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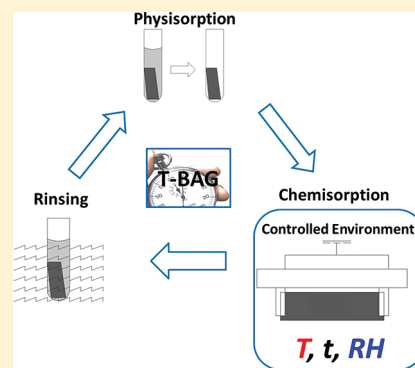
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# Environment-Controlled Tethering by Aggregation and Growth of Phosphonic Acid Monolayers on Silicon Oxide

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**ABSTRACT:** Phosphonic acid monolayers are being considered as versatile surface modification agents due to their unique ability to attach to surfaces in different configurations, including mono-, bi-, or even tridentate arrangements. Tethering by aggregation and growth (T-BAG) of octadecylphosphonic acid (ODPA) on silicon oxide surfaces has proven to be a robust method to establish a strong chemical bond. However, it requires a long processing time ( $> 48$  h) that is a substantial drawback for industrial applications. We demonstrate here that the humidity level during processing is the most important parameter controlling the reaction. Using in situ Fourier Transform Infrared Spectroscopy (FTIR), we first show that the initially physisorbed layer obtained upon immersion in ODPA is composed of well-ordered bilayers and only reacts with the  $\text{SiO}_2$  surface at  $140^\circ\text{C}$ . Importantly, we show that the presence of water at the interface (determined by the humidity level) greatly influences the reaction time and completion. In humid environments (relative humidity,  $\text{RH} > 40\%$ ), there is no reaction, while in dry environments ( $\text{RH} < 16\%$ ), the reaction is essentially instantaneous at  $140^\circ\text{C}$ . Ab initio calculations and modeling confirm that the degree of chemical reaction with the surface OH groups depends on the chemical potential (i.e., concentration) of interfacial water molecules. These findings provide a workable modification of the traditional T-BAG method consistent with many industrial applications.



## INTRODUCTION

Biomedical, energy, surface coating and protection, and sensor applications all require selective organic surface functionalization of inorganic, electronically active substrates such as silicon.<sup>1–3</sup> The exceptionally good electrical properties of Si/ $\text{SiO}_2$  interfaces and the use of glass substrates have focused attention and effort on grafting molecules via hydroxyl groups that typically terminate  $\text{SiO}_2$  surfaces after wet chemical cleaning. However, their activation is difficult for some important molecules, such as phosphonates, and therefore a roadblock for further development of a large number of devices of industrial value.

Phosphonates are of particular interest for their use in coatings, sensors, electronics (such as thin film transistors), solar panels, water repellents, and adhesive promoters,<sup>4–7</sup> and have been successfully grafted on metal oxides, involving metals such as aluminum,<sup>8</sup> titanium,<sup>9</sup> silicon,<sup>10</sup> zinc,<sup>11</sup> hafnium,<sup>12</sup> nickel,<sup>13</sup> and more specific alloys such as ITO,<sup>14</sup> AZ31,<sup>15</sup> SS316L,<sup>16</sup> and Nitinol.<sup>17</sup>

The problem arises in the grafting of phosphonates to silicon oxide. Under normal ambient conditions, phosphonate molecules do not react chemically on silicon oxide or even  $\text{TiO}_2$ . Gawalt et al. discovered that the adhesion and stability of phosphonic acid SAMs on  $\text{TiO}_2$  require thermal annealing after deposition of a thin phosphonic acid film.<sup>9</sup> It was proposed that the phosphonic acid molecules in the unheated, as deposited, film are only weakly physisorbed on the surface. Interestingly, the molecule–molecule interactions (van der Waals and hydrogen bonding) are apparently stronger than substrate–

molecule interactions in the deposited films, enhancing the order of the physisorbed SAM. Thermal energy derived from annealing fosters covalent attachment of the phosphonic acids to the substrate. Hanson et al. built on these findings to formulate a technique for grafting phosphonic acid films, referred to as the tethering by aggregation and growth (T-BAG) method.<sup>18</sup>

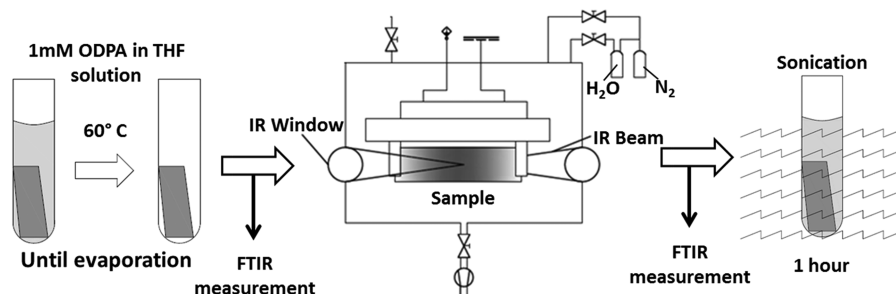
This T-BAG method was specifically developed for the deposition of self-assembled monolayers (SAMs) of phosphonic acids on native oxide surfaces of silicon. During the T-BAG process, a phosphonic acid is initially weakly physisorbed from a solution onto the oxide substrate, then chemically attached by a heating step and further rinsed to remove any remaining physisorbed multilayers present on the surface on top of the chemisorbed SAM. This is a simple and reliable method to grow SAMs of phosphonates on oxide surfaces. The physisorption step takes advantage of the organized arrangement of amphiphilic molecules at the liquid/gas interface,<sup>19</sup> and is not restricted to specific environmental conditions like silanation reactions, which makes it potentially suitable for the industry. Sample heating has been identified as the key element of the T-BAG method, as it allows conversion of the physisorbed phosphonic acid to chemisorbed phosphonate, securing a monolayer to the surface prior to ultrasonic rinsing in water. The main disadvantage of this process is the long time

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**Figure 1.** Schematic description of the T-BAG process and experimental setup.

necessary to complete it, typically more than 48 h.<sup>10,18,19</sup> Surprisingly, there has been little progress in understanding the grafting mechanism and little attention paid to the role of the environment.

We have therefore developed in situ characterization methods to monitor the chemical evolution of the layer as a function of temperature and explore the role of the environment after the initial wet chemical deposition on the oxide surface. Specifically, the phosphonic acid covered silicon oxide sample is first heated for short time periods, under humidity-controlled environments, and the evolution of the physisorbed phosphonic acid is analyzed by in situ FTIR and ex situ spectroscopic ellipsometry. Our results clearly show that the chemical reaction between the phosphonic acid and the hydroxyl terminated silicon oxide surface takes place quickly in a low humidity environment at 140 °C, without requiring a long heating period of 48 h. Interestingly, they confirm that a minimum temperature of 140 °C is indeed necessary for the formation of chemisorbed ODPa on silicon oxide, as previously established.<sup>18</sup> However, in contrast to earlier suggestions, the phosphonic acid molecules are found to be attached to silicon oxide surfaces mostly in a bidentate Si–O–P configuration, leaving one P=O group. In high humidity environments, no chemisorption takes place, as described and explained by ab initio total-energy calculations.

## EXPERIMENTAL SECTION

**Sample Preparation.** A 1.5 × 0.5 in. wafer of Float Zone (FZ) Si (111) double side polished is cleaned in piranha solution (H<sub>2</sub>SO<sub>4</sub> (Fisher 98%):H<sub>2</sub>O<sub>2</sub> (Fisher 30%) 3:1) for 30 min, intensely rinsed with deionized H<sub>2</sub>O (18.2 MΩ cm Milli Q), and finally dried in a stream of N<sub>2</sub>. Afterward the sample is immersed in a solution of octadecylphosphonic acid (ODPA powder (Aldrich 97%); 1 mM in tetrahydrofuran (THF) (Aldrich 99.9% inhibitor free)), below its critical micelle concentration (CMC) in a simple glass tube. The solution is heated in a water bath at 60 °C until complete evaporation is achieved (~3 h), as shown in Figure 1. Even though the solvent is consumed completely, the round-bottom of the tube allows the sample to dry before CMC is reached. Reaching or exceeding the CMC would lead to the formation of multilayers on the surface instead of the well-ordered bilayers.<sup>20</sup>

**In Situ Surface Analyses.** The surface analysis is performed in a Quartz chamber (shown in Figure 1) capable of working in continuous vacuum ( $p = 10^{-4}$  Torr) or under the flow of different gas phase molecules. Samples can also be resistively heated to 1000 °C. All of the heating steps in this chamber are performed resistively, making it possible to achieve chemisorption temperature (140 °C) in ~10 s. An FTIR spectrometer (Thermo Scientific, Nicolet 6700) allows in situ analysis of the sample during the execution of the process. This system was designed by the author and colleagues. FTIR measurements are performed with a deuterated triglycine sulfate (DTGS) detector with 3000 averaged scans to ensure an optimal signal-to-noise ratio. The relative humidity (RH) is calculated by setting the value in continuous

vacuum to 0% RH and comparing the water vapor peak-to-peak height shown by FTIR measurements at room conditions (~22% RH) to different working environments. For the N<sub>2</sub>/H<sub>2</sub>O gas, it is estimated to be ~90% RH, and for the N<sub>2</sub> gas, it is estimated to be ~4% RH. The calculation also considers the contribution to the spectrum due to the intrinsic humidity of the spectrometer used.

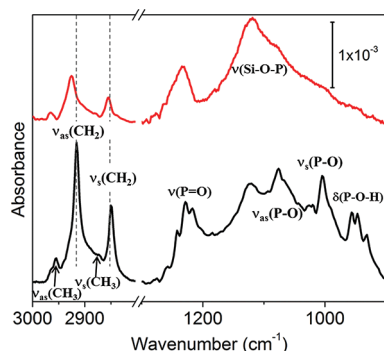
**Spectroscopic Ellipsometry.** Spectroscopic ellipsometry measurements are performed using a Jobin-Yvon UVISSEL ellipsometer, with a spectral range of 0.6–6 eV, to verify the number of ODPa layers covering a sample. Measurements are performed before the physisorption (as reference), after the physisorption, and after the T-BAG process is complete.

**Ab Initio Total-Energy Calculations.** The calculations are performed using density functional theory (DFT) within the generalized gradient approximation (GGA) as implemented in the Vienna ab initio simulation package (VASP).<sup>21</sup> The electron–ion interaction is described by the projector augmented wave scheme.<sup>22</sup> The electronic wave functions are expanded into plane waves up to a kinetic energy of 360 eV.<sup>23</sup> A fully hydroxylated SiO<sub>2</sub>(100) surface is modeled by periodically repeated slabs. Each supercell consists of 16 atomic layers within (2 × 2) periodicity plus a vacuum region equivalent to 18 Å. Further calculations contain a physisorbed methylphosphonic acid (MPA) and water. The 15 uppermost layers as well as the adsorbate degrees of freedom are allowed to relax until the forces on the atoms are below 10 meV/Å. The Brillouin zone integration is performed using 4 × 4 × 1 Monkhorst–Pack meshes. We use the PW91 functional to describe the electron exchange and correlation energy within the GGA.<sup>24</sup> It describes the hydrogen bonds in solid water (ice<sub>II</sub>) in good agreement with experiment.<sup>25</sup>

## RESULTS AND DISCUSSION

The first step of the T-BAG method is the phosphonic acid physisorption on the surface. This is achieved by immersing the sample in a solution and waiting for complete evaporation of the solvent. After the physisorption process is completed, the nature of the physisorbed layer is analyzed with IR spectroscopy. Figure 2 (bottom line) shows all of the typical spectral features of a fully protonated physisorbed phosphonic acid: the stretch mode of the (P=O) at 1227 cm<sup>-1</sup>, the asymmetric and symmetric stretch modes of the (P–O) at 1078 and 1004 cm<sup>-1</sup>, and the deformation mode of the (P–O–H) feature clearly present at 956 cm<sup>-1</sup>.<sup>8</sup> In the aliphatic region, the spectral positions of the strong asymmetric and symmetric stretch modes of the (CH<sub>2</sub>) at 2915 and 2850 cm<sup>-1</sup>, respectively, indicate an ordered arrangement on the surface. These low wavenumbers of the (CH<sub>2</sub>) vibrational modes suggest that the physisorption step takes advantage of the organized arrangement of amphiphilic molecules at the liquid/gas interface. In addition, the asymmetric and symmetric stretch modes of the (CH<sub>3</sub>) at 2966 and 2870 cm<sup>-1</sup> are present.

The treated sample is then heated resistively inside the vacuum chamber to 140 °C for ~10 s (RH ≈ 4%), and then cooled to the FTIR measurement temperature (room temper-



**Figure 2.** Transmission spectra taken after the physisorption of ODPA (bottom spectrum) and after the finishing of the T-BAG process (top spectrum); all spectra are referenced to the initial SiO<sub>2</sub> surface.

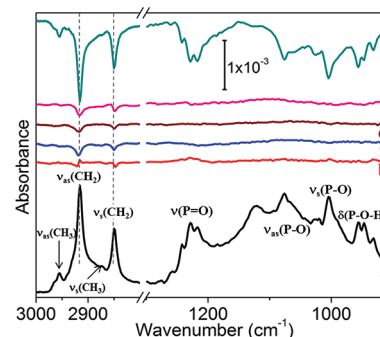
ature). After FTIR measurements, the sample is rinsed by sonication for 60 min in THF to remove extra layers of ODPA and is brought back to the vacuum chamber for FTIR measurements. The FTIR spectrum in Figure 2, top curve, shows the resulting IR spectrum at the end of the T-BAG process, referenced to the clean SiO<sub>2</sub> surface. The presence and intensity of the (P=O) mode at 1227 cm<sup>-1</sup> rules out the formation of the primarily tridentate bonding previously suggested.<sup>10,18</sup> The loss of the (P-O-H) mode at 956 cm<sup>-1</sup> rules out the monodentate configuration. On the other hand, the formation of a chemical bond to the surface is evident in the presence of the (Si-O-P) stretch modes in the 1140–1080 cm<sup>-1</sup> region. The specific frequencies, a strong mode at 1108 cm<sup>-1</sup> and a weaker shoulder at 1080 cm<sup>-1</sup>, directly support the bidentate bonding configuration, although the surface is far from being homogeneous.

Figure 2 also depicts the presence of the asymmetric and symmetric stretch modes of the (CH<sub>2</sub>) at 2915 and 2850 cm<sup>-1</sup> along with the asymmetric and symmetric stretch modes of the (CH<sub>3</sub>) at 2966 and 2870 cm<sup>-1</sup> (black bottom line). The spectra indicate that the alkyl chains are not degraded by the deposition/heating/rinsing procedure (red top line). The blue shifts of the alkyl modes from 2850 to 2852 cm<sup>-1</sup> and from 2915 to 2920 cm<sup>-1</sup> during the heating step point to some unexpected disordering. One possible mechanism for the formation of SAMs of ODPA has been described by Neves et al.<sup>20</sup> It is claimed that the ODPA multilayer deposited on the surface forms a close-knit network. Once the surface is heated, this multilayer initially separates and develops into a less closely packed monolayer. This monolayer would tend to form the most stable configuration, leading to the formation of a well-arranged self-assembled monolayer. Indeed, the values of the resulting SAM for the asymmetric (2852 cm<sup>-1</sup>) and symmetric (2920 cm<sup>-1</sup>) stretch modes of the (CH<sub>2</sub>) are still indicative of well-ordered alkyl chains.

The intensity of the IR suggests that the initially physisorbed ODPA surface is covered by multilayers of the fully protonated phosphonic acid. The decrease of the IR spectral areas of the vibrational modes after the heating and rinsing processes and the position of the remaining features in the aliphatic and phosphonate region indicate that the final surface is a phosphonic acid monolayer. To determine the number of molecular layers, we have performed spectroscopic ellipsometry at the beginning and at the end of the T-BAG process. The best-fit of the measured data is based on a five-layer model consisting of a symmetric stack around double-side polished Si

substrate (SAM-SiO<sub>2</sub>-Si-SiO<sub>2</sub>-SAM), using a tabulated dielectric function for Si and SiO<sub>2</sub> and a Cauchy model to describe SAM layers.<sup>26</sup> The fit is performed on the layer parameters of thickness *d* and the refractive index *n*. The thickness of the silicon was 500 μm. The thickness of the SiO<sub>2</sub> was determined after the piranha cleaning (and then kept fixed for the next measurements, *d* = 2.1 nm), the thickness of the bilayer was determined after the physisorption but before any heating treatment (*d* = 3.9 nm, *n* = 1.50), and the thickness of the monolayer was determined after the 140 °C heating treatment (*d* = 1.7 nm, *n* = 1.50). The estimated error in the extracted thickness values is ~20%.<sup>18</sup>

To confirm that the high annealing temperature (140 °C) is necessary and sufficient to achieve chemisorption even for short heating periods in a dry atmosphere, we have performed stepwise annealing experiments. To do so, a sample is brought into the IR chamber right after the wet chemical physisorption process, and subsequently annealed in a stepwise fashion by resistive heating of the Si substrate (RH ≈ 4%). Figure 3 shows

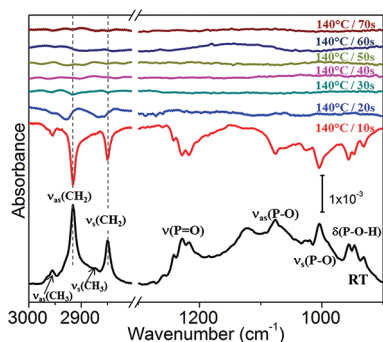


**Figure 3.** Transmission spectra taken after treating physisorbed ODPA into the silicon oxide surface at different temperatures. (a) 60 °C, (b) 80 °C, (c) 100 °C, (d) 120 °C, (e) 130 °C, (f) 140 °C. Each spectrum is referenced to the one measured before.

the FTIR differential spectra after each heating treatment. There is clearly no evidence for chemical reaction up to a temperature of 130 °C (no measurable spectral changes). As soon as the temperature of 140 °C has been reached, there is a loss in the δ(P-O-H) mode without any loss of the ν(P=O) mode, demonstrating that the phosphonic acid is chemisorbed on the surface only after heating in a dry atmosphere.

The time dependence of the whole T-BAG process is addressed next because 48 h is an exceedingly long time for most applications. To do so, we performed a series of annealing cycles to 140 °C (RH ≈ 4%), maintaining the sample at 140 °C only for 1 s each time, and cooling after each annealing cycle to perform the IR measurements, until no noticeable change in the FTIR is noted. Figure 4 shows the FTIR differential spectra of a sample, after each heating treatment. After the first annealing cycle when large changes are noted, there is no observable evolution of the surface during the subsequent heating cycles in all of the spectral regions mentioned above. This observation confirms that the heating time for the T-BAG can be lowered substantially from 48 h to a few seconds with no noticeable effect on the surface composition, as long as the heating temperature of 140 °C is reached and the humidity is negligible. It clearly shows that the T-BAG method can be modified by lowering the heating time period, yet still achieving a chemical attachment of the ODPA molecule on the surface. It

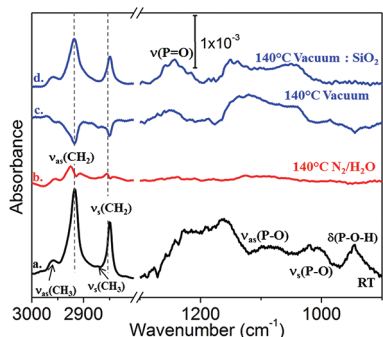




**Figure 4.** Transmission spectra taken after several heating cycles of the physisorbed ODPA on the initial silicon oxide surface; each spectrum is referenced to the previous heating cycle.

also points to the humidity level as a key factor for reaction, which we address next.

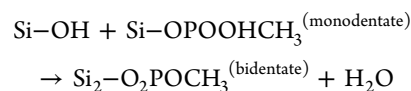
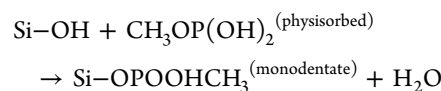
In situ FTIR characterization is therefore performed to identify the dependence of the heating step on the environment by using a dry atmosphere ( $N_2$  purged,  $RH \approx 4\%$ ) or different humidity levels achieved by adding  $H_2O$  to the  $N_2$  carrier gas ( $N_2/H_2O$  mixture, typically achieving  $RH \approx 90\%$ ). The IR measurements are performed after evacuation ( $p = 10^{-4}$  torr). Figure 5 shows the differential spectra of the surface changes



**Figure 5.** Transmission absorption spectra taken (a) after physisorption of ODPA on silicon oxide surface, and (d) after the final annealing at 140 °C under low humidity conditions, both referenced to the initial  $SiO_2$  surface. The intermediate differential spectra are (b) after heating the sample at 140 °C under high humidity conditions, referenced to (a), and (c) heating the same sample at 140 °C but now under low humidity conditions, referenced to (b). The spectra represent averages of several runs to minimize baseline and source fluctuations.

after each heating cycles, both under  $N_2/H_2O$  atmosphere and in vacuum. The spectra confirm that, after a heating period to 140 °C in high humidity environment, there is no change in the spectrum. In contrast, after the second heating period to 140 °C in dry atmosphere or in vacuum, there is a loss in the  $P=O-H$  feature without any loss of the  $P=O$  bond, indicating that the phosphonic acid is chemisorbed on the surface only after heating in dry atmosphere, and not under high humidity conditions. The features assigned to asymmetric and symmetric stretch modes of the  $(CH_2)$  at 2915 and 2850  $cm^{-1}$  do not lose intensity, but show a small shift after the first heating in the  $N_2/H_2O$  environment. In contrast, the second heating in vacuum leads to a substantial reduction of the area in the aliphatic region.

The adsorption energy  $E_{ads}$  of the chemical reaction:

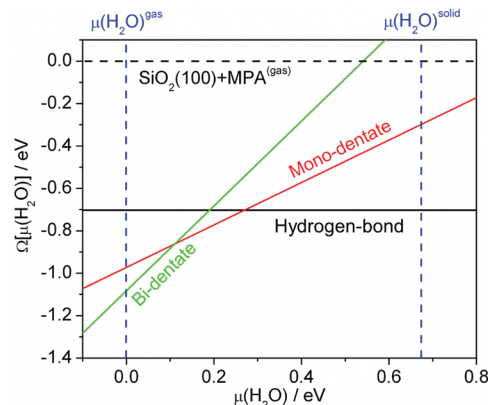


can be calculated with respect to the MPA molecule in vacuum and the clean silicon oxide slab. However, the sign of the adsorption energy alone is not sufficient to derive a firm conclusion on the stability of a specific surface structure. Rather, one has to take into account the chemical potentials  $\mu(A_i)$  of the surface constituents  $A_i$  to compare the total energies of interfaces with different stoichiometries. The ground state of the surface is determined by the minimum of the thermodynamic grand-canonical potential ( $\Omega$ ):

$$\Omega = F - \sum_i \mu(A_i) * n_{A_i}$$

where  $F = E - TS$  is the surface free energy, which we approximate by the total surface energy  $E$  at zero temperature assuming similar entropy contributions  $S$  for different adsorption configurations. In fact, the differences in vibrational free energy and electronic entropy are typically several orders of magnitude smaller than the adsorption energies calculated here.

If one assumes a flat, that is, stoichiometric, fully hydroxylated  $SiO_2(100)$  surface with a physisorbed layer of MPA, in the presence of the  $N_2/H_2O$  environment, the grand-canonical potential will only depend on the chemical potential (or concentration) of water  $\mu(\text{water})$ . Figure 6 shows the



**Figure 6.** Calculated phase diagram of the fully hydroxylated  $SiO_2(100)$ /methylphosphonic acid interface as a function of the chemical potential (i.e., local concentration) of water.

resulting phase diagram. Here, two important limiting values are indicated. The water-rich condition/limit is marked by a vertical line denoted  $\mu_{solid}(\text{water})$ . This value corresponds to the system in equilibrium with bulk water approximated here by calculations for solid water. Lower values of  $\mu(\text{water})$  indicate an increasingly dry environment. The zero-temperature calculation for gas-phase water molecules is indicated by another vertical line  $\mu_{gas}(\text{water})$ .

The phase diagram confirms the results of the measurements and in particular the need for annealing to 140 °C. Under ambient conditions, phosphonic acid molecules do not react chemically on silicon oxide. Furthermore, the  $SiO_2$ /phosphonate interface is thermodynamic stable only under very dry

conditions. As the chemical potential of water increases, water molecules start to diffuse to the interface and hydrolyze the system.<sup>27</sup> The SiO<sub>2</sub>/H<sub>2</sub>O interface gains a lot of energy due to the fact that it can build up a dense network of the hydroxyl groups on the surface, making it very stable and hence less reactive. It is also known that increasing the number of hydroxyl groups enhances the stability of the surface as well.<sup>28</sup> Consequently, high temperature processes (140 °C) like the T-BAG become necessary to break this network and allow reactions with the surface. As for any activated process, temperature is more important than time. Clearly, the reaction does not occur for ~10 s at 130 °C, requiring an additional 10 °C to be fully activated, that is, to rearrange the interface by reducing H-bonding.

Although the calculations are not strictly predictive, they can be the starting point for assessing whether the selective modification of silicon oxide with monodentate chemisorption is possible. Indeed, Mutin et al. have already shown that a selective surface functionalization with phosphonic acids is possible, taking advantage of the easily hydrolyzed SiO<sub>2</sub>/phosphonate interface.<sup>29</sup> However, they show that there are adsorption geometries energetically more favorable than other models depending on the chemical potential of water. If one could control all of the parameters of the adsorption process, the selective attachment of monodentate-bound layer seems possible. Therefore, we believe the calculations are advancing the understanding of the attachment on silicon oxide.

It is also important to state that these studies are for the case of silicon oxide, which is different from most of the other oxide surfaces. If we compare silicon oxide to another oxide surface (e.g., case aluminum oxide, see Figure 5, FH, in ref 30), we find that aluminum oxide becomes more reactive as the number of hydroxyl groups increases.<sup>31</sup> This finding is due to the fact that, in contrast to silicon oxide, the surface hydroxyl groups on aluminum oxide do not interconnect with each other, allowing them to react at lower temperatures.

## CONCLUSION

Tethering by aggregation and growth has been studied and shown to depend on the environment humidity. A high annealing temperature (140 °C) is confirmed to be necessary for activating the reaction, which readily occurs at 140 °C in a dry environment. This finding is of great value for research and industry, because shortening the heating cycle would make the T-BAG process highly suitable for industrial production processes.

It was also demonstrated that the OPDA SAM chemisorbs on the surface in a bidentate configuration. This was confirmed by the detection of the P=O and P–O modes and the loss of the P–O–H feature in the FTIR spectrum. These findings are consistent with the currently accepted model for this process, in which the well-ordered bilayers after the initial ODPA physisorption give rise to the self-assembled monolayer, once heated and then rinsed by sonication.<sup>20</sup>

The T-BAG process for phosphonic acids on silicon oxide was shown to be strongly dependent on the reaction environment. Indeed, there is no condensation reaction of the multilayer material during the first heating cycle in high humidity (RH > 40%), yet complete loss of the multilayer and chemisorption of a monolayer in low humidity (RH < 16%) upon heating. Theoretical calculations based on statistical considerations support these observations and account for the role of water at the interface.

A fundamental understanding of organic functionalization of oxide surfaces such as silicon oxide or aluminum oxide is still lacking and is definitely less developed than organic functionalization of oxide-free surfaces. This is mainly due to the difficulty in preparing well-defined surfaces that do not change in chemical composition and microstructure during the chemisorption and thus permit the formation of ordered molecular structures. Most processes on the surface of metals or alloys oxide layers lead to dissolution or coagulation of the surface, and thus disturb the process of self-assembly. So far, the T-BAG process has been plagued by inhomogeneity resulting from ill-controlled humidity levels (interface water concentrations). The new findings in low humidity environments may potentially transform its future use.

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### Notes

The authors declare no competing financial interest.

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