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Wavelength critical role during UV-activated grafting of 1-alkene on silicon and silicon nitride Si_xN_4 surfaces

M. Brunet,^{a,b} D. Aureau,^c F. Guillemot,^b A. Etcheberry,^c F. Ozanam^a and A. C. Gouget-Laemmel^{*a}

The wavelength used during photochemical grafting of alkene on silicon related surfaces influences the molecular surface coverage. Ultraviolet light leads to apparently highly dense layers on UV absorbing materials due to side reaction between alkene resulting in strongly physisorbed dimers whereas higher wavelengths lead to dense and well-controlled layers.

The covalent grafting of molecular and polymer layers onto inorganic materials is highly in demand in many fields such as glass industry, molecular electronics or biotechnology, notably to improve their wettability, their resistance towards corrosion and biofouling or to promote selective adhesion.¹⁻⁴ Though in some cases the details of the molecular arrangement does not sensitively affect the functional role of the layer, in many cases the packing density, orientation or grafting configuration of the molecules are of paramount importance. The rational design of functional molecular layers therefore demands a precise control and evaluation of these characteristics.

Various methods of surface functionalization were developed during the last two decades.^{5, 6,7} Here we focus on the photo-activated reactions of 1-alkene at solid surfaces, of widespread use since they lead to the fast and easy formation of functionalized monolayers through stable covalent bonds.⁸⁻¹⁰ These reactions were successfully applied to various inorganic substrates such as silicon, silicon nitride, germanium, carbon and even TiO_2 , ITO or stainless steel. The reactions can be promoted by UV light and even by visible light depending on the substrates. In the case of hydrogenated silicon surfaces (without their native oxide layer), the irradiation is commonly performed at 312 nm for which most 1-alkenes are essentially transparent.¹¹ In this way, densely-packed and versatile monolayers are grafted via Si-C bonds and they are not subject to hydrolysis or uncontrolled multilayer formation.^{7, 12} In the case of silicon nitride, silicon carbide or carbon (like carbon nanofibers or diamond) substrates, the hydrosilylation reaction is performed at lower wavelengths because these higher energies seemed to form monolayers with higher quantities of organic species on surfaces (generally controlled by contact angle measurements).¹³⁻¹⁵ Even if the critical role of the wavelength on the final coverage of the grafted layer is accepted, there are few

in-depth studies on the influence of the wavelength on the molecular

composition of the grafted surfaces. A quantitative information is still lacking.

We therefore focus on the UV-induced grafting of 1-alkene on a family of dielectric silicon based materials: the oxide-free silicon nitride Si_xN_4 thin films. We chose Si_xN_4 for the possibility of investigating a generic family of materials with similar chemical nature but varying optical absorption upon varying the material stoichiometry x . By using quantitative tools originally developed for crystalline silicon substrates,^{17, 18} the molecular composition of the grafted layers can be assessed as a function of the activation wavelength and as a function of Si/N ratio. The silicon nitride coatings can be conveniently deposited by magnetron sputtering. For the quasi-stoichiometric Si_3N_4 , the apparent Si/N ratio found by XPS is close to 0.85 ($x \sim 3.4$).¹⁹ By tuning the gas-ratio during the deposition, the Si_xN_4 coatings can be silicon enriched with Si/N ratios comprised between 1.25 ($x = 5$) and 2 ($x = 8$) as determined by XPS. The native oxynitride layer of Si_xN_4 can be removed from hydrogen fluoride HF chemical etching to obtain essentially unreactive Si-F bonds with very few Si-NH_x and Si-OH bonds as recently demonstrated by Chabal *et al* and Ozanam *et al*.^{19, 20} For quasi-stoichiometric Si_xN_4 thin films, no Si-H bonds are formed at the surface whereas for silicon-rich Si_xN_4 ($x = 5, 8$), Si-H bonds can be generated. Starting from these various etched Si_xN_4 surfaces, we studied their irradiation in the presence of 1-decene as model molecule at two wavelengths 254 and 312 nm for 24 h (cf S1 in the Supporting Information SI). Same irradiation procedures were also performed on the well-known hydrogenated crystalline (111)Si surfaces. We use IR spectroscopy in ATR (Attenuated Total Reflexion) geometry to quantitatively determine the molecular density of the organic chains grafted on an ATR silicon prism covered by a thin film of Si_xN_4 . Figure 1A represents the IR-ATR spectra in the 2700-3050 cm^{-1} range of an etched quasi-stoichiometric surface after the photochemical reaction under 312 or 254 nm irradiation. Wider spectral range is shown in Figure S2. The presence of the stretching vibrations of the CH_2 and CH_3 modes between 2855 and 2960 cm^{-1} confirms the grafting of alkyl chains on the quasi-stoichiometric surface (Fig. 1A).

The position of the asymmetric vibration of CH₂ located at 2926 cm⁻¹ for both wavelengths indicates that these coatings are not well-organized.* The activation at higher energy gives higher intensities of the IR bands suggesting a higher grafting density. As also observed by Zuilhof *et al.*,²¹ denser layers are formed after an optimized irradiation time of 24 h at 254 nm. However, the contact angle value of the coating obtained at 254 nm is quite low around 70° (vs 58° at 312 nm) suggesting a low packing density of decyl chains. A quantitative analysis of the peak related to ν_sCH₂ mode at 2865 cm⁻¹ in s- and p-polarization yields a molecular density of grafted chains of 1.4 nm² at 254 nm and 1 chain per nm² at 312 nm (cf Figure 1B). Such a low surface coverage can be explained by considering the chemical composition of the initial Si_{3.4}N₄ surface which is devoid of hydrogenated bonds with very few Si-NH_x and Si-OH bonds limiting the amount of surface site where an addition of the C=C bonds of the reactant can take place.

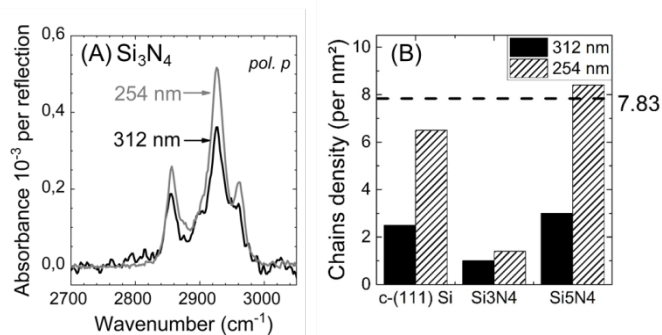


Figure 1. FTIR-ATR spectra in p-polarization in the 2700-3050 cm⁻¹ range of an etched quasi-stoichiometric surface after the photochemical irradiation of 1-decene at 312 nm (black) and 254 nm (grey) for 24 h, the reference spectra being the freshly etched surfaces (A). Calculated density of grafted decyl chains at 312 and 254 nm on c-(111)Si, Si₃N₄, Si₅N₄ surfaces. The dotted line represents the density of close packed Si atoms in a dense Si plane (B).

In order to increase the number of anchoring sites, surface Si-H species were generated by enriching the material in silicon up to x = 5. The intensities of the CH₂ vibrations for both wavelengths are much higher than those obtained on quasi-stoichiometric surfaces (up to 2-5 times), suggesting denser layers on silicon-rich Si₅N₄ layers than on Si₃N₄ layers (Figure S3C). A negative band at 2122 cm⁻¹ is also observed whereas it was absent on IR spectra of Si₃N₄ surfaces (cf Figure S3B vs S2B) confirming that Si-H bonds disappear during the grafting. The activation at 254 nm seems to be more efficient than that at 312 nm in term of the quantity of carbon-related species but the position of the ν_{as}CH₂ bands is significantly lower at 312 nm (2922 cm⁻¹) than at 254 nm (2925 cm⁻¹). After irradiation at 254 nm, the surface is covered by a larger amount of molecules but more disorderly arranged. The contact angle value increases

up to 88° at 312 nm and up to 103° at 254 nm. A further analysis of the IR bands shows that a molecular density of 3 chains.nm⁻² is obtained at 312 nm and up to 8.4 chains.nm⁻² at 254 nm (cf Figure 1B). Similarly, the photochemical hydrosilylation of 1-decene on HF-etched (111)Si surface at 312 nm for an optimized time of 3 h leads to a surface coverage of about 2.5 nm⁻²,²² and when the activation is performed at 254 nm (for 24 h) an approximate density of 6.5 nm⁻² is found. The maximum achievable packing density of alkyl chains at a surface, derived from their steric volume in alkane crystals, is 5.4 nm⁻².²³ At a flat silicon surface, where alkyl chain should be in registry with surface Si atoms for covalent bonding, this density reduces to ~3.9 nm⁻².²⁴ Therefore, irradiation at 254 nm of Si or Si-rich Si_xN₄ leads to the presence of molecules at the surface in excess of one monolayer. Such a high density is not observed for a quasi-stoichiometric silicon nitride layer.

To gain information on the chemical nature of these extra species, TOF-SIMS measurements were performed on the enriched Si₅N₄ and c-Si(111) after irradiation with 1-decene at 254 nm. The main fragments are attributed to residues of the decyl chains (from C₆H₉⁺ to C₁₀H₁₇⁺) for both surfaces (C and E). However, heavier fragments attributed to C₂₀H₃₇⁺ (D and F) are also detected suggesting the formation of dimers during the functionalization. On the other hand, only short fragments are observed on the well-known decyl-terminated (111)Si surface (obtained at 312 nm for 3h) with no formation of fragments higher than 10 carbons (Fig. 2A-B). The irradiation at higher energy promotes the formation of layers consisting of C₁₀ and C₂₀ molecules.

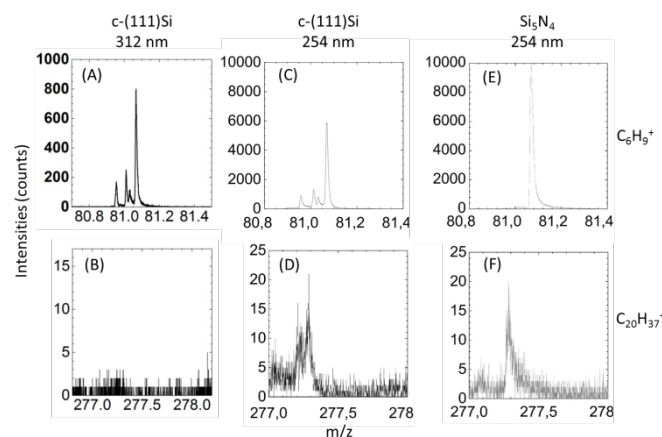


Figure 2. TOF-SIMS spectra in positive mode of c-(111)Si (A-B-C-D) and Si₅N₄ (E-F) surfaces functionalized with 1-decene at 312 nm (A-B) and at 254 nm (24h for Si₅N₄ and 3h for c-(111)Si).

To get insight into the organization of these layers, AFM experiments were performed after various post-rinsing procedures, including mechanochemical conditions (THF rinse with cotton swab, cf SI). Figure 3 displays the AFM images obtained for the quasi-stoichiometric Si₃N₄, Si₅N₄ and c-(111)Si surfaces after their irradiation at 254 nm followed by mechanochemical treatment.

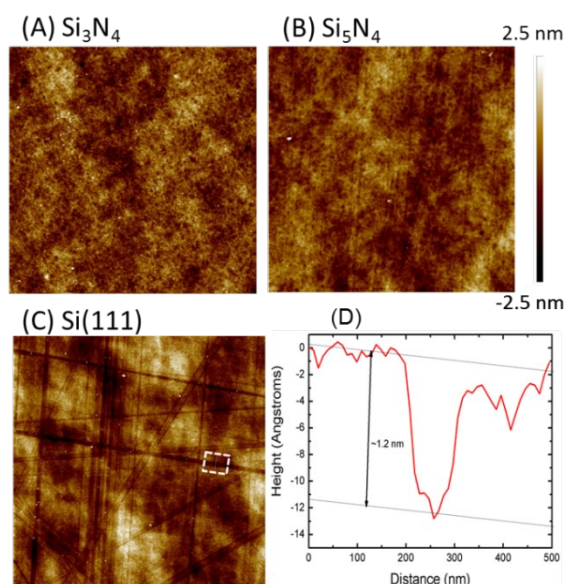


Figure 3. AFM images ($5 \times 5 \mu\text{m}^2$) of Si_3N_4 (A), Si_5N_4 (B), and c-(111)Si (C) surfaces modified with 1-decene at 254 nm after mechanochemical treatment. AFM depth profile (D) of a line taken on image (C) with an apparent width of $0.1 \mu\text{m}$ and depth of 1.2 nm.

All silicon nitride surfaces present a similar roughness after chemical etching (cf Fig. S4A-B) and their functionalization with standard chemical rinses (cf Fig. S4C-D). After mechanochemical rinses, straight scratches appear on enriched Si_5N_4 (Fig. 2B) and crystalline (111)Si (Fig. 2C) surfaces. These scratches are more pronounced on the richer silicon Si_8N_4 thin film for which a density of 7.4 nm^2 decyl chains is obtained (data shown in S5). The scratches do not appear after a mechanochemical treatment of quasi-stoichiometric Si_3N_4 surfaces or of etched Si_5N_4 surfaces before functionalization (Figure 2A and Figure S4C). It indicates that the scratches are located within the molecular layer and are not due to the substrate abrasion by the mechanochemical treatment. Moreover, when scratches are present, the mechanochemical treatment results in a lowering of the intensity of the alkyl chain signatures in the ATR-FTIR spectra. The treatment therefore appears to remove efficiently unreacted molecules evidencing the presence of physisorbed molecules. The AFM depth profile shown in Figure 2D suggests a removal of 1.2 nm which corresponds to a layer of decyl molecules. For Si_8N_4 substrates, the AFM depth profiles range between 1 and 2.4 nm, confirming the presence of multilayers at the surface.

Such results confirm that the irradiation at 254 nm for Si and Si-enriched substrates promotes the inter-reaction between decene molecules leading to the formation of unorganized layers with grafted and physisorbed C_{10} and C_{20} chains. Interestingly, such multilayers are not formed at 312 nm and at 254 nm for the quasi-stoichiometric materials.

Although 1-decene is strongly absorbing at 254 nm and not at 312 nm, no degradation of 1-decene is detected by ^1H NMR spectroscopy in CDCl_3 after irradiation at 254 nm for 24h: no change of the peak positions and integrals is observed as compared to the 1-decene spectrum recorded before irradiation, suggesting that no fragmentation nor polymerization takes place. Therefore the difference between the final surface coverage after photoactivation at higher energy plausibly arises from the distinct optical properties of the substrates. The complex optical indexes of both silicon nitride layers were therefore measured by ellipsometry. Figure 4 shows that the quasi-stoichiometric material is slightly absorbing at 312 nm and four times more at 254 nm, with an imaginary part k close to 0.05. On the opposite, silicon-rich Si_5N_4 is strongly absorbing at 312 nm in comparison with Si_3N_4 but even more (22 times more) at 254 nm with $k \sim 0.86$.

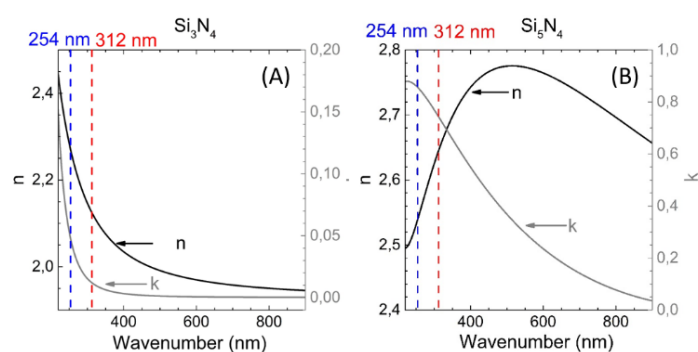


Figure 4. Optical indexes n and k of Si_3N_4 and Si_5N_4 layers deduced from ellipsometry measurements.

On Si_3N_4 , the activation at 254 nm probably creates a surface radical allowing for the attack of the alkene unsaturated bond and the grafting of the corresponding alkyl chain at the surface, as suggested by Chidsey *et al.* for crystalline silicon.^{13, 25} On Si_5N_4 , the higher UV absorption generates surface radicals in larger amounts and/or at higher energies, which initiates side reactions between the 1-decene molecules. This way, the stronger absorption at 254 nm as compared to 312 nm, especially effective on the Si-rich layers, may explain the presence of unwanted molecule, either chemisorbed or physisorbed at the surface.

To conclude, on strongly UV absorbing materials, the activation at 254 nm leads to the formation of apparent highly dense layers due to the presence of dimerized molecules, grafted or physisorbed at the surface. In particular, this unwanted situation takes place on Si substrates. The activation at 254 nm is efficient for non-absorbing materials as quasi-stoichiometric silicon nitride whereas higher wavelengths are necessary on UV absorbing materials to ensure the formation of dense monolayers.

Conflicts of interest

There are no conflicts to declare.

Notes and references

* As a reference, such a band is located at 2917 cm^{-1} for crystalline polyethylene and at 2926 cm^{-1} for liquid alkane.

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