

Adsorption of silanes bearing nitrogenated Lewis bases on SiO₂/Si (100) model surfaces

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Abstract

The present paper describes the one-pot procedure for the formation of self-assembled thin films of two silanes on the model oxidized silicon wafer, SiO₂/Si. SiO₂/Si is a model system for other surfaces, such as glass, quartz, aerosol, and silica gel. MALDI-TOF MS with and without a matrix, XPS, and AFM have confirmed the formation of self-assembled thin films of both 3-imidazolylpropyltrimethoxysilane (3-IPTS) and 4-(*N*-propyltriethoxysilane-imino)pyridine (4-PTSIP) on the SiO₂/Si surface after 30 min. Longer adsorption times lead to the deposition of nonreacted 3-IPTS precursors and the formation of agglomerates on the 3-IPTS monolayer. The formation of 4-PTSIP self-assembled layers on SiO₂/Si is also demonstrated. The present results for the flat SiO₂/Si surface can lead to a better understanding of the formation of a stationary phase for affinity chromatography as well as transition-metal-supported catalysts on silica and their relationship with surface roughness and ordering. The 3-IPTS and 4-PTSIP modified SiO₂/Si wafers can also be envisaged as possible built-on-silicon thin-layer chromatography (TLC) extraction devices for metal determination or *N*-heterocycle analytes, such as histidine and histamine, with “on-spot” MALDI-TOF MS detection.

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1. Introduction

In the earlier 1980s the pioneering work of Sagiv introduced the formation of self-assembled monolayers (SAMs) from siloxane compounds [1], opening a whole new area for the application of these compounds. A wide variety of

organosilanes have been used in the chemical modification of the surfaces [2,3]. For this purpose, the silanes usually consist of three surface reactive groups, with labile alkoxide or chlorine, at one extremity. The surface grafting occurs when one or more groups in the silane chain can be hydrolyzed and subsequently bound to the surface. The other extremity of the silanes typically bears an organofunctional group able to bind to a variety of ligand units, acting as Lewis bases. This modification strategy can be applied to prepare hydrophobic surfaces [1,4] and stationary phases for reverse-phase chromatography [5,6] and used to design biocompatible surfaces [7,8] and sensors [9,10].

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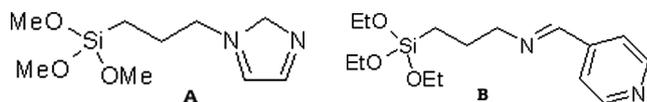


Fig. 1. Structure of 3-IPTS (A) and 4-PTSIP (B).

The present paper describes the organomodification of wet-chemically grown SiO_2 layers on *n*-type Si (100), named SiO_2/Si , using 3-imidazolylpropyltrimethoxysilane (3-IPTS) and 4-(*N*-propyltriethoxysilane-imino)pyridine (4-PTSIP) silanes (see Fig. 1), and the characterization of the structure of 3-IPTS and 4-PTSIP silane layers by both X-ray photoelectron spectroscopy (XPS) and matrix-assisted laser desorption/ionization mass spectroscopy (MALDI-TOF MS). To our knowledge, for the first time MALDI-TOF MS has been used to characterize silane layers, providing a clear picture of the actual molecular structure. The morphology of these silane layers was also investigated by atomic force microscopy (AFM). Gushikem and co-workers [11–13] previously reported the adsorption of the 3-IPTS on silica gel using the one-pot setup to graft the 3-IPTS in order to use it in metal chloride uptake from ethanolic solutions. We have adapted their methodology as well as developing a two-step technique in our laboratory [14] to produce the 3-IPTS modified silicon wafer surface.

2. Materials and methods

2.1. Materials

Plates of 1 cm^2 were cut from Si (100) wafers (Goodfellow Cambridge Ltd.). The chemicals used in this study were imidazole, 3-chloropropyltrimethoxysilane (3-CIPTS), 3-aminopropyltriethoxysilane (3-APTS), 4-pyridylcarboxyaldehyde (4-PCA), and tetrabutylammonium fluoride supported on silica gel ($\text{Bu}_4\text{NF}/\text{SiO}_2$) from Aldrich, HF 40% from Synth, H_2O_2 30%, toluene, acetonitrile, H_2SO_4 98%, dichloromethane (CH_2Cl_2), and NH_4OH 24% from Mallinkrodt, and deionized water ($18.2 \text{ M}\Omega \text{ cm}$). All reagents were used as received, except toluene, which was freshly distilled.

2.2. Silicon wafer preparation

The silicon surface was previously treated according to the procedure reported [15] in order to obtain smooth and clean surfaces of SiO_2/Si .

2.3. Preparation of organosilane film

2.3.1. 3-IPTS

To prepare the 3-IPTS/ SiO_2/Si , the one-pot adsorption procedure used was adapted from a previously reported method [11]. Although the two-step procedure reported by Andresa et al. [14] has shown higher surface yields, our attention has been devoted to the one-pot method, as it is an

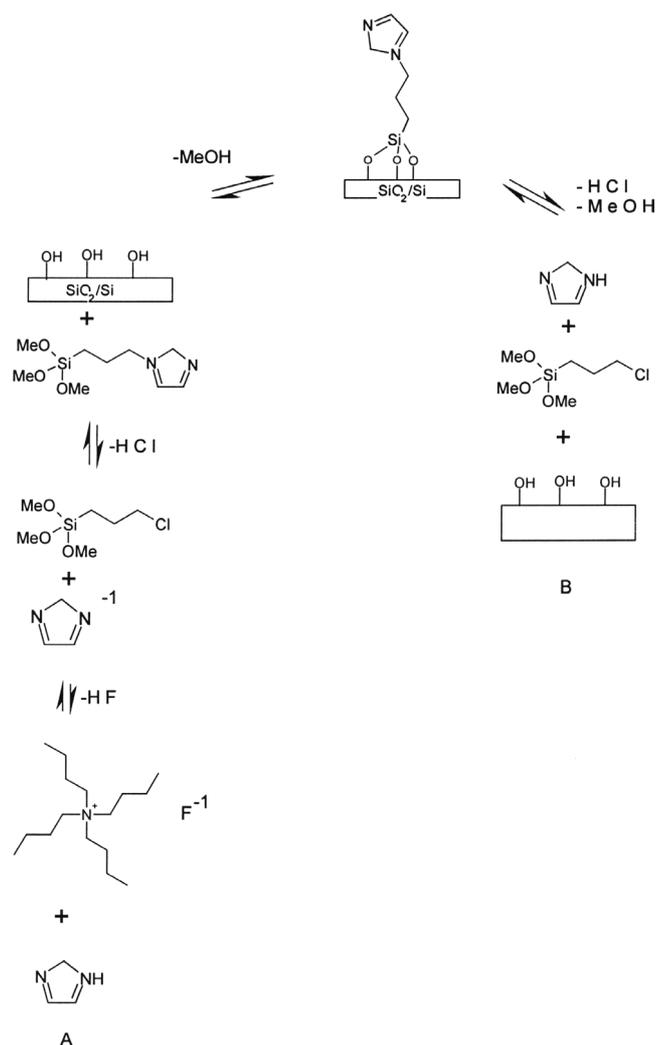


Fig. 2. Schematic representation of two-step (A) and one-pot (B) procedures for the synthesis of 3-IPTS/ SiO_2/Si .

easier and more reliable procedure. Fig. 2 shows the one-pot and two-step procedures schematically.

XPS was employed in order to obtain the optimum reaction/adsorption time for good surface coverage of 3-IPTS. The N/Si atomic ratio was plotted as a function of time for the 3-IPTS solutions. The time scale observed was in the range of 0 to 150 min.

2.3.2. 4-PTSIP

To synthesize the 4-PTSIP silane in a typical procedure, 2.5 ml of 3-APTS (10.7 mol) and 1.0 ml of 4-PCA (10.5 mol) were mixed in acetonitrile for 3 h under reflux at 80°C . A two-step work-up procedure was used, as previously reported [14], and the product was characterized by GC-MS (EI): m/z 310 ($\text{M}^+\bullet$).

After the adsorption of the silanes, the layers were ultrasonically washed for 30 min with toluene and acetonitrile for 3-IPTS and 4-PTSIP, respectively, for 30 min to remove the physically adsorbed silane overlayer and dried under a dry nitrogen stream at room temperature.

2.4. X-ray photoelectron spectroscopy

The XPS measurements were performed using a Kratos XSAM HS spectrometer with nonmonochromatic AlK α radiation (1486.6 eV, power 140 W). The base pressure in the chamber was in the range of 10⁻⁹ Torr. The spectra were charge-corrected and the chemical compositions of the films were verified as previously described [15,16].

The N/Si atomic ratio was obtained by measuring the total area under all the fitted peaks components of the N1s and Si2p high-resolution spectra. The accuracy for the atomic ratio values is $\pm 10\%$, i.e., up to 0.03 in N/Si atomic ratio values, and ± 0.2 eV for the binding energy.

All XPS peaks, in insulating samples were fitted according to Leclercq and Pireaux's method, using Gaussian–Lorentzian peaks [17].

2.5. Matrix-assisted laser desorption/ionization mass spectroscopy

The mass spectra were obtained by a Micromass MALDI-TOF Instrument (UK) in the positive ion mode using the reflection mode and a QSTAR Pulsar quadrupole time-of-flight (QqTOF) instrument equipped with an orthogonal MALDI source. The main settings were pulse voltage, 2450 V; delay extraction, 100 ns; accelerating voltage, 15 kV; and reflectron voltage, 2 kV [18].

2.6. Atomic force microscopy

The AFM experiments were carried out with an Explorer model from Topometrix Inc. To minimize the surface deformation and material removal, the experiments were performed in intermittent contact mode (tapping mode), using a silicon cantilever with a spring constant of ~ 70 N m⁻¹ at a scan rate of 1 Hz. All measurements were taken under air at room temperature, employing the root-mean-square roughness (R_{rms}) to compare the surfaces quantitatively and evaluate the morphological changes on the plates [19]. As the roughness value depends on the observation scale, all experiments were carried out on a scale of 1 μm .

3. Results and discussion

3.1. 3-IPTS

To understand the grafting mechanism of the 3-IPTS on the SiO₂/Si surface and obtain the optimum reaction/adsorption time to achieve good surface coverage, the N/Si atomic ratios were measured by XPS as a function of reaction/adsorption time of the imidazole/3-CIPTS solution.

However, Fig. 3 reveals unexpected behavior for the 3-CIPTS adsorption and 3-IPTS formation. Both processes occur only after 30 min of plate immersion; before this period of time neither the Cl2p nor the N1s peak could

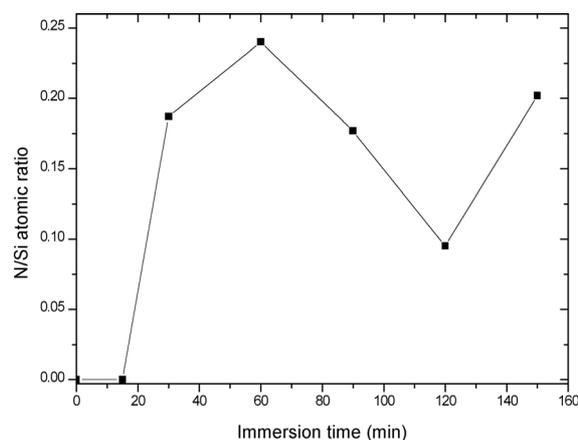


Fig. 3. N/Si atomic ratio obtained by XPS vs reaction/adsorption time on SiO₂/Si surface.

be detected. This shorter reaction time for the 3-IPTS formation by the one-pot procedure is a remarkable indication of the role of the surface in the reaction when compared with the reaction time for the off-surface synthesis (30 h). When the silane molecule is not attached to the surface, the terminal alkoxy groups may be freely orientated and hinder the electrophilic halogenated carbon atom sterically. Thus, this steric hindrance would result in lower kinetic rates and longer reaction times. However, once on the surface, the 3-CIPTS is attached to the surface by siloxane Si–O–Si bonds. It turns out that there is no alkoxy group to exert steric hindrance, resulting in faster reaction times.

The 3-CIPTS can also be adsorbed with the Cl atom oriented toward the solution–surface interface. Indeed, Kornherr et al. [20] studied by molecular dynamics (MD) calculations the adsorption of octyltrihydroxysilane, 3-aminopropyltrihydroxysilane, and 3-mercaptopropyltrihydroxysilane (3-MPTS) single molecules on ZnO surface from isopropanol solution. They showed that the more polar silane adsorbs on the surface with the backbone parallel to the oxide surface, therefore maximizing the interaction between the two polar groups, –OH and –NH₂, and the surface acid sites, –OH. For instance, the other two silane molecules showed parallel and orthogonal adsorption, with higher stability for the orthogonal adsorption mode. As the silane molecules used in this procedure are 3-CIPTS with dipole moment similar to 3-MPTS, 0.92 D and 0.87 D, respectively, as estimated from molecular mechanics calculations (MM⁺), a similar orientation can be expected for grafted 3-CIPTS on SiO₂. This “fixed” orientation of the molecule exposes the chlorine atom to the attack of imidazole molecules, influencing the reaction rate positively. Therefore, surface “fixed” orientation and the elimination of alkoxy groups are responsible for these shorter reaction times.

Fig. 4 illustrates the explanation for the kinetic differences observed between the one-pot and two-step procedures.

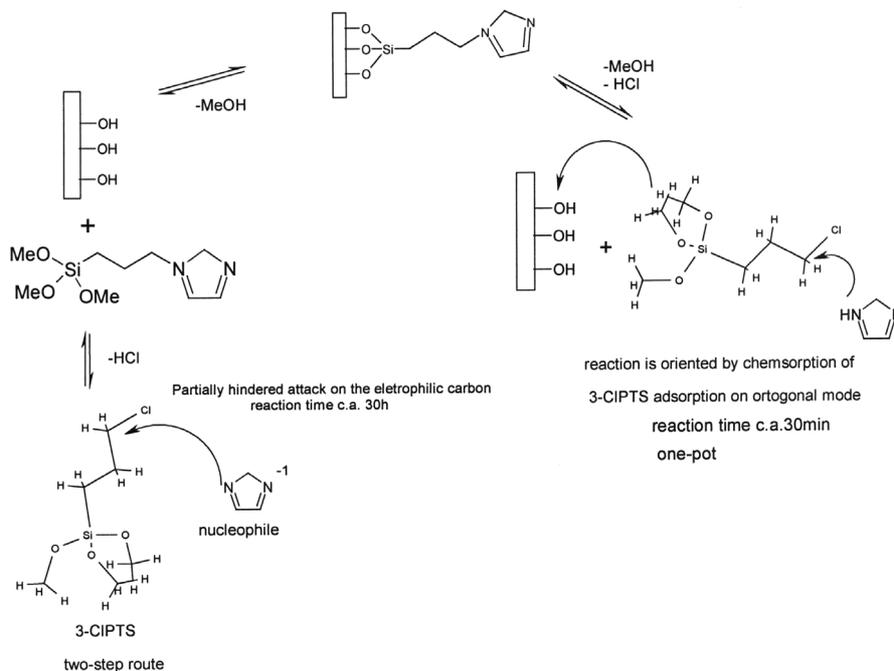


Fig. 4. Schematic procedures for one-pot and two-step procedures, emphasizing different reaction times and kinetic mechanisms.

The N/Si atomic ratio also shows a step decrease in the silane concentration after 80 min, and this decrease in concentration can be explained by assuming that the nonreacted 3-CIPTS is adsorbed on top of the 3-IPTS layer. At this time a large number of imidazole and 3-CIPTS molecules should not react yet. This adlayer of 3-CIPTS would result in an artificial decrease in the N/Si ratio due to increased layer thickness [21]. The increase in the N/Si ratio after 120 min is still shorter than the reaction time for 3-CIPTS and imidazole molecules in solution; therefore it is possible to infer that this increase is due to the formation of 3-IPTS at the adlayer of 3-CIPTS. Compared to the chemically bonded 3-CIPTS, this longer reaction time for the adlayer should be due to a higher degree of freedom of the molecules in the adlayer.

The XPS N1s spectra for the grafted 3-IPTS showed an asymmetric and wide peak, Fig. 5, which was fitted with two components at 399.7 and 401.9 eV, assigned to nonprotonated and protonated imidazole groups, respectively. The protonation could result either from the interaction between the bent 3-IPTS and the surface silanol groups with a consecutive proton transfer [14,15,22], or from the reaction with the hydrogen chloride obtained as a by-product from the reaction of 3-CIPTS and imidazole, or by proton transfer from adlayer water.

The root-mean-square roughness (R_{rms}), measured by AFM, of the 3-IPTS samples obtained by the one-pot or two-step method, for an adsorption temperature of 298 K, is almost the same, i.e., 0.47 and 0.70 nm, respectively. For one-pot adsorption at 323 K the 3-IPTS layer shows rougher surfaces, $R_{\text{rms}} = 1.16$ nm, probably due to thermally induced disorder in the adsorption of the silanes. Based on the Kornherr model [20], one can assume that a higher tem-

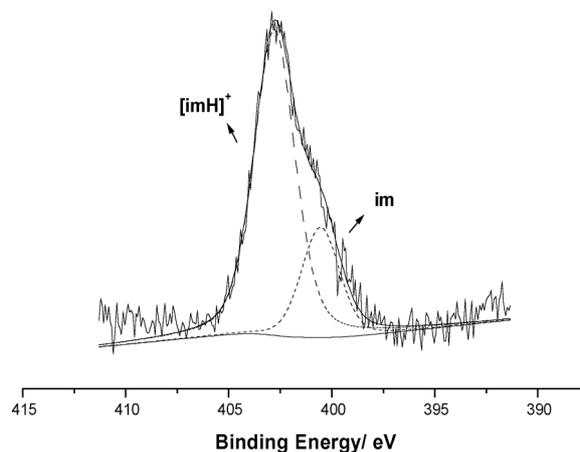


Fig. 5. XPS N1s spectrum for SiO₂/Si surface after the adsorption of 3-IPTS, where [im] stands for 3-IPTS and [imH]⁺ represents the protonated 3-IPTS.

perature induces a more spread distribution of orientations of adsorbed molecules. If the orientation of the molecules on the surface depends on energetic factors, the orthogonal and more stable adsorption orientation is favored at lower temperatures. The increase in the temperature can induce the adsorption in the less stable and parallel orientation. This increase in the population of parallel adsorption would result in a slighter rougher surface, as observed. Also, comparing the AFM images of the SiO₂/Si substrate (Fig. 6E) with the 3-IPTS/SiO₂/Si, 15 min of adsorption time (Fig. 6C), one can see that the surface morphology is not altered by the 3-IPTS layer. Therefore it is possible to conclude that the 3-IPTS layer grows following the surface morphology. Higher adsorption times of 3-IPTS result in rougher sur-

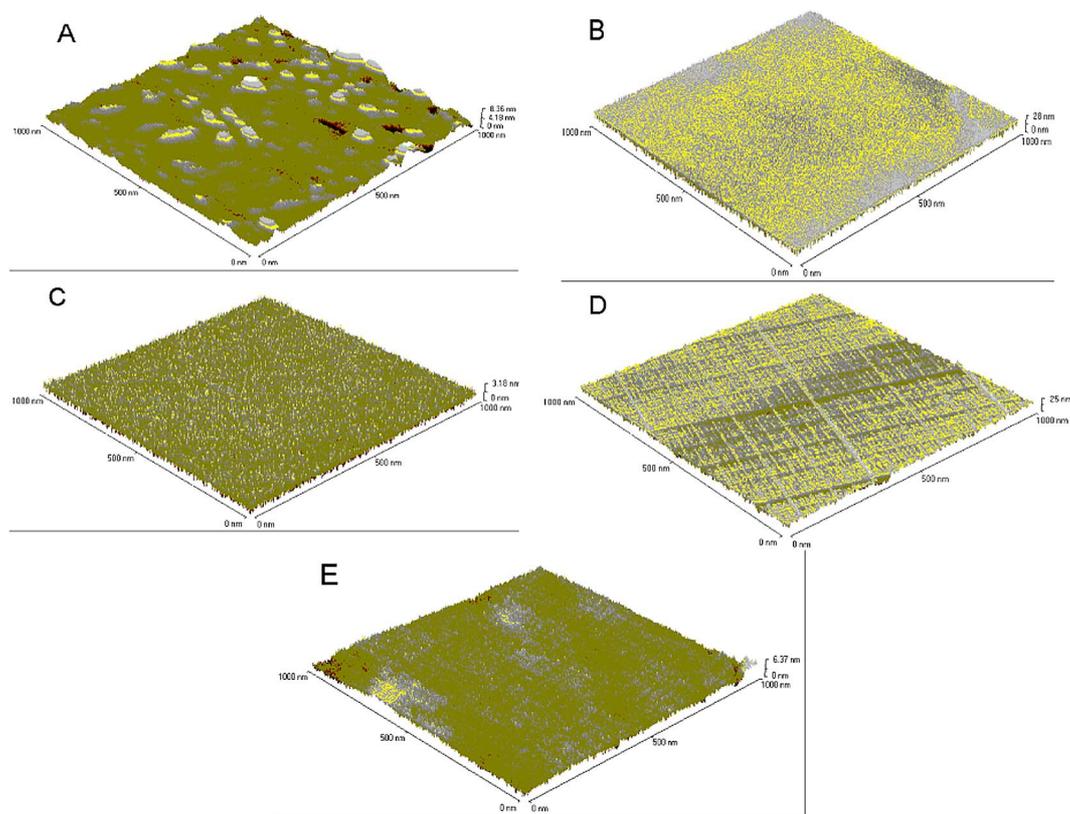


Fig. 6. AFM images of two different procedures of 3-IPTS adsorption: one-pot with 150 min of adsorption time (A), two-step (B), one-pot with 15 min of adsorption time (C), 4-PTSIP/SiO₂/Si two-step with 15 min of adsorption time (D), and SiO₂/Si (E) (1 μm scale).

faces, Fig. 6A, with agglomerates of 10–30 nm distributed randomly on the surface on top of the flat layer. These higher adsorption times probably lead to the adsorption of 3-CIPTS and/or imidazole, as described before on the 3-IPTS layer in a disordered way. This second layer of silanes has no contact with the SiO₂/Si surface, resulting in an unstable layer that could hydrolyze and polymerize along time, resulting in the globular deposits observed.

3.2. 4-PTSIP

The most important feature of the long-scan XP spectra for the immobilization of 4-PTSIP on the SiO₂/Si surface is the presence of the N1s peak, confirming the organomodification of the surface (not shown).

The N1s spectra (Fig. 7) show an asymmetric and wide peak, which is fitted with three components at 399.7, 400.7, and 402.1 eV, with 49, 15, and 35% of the total area of the peak, respectively. The components were assigned to the imine, pyridine, and protonated pyridine groups, respectively. These assignments were executed by comparing the experimental results with the reported N1s peaks of some molecules containing pyridine and imine groups, as showed in Table 1.

The AFM image of 4-PTSIP/SiO₂/Si surfaces (Fig. 6D) shows a pattern similar to 3-IPTS at 15 min with the same R_{rms} .

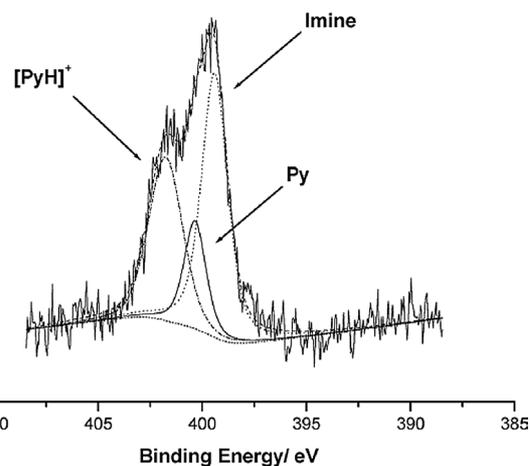


Fig. 7. XPS N1s spectrum for the SiO₂/Si surface after the adsorption of 4-PTSIP.

Table 1
N1s binding energy values relative to some compounds having pyridine and imine groups

Compound	N1s binding energies (eV)	Reference
2,2'-Bipyridine	399.4	[23]
Poly(2-vinylpyridine)	399.3	[24]
Poly(ethyleneimine)	399.1	[24]
Pyridine trifluoroborate	401.4	[25]

3.3. MALDI-TOF MS

The broad success of matrix-assisted laser desorption/ionization (MALDI) [26] has been related mainly to the ability of the matrix to incorporate and transfer the laser radiation energy to high-molecular-weight (MW) molecules such as polymers, sugars, and proteins [27,28]. In MALDI, the analyte is normally dissolved into a solid ultraviolet-absorbing organic matrix, which vaporizes upon laser radiation, carrying the analyte with it [29]. Owing to the chemical noise from matrix ions in the low- m/z range, MALDI is, however, not so widely applicable for low-MW compounds, unless, for instance, matrices that produce almost no noise, such as ionic liquids, are employed.

To accomplish the silicon plate analysis of immobilized low-MW organic compounds, it was necessary to test both the use of an ionic liquid matrix of α -cyano-hydroxycinnamate and tetraethylammonium (α -CHCA·Et₃N) and

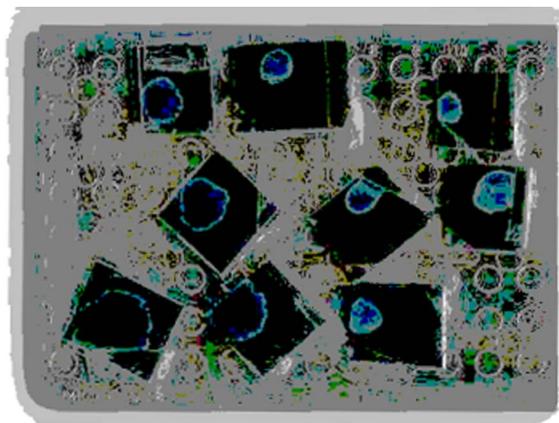


Fig. 8. Photography of a modified silicon wafer attached to the MALDI sample holder.

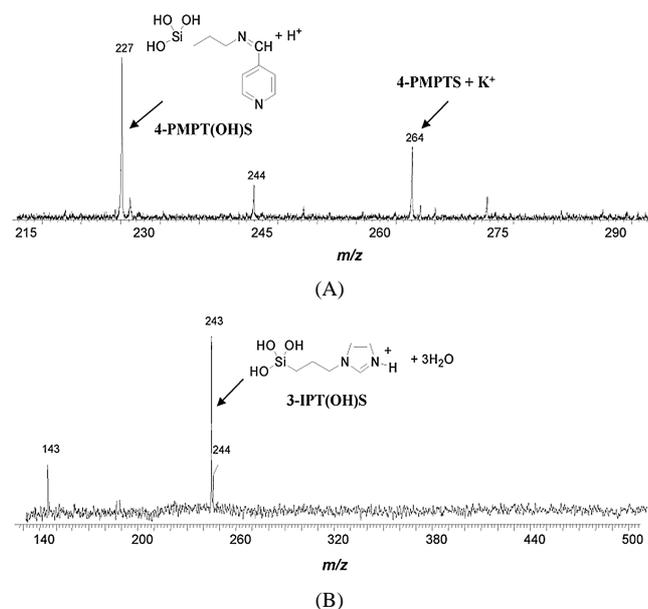


Fig. 9. MALDI-TOF mass spectra of 4-PTSIP/SiO₂/Si (A) and 3-IPTS/SiO₂/Si (B) wafers. The inset shows the proposed structures of the ions arising from laser ablation and ionization of surfaces.

the direct analysis of silicon plate, since the silicon surface could act as the matrix in the direct ionization on silicon (DIOS) technique [30–32]. Both approaches furnished good results, but cleaner spectra and more abundant peaks were obtained by direct laser radiation onto the surface. Fig. 8 shows the silicon plate resting on a MALDI sample plate, and Fig. 9 shows the mass spectra, displaying ions of great abundance arising from analyte ionization. The breaking of the Si–O–Si bonds that held the silanes to the surface produces ions of m/z 227 and 264 for the 4-PTSIP surface and m/z 243 for the 3-IPTS surface. The proposed structures of such ions are shown in Figs. 9A and 9B for 4-PTSIP and 3-IPTS, surfaces respectively. Note the formation of trihydrated ions with the 3-IPTS molecular ions in Fig. 9B.

The detection of hydrated species in the MALDI-TOF mass spectra for both 4-PTSIP and 3-IPTS surfaces is quite informative; therefore the protonated species observed in the N1s XP spectra of the samples could be explained by the presence of the water adlayer acting as a sink of protons for the silane layers. The hydrophilic nature of the silane layers was also confirmed by measuring the water static contact angles. The 3-IPTS/SiO₂/Si and the 4-PTSIP/SiO₂/Si wafers show $(53.4 \pm 2.7)^\circ$ and $(61.8 \pm 1.8)^\circ$, which are compatible with hydrophilic surfaces.

4. Summary

The molecular structure of silane layers of 3-IPTS and 4-PTSIP on silicon wafers was demonstrated by the application of direct MALDI-TOF mass spectrometry, with the silicon surface acting as the matrix in a DIOS process. N1s XP spectra show the presence of protonated and nonprotonated *N*-heterocycle nitrogen in the layers, and as evidenced by the MALDI-TOF mass spectra (formation of trihydrated ion), the water adlayer is the main ensemble responsible for this protonation. The AFM of the layers shows smooth surfaces following the morphology of the SiO₂/Si substrate. The AFM shows the formation of rougher and disordered layers, with 10–30 nm large globule formation on the surface for long adsorption times, i.e., 150 min. Due to the small size of the globules, we believe they are deposits of nonreacted silanes, since the reaction of 3-CIPTS with imidazole in solution takes more than 180 min to achieve very low yields. The results reported herein are useful for a better understanding of the adsorption mechanism of these silanes on other surfaces of similar materials, such as glass, quartz, and silica gel, since they have the same functional groups, but rougher surfaces.

Acknowledgments

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