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Experimental Study of Thermodynamic Surface Characteristics and pH Sensitivity of Silicon Dioxide and Silicon Nitride

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In this report, we have introduced a revision of the chemical treatment influence on the surface thermodynamic properties of silicon dioxide (SiO_2) and silicon nitride (Si_3N_4) solid thin layers. Some characterization techniques might be used to quantify the thermodynamic properties of solid surface and predict its ability in the adhesion phenomenon. In this work, we have used static and dynamic contact angle (CA) measurements to characterize both dioxide solid surfaces being treated by using the two procedures of cleaning and chemical activation. Qualitative and quantitative concepts of analysis, using the Van Oss approach, are based on the determination of dioxide surface hydrophilic and hydrophobic features and the thermodynamic parameters such as free energy, acid, base, and Lewis acid–base surface tension components. Electrochemical capacitance–potential measurements were carried out to study the reactivity of both silicon dioxide and silicon nitride surfaces for pH variation. Furthermore, the surface roughness of these insulators was examined by using the contact angle hysteresis (CAH) measurements and atomic force microscopy (AFM). It was concluded that CA technique can be used as a suitable and base method for the understanding of surface wettability and for the control of surface wetting behavior.

1. Introduction

Actually, silicon nitride and silicon dioxide thin films are attractive and extensively used in the development of physical and electrochemical devices. These insulator layers are used in the field of effect transistor (ISFET) devices and electrolyte–insulator–semiconductor (EIS) structures in order to electronically record signals from cells or to detect biomolecular interactions at the solid liquid–interface. In literature, many studies were carried out using silicon dioxide and silicon nitride as transducer materials to make sensors and biosensors.^{1–3} Besides, both insulator layers need chemical or physical treatments to get clean and highly active surfaces, aiming at enhancing the adhesion of chemical or biochemical species on the solid surface. Therefore, the surface properties of an affinity matrix are meant to explain its interactions with chemical or biological species. The hydrophobic or polar character can be determined by measuring contact angles of different test liquids on a dioxide surface.

However, in the natural state, material surfaces are not active or are less active. To make a surface more active, it is necessary to make the atoms hidden in volume accessible. In general, solid surface reactivity is measured by the nature and the number of active sites such as $-\text{OH}$, $-\text{COOH}$, $-\text{NH}_2$, $-\text{SH}$, and so on. The presence of these sites may influence the surface energy and can be desirable or undesirable in the adhesion and friction phenomenon at solid surfaces, depending on the practical situation. To quantify surface energy, the contact angle measurements are largely

used.^{4–8} The latter has been widely used for the characterization of the interfacial phenomenon, including wetting/dewetting of solid surfaces, capillary penetration into porous media, coating, and painting. At the base of contact angle research is Young's equation, which is valid for an ideal solid surface, namely, a perfectly smooth, chemically homogeneous, rigid, insoluble, and nonreactive surface. The contact angle is expressed by the well-known Young equation which was introduced in 1805.⁹

$$\gamma_{\text{LV}} \cos \theta + \gamma_{\text{SL}} - \gamma_{\text{SV}} = 0 \quad (1)$$

where θ is the Young contact angle and γ_{LV} , γ_{SV} , and γ_{SL} are the surface tensions of the liquid–vapor, solid–vapor, and solid–liquid interfaces, respectively.

Contact angles are often used simply as empirical parameters to quantify the wettability in technical solid–liquid systems. However, it is not only of great importance but also of practical interest to know how the contact angle depends on the chemical composition of both the solid and the liquid.

In the present work, we report the characterization of surfaces of silicon dioxide and of silicon nitride thin layers using contact angle (CA) measurements. Both insulator surfaces were treated in the same experimental conditions using optimized chemical cleaning and activation procedures. Therefore, we have used the sessile drop method to determine the thermodynamic surface properties such as surface energy, acid, base, and Lewis acid–base components. Indeed, contact angle measurements were carried out in saturated and unsaturated media with the test liquid vapor.

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Table 1. Surface Tension Components (mJ/m^2) of Liquids Used for Contact Angle Measurements^{11,12}

surface tension (mJ/m^2)	$\gamma_{\text{L}}^{\text{p}}$	$\gamma_{\text{L}}^{\text{d}}$	γ_{L}
distilled water (H_2O)	51.01	21.8	72.8
formamide (CH_3CO)	41.9	39	58
diiodomethane (CH_2I_2)	0	50.8	50.8

The surface free energy parameters were calculated from the contact angles of sessile drops of apolar and polar liquids on dioxide samples using the acid–base method of van Oss.¹⁰ Furthermore, the electrochemical C – V measurements were carried out to corroborate the wettability analysis and to explain the effect of cleaning and the activation procedures on both insulator surfaces for sensitivity to pH variation. In addition, hysteresis technique was used to examine the physical and chemical heterogeneity/homogeneity of such dioxide surfaces. Moreover, both silicon dioxide and silicon nitride surfaces were examined by atomic force microscopy to study the change in surface topography before and after the chemical treatment.

2. Experimental Section

2.1. Materials. Silicon dioxide and silicon nitride samples (1 cm^2) used in this work were purchased from LAAS-CNRS Toulouse. These substrates were obtained by deposition of a 100 nm silicon nitride layer by low pressure chemical vapor deposition (LPCVD) method or of a 50 nm layer of thermally grown silicon dioxide on a p-type silicon substrate, $400 \mu\text{m}$ thickness.

For contact angle measurements, three probe liquids with different polarities were chosen as the test liquids: distilled water, formamide (Sigma Chemical Co.), and diiodomethane (Sigma Chemical Co., St. Louis, MO). All of them were reagent grade, and their surface tension components are listed in Table 1.

2.2. Surface Treatment. Both insulator surfaces were treated in the same conditions using cleaning and chemical treatment procedures as follows:

Ultrasonic Degreasing (S1). The substrates were successively washed in an ultrasonic bath of trichloroethylene, acetone, and isopropyl alcohol for 15 min, rinsed with deionized water, and dried under nitrogen flow.

Sulfochromic Mixture (S2). After ultrasonic degreasing (S1), the substrates were dipped into a sulfochromic mixture ($\text{H}_2\text{SO}_4 + \text{K}_2\text{Cr}_2\text{O}_7$) for 15 min at room temperature, then rinsed with deionized water, and finally dried under nitrogen flow.

2.3. Characterization Techniques. Static contact angle measurements were performed on silicon nitride and silicon dioxide surfaces using the sessile drop method with an apparatus provided by GBX Scientific Instrument (Romans, France). An image of the drop deposited on the solid surface (Figure 1A) was registered by a video camera, and an image analysis system calculated the contact angle (θ) from the shape of the drop. All measurements were done in an unsaturated or a saturated atmosphere chamber with the liquid vapor (before measuring the contact angle, a small quantity of the probe liquid must be placed in the chamber to generate a saturated vapor area). The dynamic contact angle hysteresis measurements were carried out using the 3S tensiometer and the corresponding software (GBX, France). The theoretical background of the Wilhelmy experiment and the

calculation of the contact angles have been described in detail elsewhere.^{13,14} For these experiments, such a solid sample prepared on both sides was immersed and withdrawn into and out from a liquid while simultaneously measuring the force acting on the solid sample. The dynamic contact angle hysteresis was determined at 20°C for each dioxide and five wetting/dewetting cycles at a speed of $50 \mu\text{m/s}$. The advancing and receding contact angles could then be determined from the obtained force curve.

3. Results and Discussion

3.1. Effect of the Chemical Cleaning Procedure on Surface Properties and Contact Angle. In general, cleaning methods for solid surfaces such as glass, metal, dioxide, or nitride materials include wet chemical,¹⁵ UV-ozone,¹⁶ and plasma cleaning procedures.^{17,18} In this work, we have used chemical cleaning and activation procedures for the treatment of silicon nitride and silicon dioxide surfaces. First, the terms “hydrophobicity” and “hydrophilicity” should be defined in a quantitative manner. Both hydrophobicity and hydrophilicity are only determined in the context of solutes, macromolecules, particles, or other solids, when immersed in water. In fact, if the contact angle is higher than 60° , the surface of the solid is considered to be hydrophobic; when the contact angle is between 40° and 60° , the surface is more or less hydrophobic; and if the contact angle is lower than 40° , the surface is considered to be hydrophilic. Consequently, water was used as probe liquid to determine the hydrophobicity or the hydrophilicity features of silicon dioxide and silicon nitride surfaces. Figure 1A is a schematic illustration of a water drop spreading on a treated silicon nitride surface. It should be noticed that commercialized silicon nitride and silicon dioxide substrates are characterized by hydrophobic surfaces (Figure 1B). For this reason, cleaning or activation steps are essential for enhancing surface properties and for removing different kinds of contamination such as organic or metallic impurities and various dust particles, that are fixed to the surface by weak electrostatic forces or by van der Waals forces. Contact angle (CA) measurements were carried out in a saturated and an unsaturated atmosphere of test liquid. As a beginning step, we have studied the evolution of the hydrophilic character of silicon dioxide (SiO_2) and silicon nitride (Si_3N_4) surfaces using distilled water as test liquid. Figure 2A shows the CA variation of a water drop ($2 \mu\text{L}$) deposited on silicon dioxide and silicon nitride surfaces under unsaturated atmosphere with liquid vapor. We note that both untreated surfaces show high hydrophobic features predicted by high CA values. Moreover, when the surfaces are treated by ultrasonic cleaning using trichloroethylene, acetone, and isopropanol (TAI), we can observe a weak change in the contact angle values as shown in Figure 2A. This result demonstrates that organic solvents have a limited effect on these surface properties. Then, both surfaces are highly hydrophilic once treated successively with organic solvents, hot sulfochromic mixture (TAIS) for 15 min, and hydration under ultrapure water. In fact, the water wettability is lower for silicon nitride in comparison to silicon dioxide surface. It is possible to increase the hydrophilic character of the silicon nitride surface by hydration under ultrapure water for 24 h. This result justifies that the silicon nitride surface, when put in contact with water for a long time, acquires a behavior

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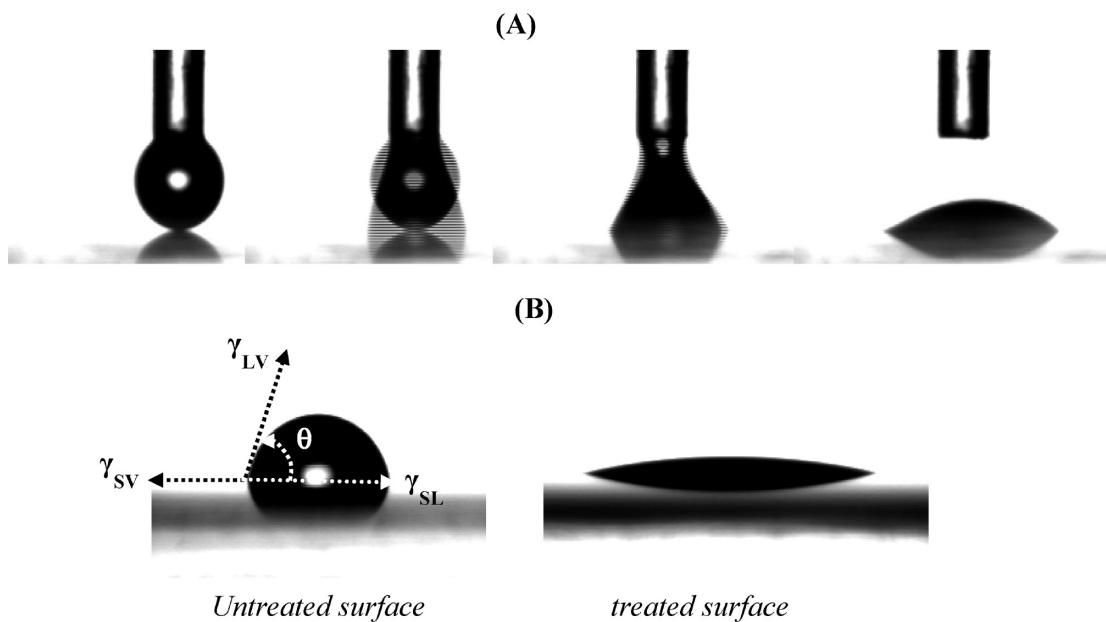


Figure 1. Camera pictures of a small water droplet ($2\ \mu\text{L}$) deposited on a silicon nitride substrate surface: (A) succession of droplet profile; (B) before and after chemical treatment (S2 procedure).

similar to that of the silicon dioxide surface.¹⁹ Hence, the decrease of the contact angle value is caused by the increase of the hydrophilic character of silicon nitride and silicon dioxide surfaces. The change in wetting phenomenon on both silicon-based substrate surfaces proves the presence of a large number of hydrophilic active sites ($-\text{OH}$ for silicon dioxide and both $-\text{OH}$, $-\text{NH}_2$ sites for silicon nitride). In a previous work, the number of the hydroxyl groups at the silicon dioxide surface was estimated to be $4.6\text{--}5$ sites of OH/nm^2 , $3\text{--}4.95\ \text{OH}/\text{nm}^2$, and $0.05\text{--}2\ \text{NH}_2/\text{nm}^2$ for the silicon nitride surface.²⁰

To study the influence of the atmosphere on the wetting properties, contact angle measurements were performed in a saturated atmosphere. Figure 2B shows the variation of the contact angle under the effect of the cleaning procedure in the presence of water vapor. The results obtained in this case are characterized by the increase of the contact angle in comparison with those obtained in unsaturated atmosphere. This will lead us to conclude that water vapor has a noticeable influence on the contact angle variation. Consequently, its presence affects the interaction at the vapor–liquid and vapor–solid interfaces, and by the way it reduces the wetting of both silicon dioxide and silicon nitride surfaces. In fact, when the surface tension of the solid–vapor (γ_{SV}) increases, θ decreases. This may lead to a higher $\cos \theta$ described as follows:

$$\cos \theta = \frac{\gamma_{\text{SV}} - \gamma_{\text{SL}}}{\gamma_{\text{LV}}} \quad (2)$$

An increase in θ means a decrease in $\cos \theta$. A decrease in $\cos \theta$ for γ_{LV} is equal to constant, which means that $\gamma_{\text{SV}} - \gamma_{\text{SL}}$ must decrease. The reduction of the surface free energy due to adsorption of vapor molecules is well-known.²¹ A lower γ_{SV} value for the surface in the presence of vapor water means that the system prefers to maximize the solid–vapor surface area.

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3.2. Effect of pH on the Wettability of Silicon Nitride and Silicon Dioxide Surfaces. Many factors can extensively affect the wettability of a solid surface such as temperature, humidity, and pH.^{22,23} In this work, we have studied the effect of pH on the wettability of silicon nitride and silicon dioxide surfaces. In a previous work,^{24,25} it was shown that a solid surface containing acid sites can interact with the base sites of the test liquid. Similarly, the surface containing base sites interacts with the acid sites of the test liquid. For silicon nitride and silicon dioxide, silanol ($\equiv\text{SiOH}$) and silylamine ($\equiv\text{SiNH}_2$) polar groups have acid–base features, and when they are created at the solid surface the reactivity for water is improved consequently. Figure 3 shows the variation of the contact angle depending on the pH variation. For acidic pH values, the CA of the deposited drop varies slightly when the pH increases, and it is demonstrated that silicon nitride and silicon dioxide present less hydrophobic surfaces (high contact angle). Comparatively, for acidic pH values, the silicon nitride surface is more hydrophobic than the silicon dioxide surface. This difference can be attributed to the presence of the generated $\equiv\text{SiNH}_3^+$ positive sites on the silicon nitride surface at acidic pH. For basic pH values, silicon dioxide and silicon nitride surfaces acquire a more hydrophilic feature and we can observe a high decrease of the CA for alkaline pH. The noticeable wettability change is due to the high dioxide surface polarity given by the generated sites such as $\equiv\text{SiO}^-$ for both studied surfaces and the residual $\equiv\text{SiNH}_2$ only for the silicon nitride surface. The high decrease of contact angle, in the case of silicon nitride, can be attributed to the $\equiv\text{Si}_2\text{N}^-$ negative sites appearing in alkaline media.

In fact, the reactivity of surface dioxide is given by the repartition of charge between the solid surface and the liquid (water drop). In the case of silicon dioxide, the reactivity of the

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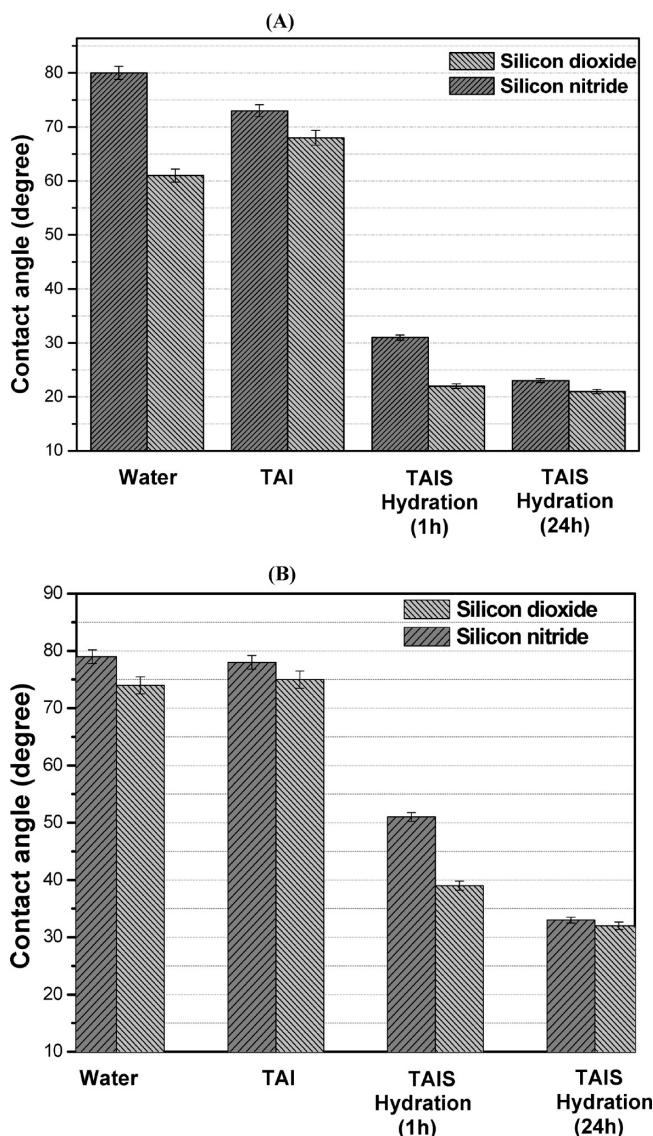


Figure 2. Bar graphs for contact angles at each different step of the cleaning procedure (TAIS: trichloroethylene, acetone, isopropanol, sulfochromic mixture) for different surfaces measured by sessile drop method in (A) unsaturated and (B) saturated atmosphere with water vapor.

surface is especially caused by the presence of amphoteric silanol ($\equiv\text{Si}—\text{OH}$) groups. The latter, in contact with water, gives the following equilibria 3 and 4, with the isoelectric point being around pH = 2 or less.²⁶



In the case of silicon nitride, the reactivity of the surface is given by the simultaneous presence of both sites such as silylamine ($\equiv\text{Si}—\text{NH}_2$) groups with a basic feature and silanol groups with an amphoteric feature ($\equiv\text{Si}—\text{OH}$). In contact with water, the

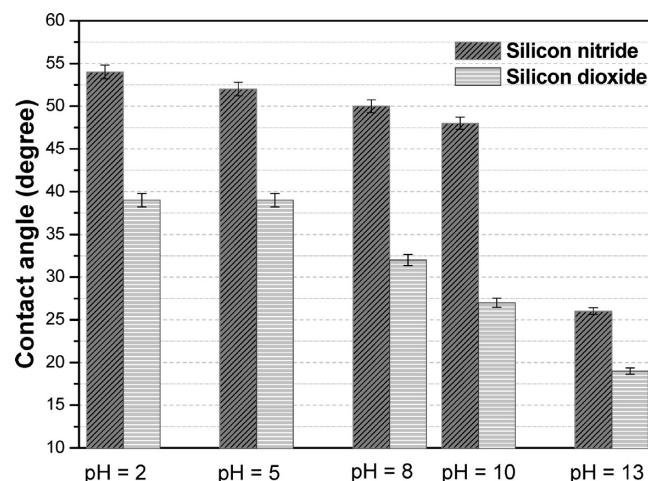


Figure 3. Bar graphs for contact angles versus pH variation for silicon nitride and silicon dioxide surfaces treated with the S2 procedure.

silicon nitride surface gives the following equilibria 5–7,^{27,28} with the isoelectric point being around pH = 8.



The change of the contact angle versus the pH variation for silicon nitride and silicon dioxide can be explained by a qualitative argument. Above the isoelectric point, water molecules interact with a negatively charged surface, while below the isoelectric point water molecules interact with a positively charged surface; it is useful to consider the interaction of a H_2O molecule with surface hydroxyls (hydrogen bonds) versus the interaction of a H_2O molecule with a surface dipole (NH_3^+ or OH_2^+). This comparison can be done by considering the electrostatic interaction energy in each case in terms of the distance of interaction. Hydrogen bonding is considered by van Oss et al.²⁹ and by Fowkes³⁰ to be an acid–base interaction, but within the present context hydrogen bonding with surface hydroxyls (OH) or amines (NH_2) can be viewed as a dipole–dipole interaction.

3.3. pH Sensitivity of Silicon Nitride and Silicon Dioxide Surfaces. The sensitivity of both surfaces for pH variation was determined using the electrochemical capacitance–potential (C – V) method.³¹ The electrochemical capacitance measurements were performed in a conventional electrochemical cell containing a three-electrode system: the substrate (silicon nitride or silicon dioxide layer) was used as the working electrode, and a platinum plate electrode and a standard calomel electrode (ECS) were used as counter and reference electrode, respectively. The electrochemical cell was connected to an amplifier system VoltaLab 40 (Radiometer Analytical SA Villeurbanne, France). The capacitance measurements were carried out at a frequency of 10 kHz with a signal amplitude of 10 mV.

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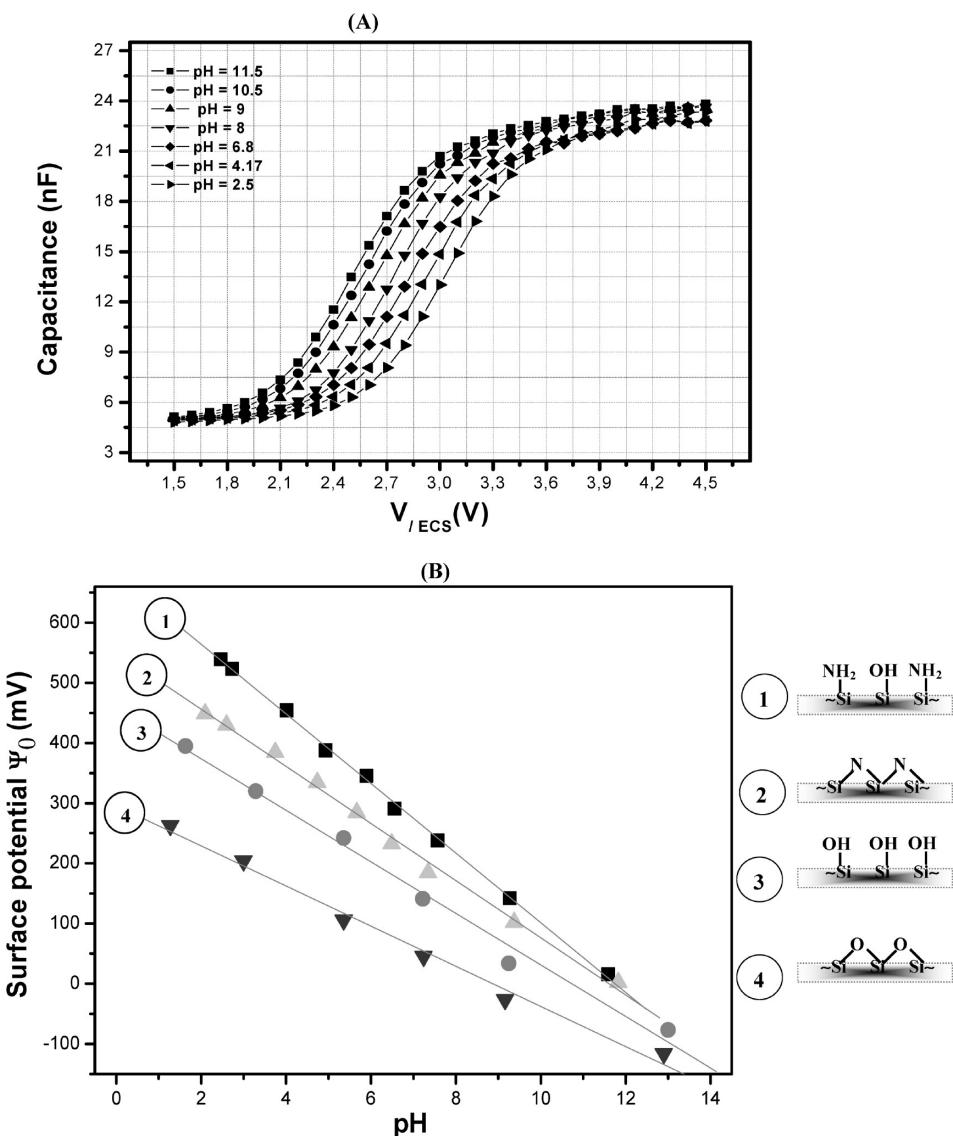


Figure 4. Electrochemical characteristics. (A) Capacitance–potential spectra of silicon nitride, (B) pH effect on the surface potential of such dioxide transducers and surface polarity correspondence. (1) Treated and (2) untreated silicon nitride surface. (3) Treated and (4) untreated silicon dioxide surface.

When the pH of the electrolyte varies in the electrochemical cell, the charge of the dioxide surface changes, according to equilibria 3–7, and consequently the surface potential ψ_{surface} is modified as follows:

$$\psi_{\text{surface}} = \psi_0 + \left(\frac{RT}{z_i F} \right) \log a_i \quad (8)$$

where ψ_0 is the initial surface potential before adding H^+ or OH^- , a and z are the activity and the charge of the analyte i , respectively, R is the universal gas constant, F is the Faraday constant, and T is the absolute temperature in Kelvin.

In Figure 4A, we report the C – V spectra of the silicon nitride structure for different pH values. The pH of the solution in the electrochemical cell was adjusted by adding NaOH or HCl solution (1 M). Figure 4B shows the variation of the surface potential ψ_0 when the pH varies for both silicon nitride and silicon dioxide surfaces. In the case of untreated surfaces, we observe a low sensitivity for pH variation. Nevertheless, supersensitivity for pH variation was observed once the surfaces were treated with the sulfochromic mixture. This observation corroborates with the result obtained by contact angle measurements. The high sensitivity of the

treated surfaces to pH change after the activation process demonstrates the presence of highly active sites such as silanol and silylamine groups. For lower pH values, both surfaces are less hydrophilic (surface potential varies averagely) and the contact angle changes slightly. This result is due to the generated positive sites created at the surfaces such as $\equiv \text{SiOH}_2^+$ for silicon dioxide, and $\equiv \text{SiOH}_2^+$ and $\equiv \text{SiNH}_3^+$ for silicon nitride. In contrast, for high basic pH values, the contact angle decreases greatly, showing good wetting surfaces due to the presence of negative sites ($\equiv \text{SiO}^-$) for silicon dioxide and ($\equiv \text{SiO}^-$, $\equiv \text{SiNH}_2$) for silicon nitride surfaces. The reactivity of both surfaces for pH variation and especially that of silicon nitride demonstrates its importance to design a pH sensor.³² In addition, silicon dioxide and silicon nitride were extensively used as simple transducers for biosensor devices to detect biological reaction inducing pH variation.^{3,33}

3.4. Evolution of the Thermodynamic Surface Properties with the Cleaning Procedure.

Surface affinity and interface

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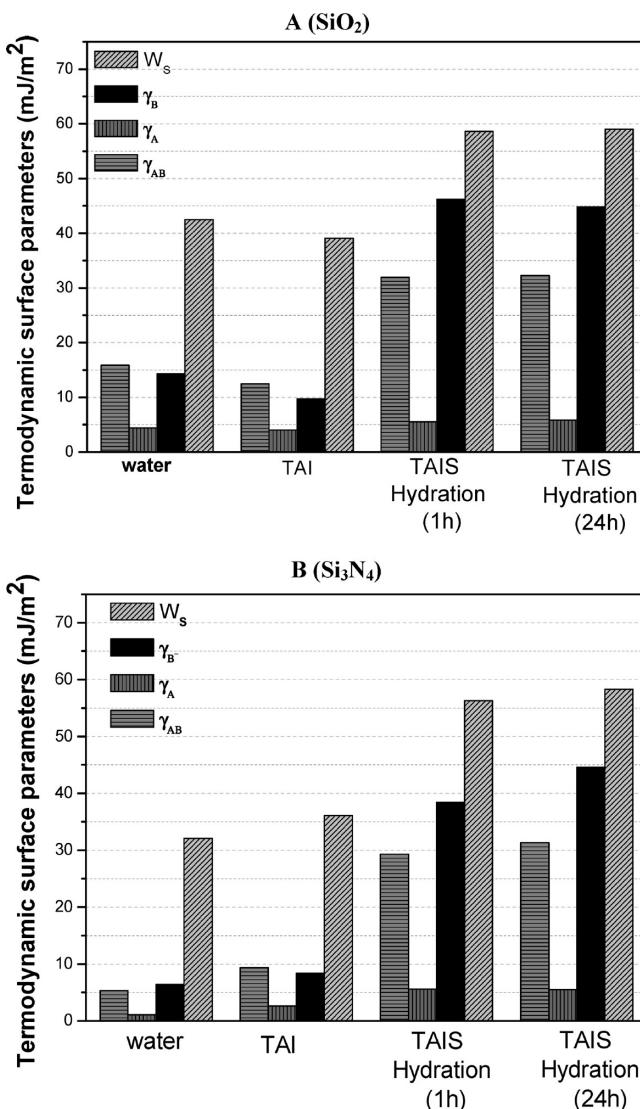


Figure 5. Bar graphs for total free energy, acid, base, and Lewis acid–base components (W_s , γ_A , γ_B , and γ_{AB}) for both dioxide substrates measured by the sessile drop method in unsaturated atmosphere with liquid vapor test: (A) silicon dioxide and (B) silicon nitride.

phenomena can be influenced by the thermodynamic parameters, such as surface free energy, acid, base, and Lewis acid–base components. However, surface energy depends on the hydrophobic (low-energy) or hydrophilic (high-energy) feature. Nevertheless, the free energy of adhesion ($-\Delta G_{SL}^{\text{adh}}$) between solid surface and water is

$$W_s = \gamma_{LV}(1 + \cos \theta) = -\Delta G_{SL}^{\text{adh}} \quad (9)$$

The free energy or total surface energy W_s can be described by the entire polar part of the surface tension of those materials such as the γ_{AB} (acid–base) component. The latter is composed of two different surface tension parameters, namely, the parameter representing its electron-accepticity (acidic), designated as γ_A , and the parameter representing its electron-donicty (basic), designated as γ_B , such as

$$\gamma_{AB} = 2\sqrt{\gamma_A \gamma_B} \quad (10)$$

In general, the acid component is given by the contribution of all positive charges resulting from the active site protonation.

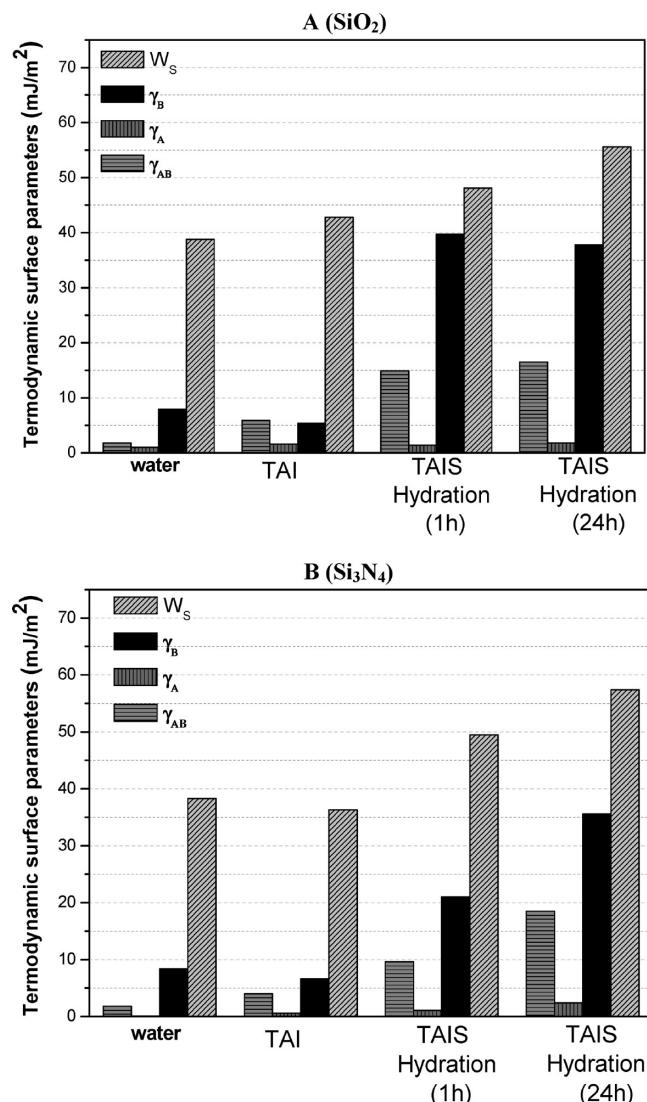


Figure 6. Bar graphs for total free energy, acid, base, and Lewis acid–base components (W_s , γ_A , γ_B , and γ_{AB}) for both surfaces measured by the sessile drop method in saturated atmosphere with test liquid vapor: (A) silicon dioxide and (B) silicon nitride.

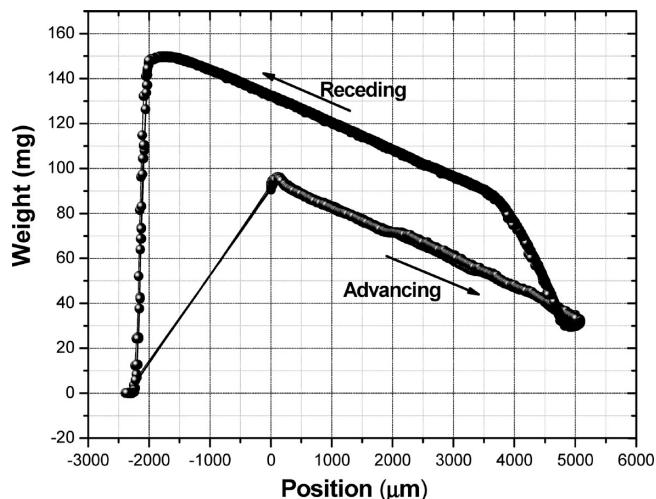


Figure 7. Five wetting/dewetting cycles obtained by hysteresis measurements performed on silicon nitride substrate.

For silicon dioxide, this component can be written as $\gamma_A = \gamma_{OH_2^+}$. In the case of silicon nitride, the acid component can be written as $\gamma_A = \gamma_{OH_2^+} + \gamma_{NH_3^+}$. The base component is given by the negative charge resulting from the deprotonation or the Lewis electron of the active sites. For silicon dioxide, the base component can be written as $\gamma_B^- = \gamma_{O^-}$ and for silicon nitride as

$$\gamma_B^- = \gamma_{O^-} + \gamma_{NH_2^-} \quad (11)$$

Table 2. Dynamic Contact Angle Values for the Silicon Nitride Surface

liquid	θ_a (°)	θ_r (°)	$\Delta\theta$ (°)
distilled water	67.5 ± 2	58.7 ± 1.5	8.4 ± 0.9
formamide	66.2 ± 1.4	65 ± 1.6	1.2 ± 0.2
diiodomethane	54.3 ± 2.1	53.2 ± 1.7	1.1 ± 0.4

Table 3. Dynamic Contact Angle Values for the Silicon Dioxide Surface

liquid	θ_a (°)	θ_r (°)	$\Delta\theta$ (°)
water	66.3 ± 1.5	61.8 ± 2.3	4.5 ± 0.8
formamide	60.7 ± 2	59.3 ± 1.7	1.4 ± 0.3
diiodomethane	57.4 ± 1.8	56.8 ± 2	0.5 ± 0.1

Thermodynamic surface components were determined by measuring contact angle of different liquids (water, diiodomethane, and formamide). Figure 5 shows the variation of surface free energy, acid, base, and Lewis acid–base components with the cleaning procedure of both surfaces in unsaturated atmosphere with liquid vapor. We observe that the cleaning chemical procedure has a significant effect on the thermodynamic properties of both silicon dioxide and silicon nitride surfaces. For untreated dioxide surfaces, a low free energy (high contact angle) was determined due to the inactive and less hydrophilic surfaces. When both surfaces were cleaned with organic solvent, the free surface energy increased slightly. This result is related to the limited effect of the organic solvents on the surface wettability. Once sulfochromic treatment takes place, the surface free energy of both solid surfaces increases widely. During these steps of the chemical treatment, the same trend was observed for the acid, base, and Lewis acid–base components. Indeed, for both solid surfaces, the base component has changed with varying degree before and after the chemical treatment. Furthermore, the base component was considerably higher than the acid component for silicon dioxide and silicon nitride surfaces. All these thermodynamic parameters are different from those obtained in saturated atmosphere with test liquid vapor (Figure 6). We observe that the atmosphere has a remarkable effect on the thermodynamic surface energy parameters. Consequently, the

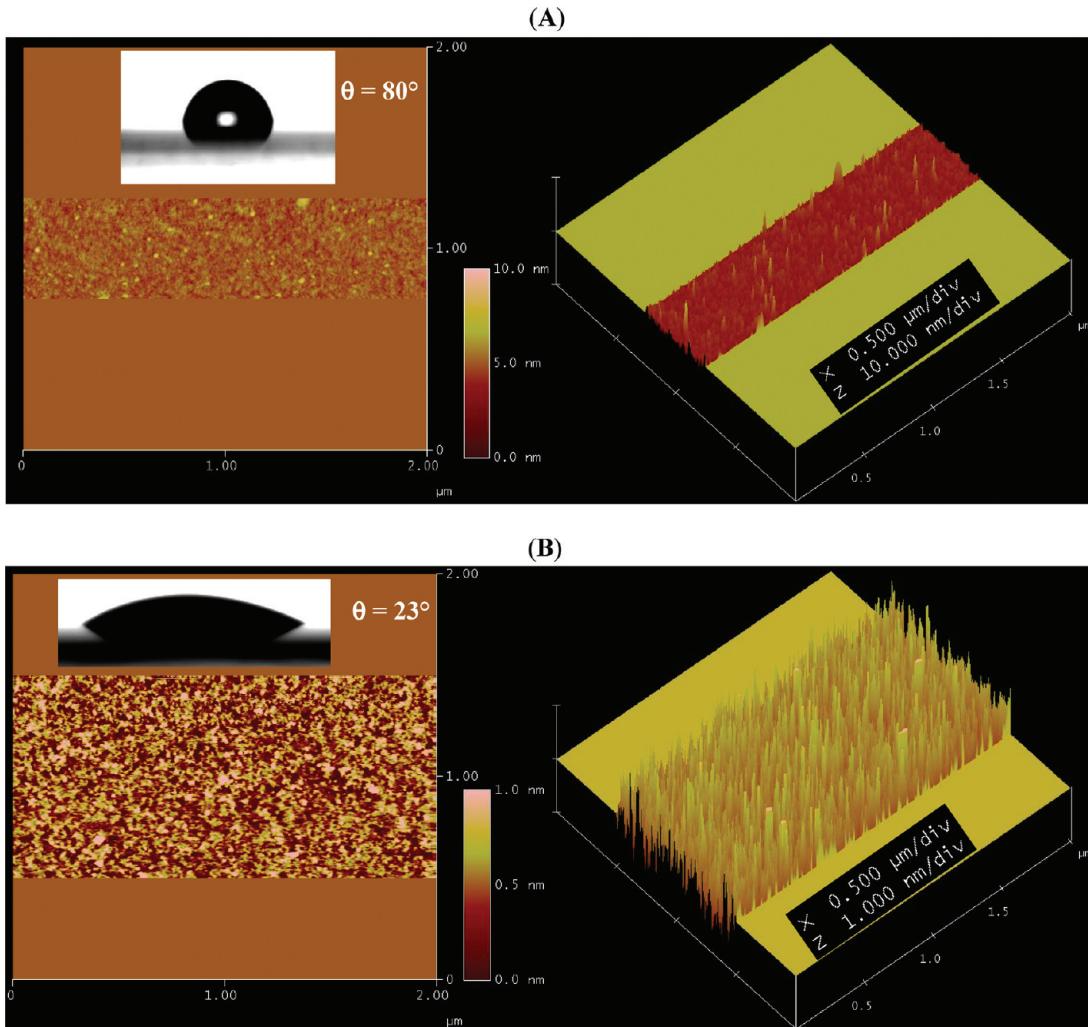


Figure 8. AFM 2D and 3D topographic images of treated silicon nitride surface: (A) cleaned with water and (B) cleaned with trichloroethylene, acetone, isopropanol, and sulfochromic mixture.

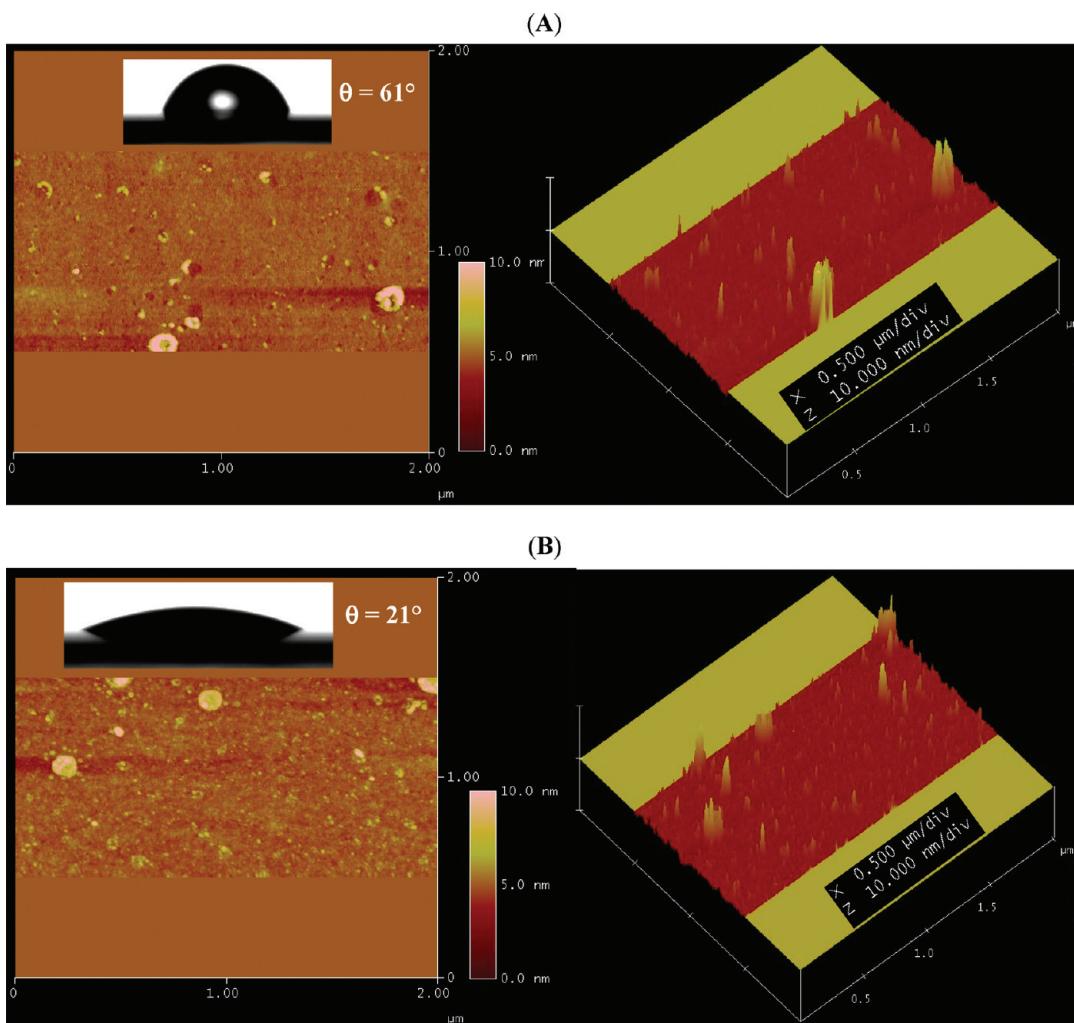


Figure 9. AFM 2D and 3D topographic images of treated silicon dioxide surface: (A) cleaned with water and (B) cleaned with trichloroethylene, acetone, isopropanol, and sulfochromic mixture.

presence of test liquid vapor reduces the atmosphere spreading pressure effect and decreases the surface energy parameters. In previous work,¹⁵ it was shown that atmosphere has a great effect on the wettability of the solid surface by adsorbing an external layer. The atmosphere effect can be taken into account when the surface free energy reaches nearly 60 mJ/m².

3.5. Surface Roughness and Contact Angle Hysteresis Measurements. The thermodynamic hysteresis model developed by Long et al.³⁴ is of practical importance to study the homogeneity or the heterogeneity of the solid surface. The heterogeneity of a surface has a specific signification in both physical (roughness) and chemical (presence of different reactive sites) approaches.^{35–37} Moreover, hysteresis is the difference between the advancing angle (θ_a) and the receding angle (θ_r) as follows:

$$\Delta\theta = \theta_a - \theta_r \quad (12)$$

$$\theta_a = R\theta_r \quad (13)$$

where R is the roughness coefficient. In the case where R is equal

to 1, we can deduce that the solid surface is smooth, and if it is different from 1, we can deduce that the surface is rough.

For example, Figure 7 shows the hysteresis profiles which are stable and repeatable over five successive immersion cycles observed for the silicon nitride substrate. However, the standard deviation of contact angles, typically $\pm 2^\circ$, represents the reproducibility of sample preparation. We observe a low hysteresis for both surfaces as shown in Tables 2 and 3. The calculated roughness coefficient ($R = \theta_a/\theta_r$) values were equal to 0.93 and 0.87 for silicon dioxide and silicon nitride surfaces, respectively. Consequently, the rough coefficient value was close to 1 for both surfaces, and this result demonstrates that both surfaces are smooth. We conclude therefore that the small difference in the roughness coefficient for both surfaces can be attributed to chemical heterogeneity in the case of the silicon nitride surface (silanol and silylamine sites) and chemical homogeneity in the case of the silicon dioxide surface (silanol sites).

3.6. Surface Topography Characterization by Atomic Force Microscopy (AFM). The surface morphology of treated silicon dioxide and silicon nitride surfaces was examined at the nanometer scale using atomic force microscopy (AFM). Different areas were studied for each sample in order to obtain representative information. The AFM images were recorded in tapping mode by using a Digital Instruments NanoScope from Park Scientific Instruments, using a 2 μm scan size and scan rate of

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 (35) Johnson, R.; Dettre, R. *J. Phys. Chem.* **1964**, *68*, 1744.
 (36) Joanny, J.; De Gennes, P. *J. Chem. Phys.* **1984**, *81*, 552.
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1 Hz/line. All scans were acquired at room temperature at atmospheric pressure and characterized by measuring the root-mean-square roughness (R_{rms}). Figures 8 and 9 show the surface topography of both silicon nitride and silicon dioxide thin films before and after chemical treatment. From AFM images, it is clear that chemical cleaning has a significant effect on dioxide surface morphology and especially in the case of the silicon nitride surface where we can observe a net change in surface morphology once treated with sulfochromic mixture. The latter has a double role on the surface:

- (i) The first role is to clean and remove the native layer (oxide layer) formed on the silicon nitride surface resulting from the atmosphere effect.
- (ii) The second is the major role, and it is attributed to the reaction of the sulfochromic mixture with Si–Si (for silicon dioxide) or Si–NH–Si (for silicon nitride) bonds and generation of native Si–O or/and Si–N bonds at the top surface to create the active sites after the hydration process.

AFM images demonstrate that untreated silicon nitride has a surface topography similar to that of the silicon dioxide surface. This result matches well with contact angle and electrochemical measurements.¹⁹ AFM measurements show that both surfaces have high homogeneous and very smooth surfaces with root-mean-square roughness values of 0.5 and 0.7 nm for silicon dioxide and silicon nitride, respectively.

4. Conclusion

This study focused mainly on the thermodynamic surface properties of both silicon nitride and silicon dioxide thin layers. We have tried to correlate the behavior of silicon-based transducers in response to step-pH variations to their thermodynamic surface characteristics. The contact angle and the surface free energy were carefully evaluated using the contact angle approach of van Oss. It has been shown that surface free energy, acid, base, and acid–base components of such surfaces can vary after the chemical treatment procedure and depend on the atmosphere nature. The surface free energy of treated surfaces was increased up to 58 mJ/m², and it was supported mainly by the base component (~45 mJ/m²) and weakly by the acid component (~5 mJ/m²). In addition, the wettability results were in good agreement with the electrochemical measurements to explain the evolution of both surfaces' sensitivity to pH variation. It should be noticed that the affinity of these studied surfaces depends on the nature and the number of functional groups (amine and hydroxyl groups). The contact angle hysteresis measurements and AFM analysis allow that both surfaces are smooth and are characterized by low root-mean-square values. In addition, the chemical cleaning procedure used in this work represents an adequate procedure for oxide surface treatment adding to other cleaning and etching procedures based on the attack of the oxide by hydrofluoric acid (HF) solutions. Finally, it will be interesting to study and to understand deeply the surface properties of both silicon dioxide and silicon nitride layers. These are of great importance and are mostly used as sensitive layers for silicon-based transducers such as ISFET and EIS potentiometric sensors.