the surface site density of Si(111). The measured peak intensities were related to the C 1s emission signal of Si(111) terminated with a methyl monolayer. The white empty and blue filled circles represent the layer thicknesses in ML and Å, respectively, and the arrows are used to indicate the type of thickness.

4. Discussion

Figure 3 shows the atomic concentration (expressed as a percentage) on the modified Si surfaces (Figure 3a) and the layer thicknesses in monolayers (ML) and angstroms (Å) (Figure 3b), respectively, as obtained from SXPS measurements.89 The overall surface coverage of the ethynyl derivatives is ~5 ML (only ~2 ML for –CD$_3$). Some SiOx species are present at the interface, as reflected by the O 2s and Si 2p suboxide signals. The attendance of halogen moieties has also been detected by the Br 3d (or Cl 2p) contributions related to Si oxide or suboxide species have been detected only in a very low quantity,63,67 with the exception of the Si surfaces modified with bromine species via reaction schemes 3a, 3b, and 3c (or via reaction scheme 3d). Therefore, the amount of Si–Br species formed via oxidation of the Br(Cl)MgX–C bond (ideal case, reaction scheme 1 and 2), but also via the breaking of the C≡C bond (reaction schemes 3a–e) and via the reaction of halogen atoms with the Si surface (reaction scheme 3d). The Si dangling bonds (reaction scheme 1) formed, which are positively charged (δ+), can easily react with the halogen atoms (strongly negatively charged, (δ–)) contained in the Grignard compounds (reaction scheme 3d). This reaction then is in competition with the main reaction (ideal case, scheme 2) and also with the oxidation of the C≡C bond. Typically, the Si–X surface species will react with the Grignard compound (reaction scheme 3e). However, reaction via reaction schemes 3a, 3b, and 3c (or via reaction schemes 3a, 3b, and 3c′) will lead to a steric hindrance of further reaction of neighboring Si–X species formed via reaction scheme 3d. Therefore, the amount of Si–Br at the interface is increased, compared to Si–Cl for grafting of the smaller ethynyl group by the MgCl compound.

(1) Initial reactions by formation of Si dangling bonds on the surface.

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(2) Main reaction by bonding of an organic radical (anodically formed via reaction scheme 1a) with a Si dangling bond.

(a) $Si\cdot\cdot\cdot h^+ + R–C \equiv C–MgX \rightarrow Si\cdot\cdot\cdot C \equiv C – R + MgX^+$

(3) Side reactions with Grignard compound, which lead to halogen incorporation in the layer.
Halogenation of the organic radical formed via 1a.\(^9\)

(a) \( \text{R–C} + \text{C–MgX}_2^{-} + h^{+} \rightarrow \text{R} + \text{C–MgX} \)

\( \text{X} + \text{C} \rightarrow \text{X} + \text{C} \)

and reaction of the polarized \(-\text{C}–\text{C}–\text{X} \) bond with a Si surface dangling bond by splitting of the \( \text{C}–\text{C} \) bond and hydrogen capture from the solvent, for example,

(b) \( \equiv \text{Si} + \text{R} + \text{C} \equiv \text{C} \rightarrow \equiv \text{Si} + \text{C} \equiv \text{C} \)

\( \equiv \text{H} + \text{C} \equiv \text{C} \equiv \text{H} \)

or via an addition/rearrangement reaction, as outlined by Fellah et al.\(^{10} \)

\( \equiv \text{Si} + \text{C} \equiv \text{C} \rightarrow \equiv \text{Si} + \text{C} \equiv \text{C} \)

\( \equiv \text{H} + \text{C} \equiv \text{C} \equiv \text{H} \)

A reaction of the halogen radicals formed via reaction scheme 3a or direct reaction of a Si dangling bond with the Grignard compound by abstracting the halogen atom is also possible:

(d) \( \equiv \text{Si} + \text{C} \equiv \text{C} \rightarrow \equiv \text{Si} + \text{X} \rightarrow \equiv \text{Si} + \text{X} \)

\( \equiv \text{Si} + \text{MgX} \equiv \text{C} \equiv \text{C} \rightarrow \equiv \text{Si} + \text{C} \equiv \text{C} + \text{MgX} \)

A similar trend can be seen in Figure 3, where the layer thickness decreases as the size of the end group increases. The formation of these thin polymeric layers is supposed to arise via oxidation of the \( \text{C}–\text{C} \) bonds, as well as from reactions via halogen atoms with the Si surface and not only via oxidation of the \( \text{Br(Cl)Mg–C} \) bond from the Grignard compounds.

5. Conclusions

The anodic grafting of ethynyl derivatives onto Si(111) surfaces in a one-step electrochemical Grignard route has been characterized by infrared spectroscopic ellipsometry (IRSE), scanning electron microscopy (SEM), and synchrotron X-ray photoelectron spectroscopy (SXPS) studies. The SXPS data of the C 1s core level spectra give evidence of the anchoring of these ethynyl derivatives onto Si(111) surfaces by the presence of a peak at \( \sim 283.7 \) eV, which is attributed to Si–C bonds. In addition, IRSE spectra, combined with SEM micrographs, clearly reveal the formation of polymeric layers on Si surfaces using these ethynyl derivatives for the electrochemical grafting process. The thicknesses of the polymeric layers are dependent on the charge flow and the end standing group of the Grignard reagent, but they are also dependent on the halogen atom present in the Grignard compound. Interestingly, the results obtained here show that the grafting of \( \text{H}–\text{C}–\text{C}– \) onto the Si(111) surface from the \( \text{H}–\text{C}–\text{C}–\text{MgCl} \) electrolyte leads to the formation of a 20 nm thick polymeric layer, whereas polymeric layers made from \( \text{H}–\text{C}–\text{C}–\text{MgBr} \), \( \text{CH}–\text{C}–\text{C}–\text{MgBr} \), and \( \text{C}–\text{C}–\text{MgBr} \) have a thickness of \( \sim 10 \) nm after passing the same amount of charge flow (450 mC/cm\(^2\)). In addition, it was also found that the larger the end group of the ethynyl derivatives, the thinner the thickness of the polymeric layer obtained for such organically modified Si surfaces. This particularity, and the possibility of varying the thickness and the composition of such polymer layers, could be of interest for potential applications, such as the click chemistry method or polymers films in biosensors.

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(90) Evans, W. V.; Pearson, R. J. Am. Chem. Soc. 1942, 64, 2865–2871.