

Characterization of Silanated Glass Surfaces by Atomic Force Microscopy : Influence of Local Surface Energy Heterogeneities on the Apparent Molecular Topography

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Introduction

The silanation of surfaces involves the reaction of alkyl-silanes with surface hydroxyl groups, through which organic moieties are covalently bonded to the inorganic solid surface : this process has long been in use to impart a hydrophobic character to otherwise hydrophilic solids such as silicon and aluminium oxides and glasses [1, 2]. Silanes are also widely used as coupling agents, favouring the adhesion of organic polymers to mineral surfaces [3].

In order to acquire information on the organization of silanated glass surfaces according to the silanation procedure, we have undertaken a study comprising characterization by atomic force microscopy (AFM) and contact angle measurements. The AFM allowed the exploration of surface topographies at scales as small as 2×2 nanometers.

In the case of glass silanated with hexamethyldisilazane (HMDS), it showed surface features compatible with the calculated van der Waals envelope of grafted alkyl groups, as far as the topview diameter was concerned. Surface densities were in line with the surface densities expected for superficial hydroxyl groups on acid activated glass.

However, the apparent heights of these features were more than three times greater than the calculated ones : we discuss these results in terms of an effect of local heterogeneities of the substrate's surface energy on the AFM image. To our knowledge, this effect has not been reported previously.

Experimental methods

Preparation of samples

All samples were prepared starting from 24 mm \times 32 mm Rouvier glass slides for light microscopy, taken from the same box. The slides were treated for two hours in a boiling mixture composed of equal volumes of nitric and sulphuric acids, rinsed with permuted water, then dried overnight under primary vacuum at 80 °C. This treatment had two purposes : to clean the slides from possible contamination, and to activate hydroxyl groups on the glass surface. The acid activated slides will be now denoted as AA.

The acidic treatment is expected to activate an average of 5 -OH groups per square nanometer of solid surface [4]. Little is known about the lateral distribution of these groups up to now, but it is unlikely that any kind of segregation occurs. It was expected that the distribution of -OH groups would be found homogeneous down to the nanometer scale.

The AA slides were silanated by immersion in a 15 % vol solution of silanating agent in refluxing toluene, overnight. The sila-

nated slides were then rinsed in dry toluene, followed by tetrahydrofuran (THF), mixtures of water and THF and finally permuted water. This silanation procedure, adapted from reference [1], was selected because it proved to be suitable to confer a marked, and moreover very stable, hydrophobic character to various silicate based materials involved in separate studies of multi-phase flows in porous media.

The silanating agent we used for the present study is hexamethyldisilazane (HMDS). It is monofunctional, one molecule reacting formally with two hydroxyls, liberating one molecule of ammonia and leaving two grafted groups on the glass surface. In principle, the polymerization of HMDS is not possible.

HMDS silanated AA slides, will be further denoted as AAHMDS.

Measurement of contact angles

As a measure of hydrophobicity, advancing contact angles in permuted water (Elgastat) under n-heptane (Prolabo Normapur), were recorded according to the sessile drop method, using a G40 Kruss goniometer. The reported values are averages for each side of at least 3 drops. The standard deviation gave an estimate of the magnitude of the contact angle hysteresis and of the macroscopic homogeneity of the surface properties for each sample.

Atomic force microscopy (AFM)

We used an optical beam deflection type AFM in the attractive contact mode (Nanoscope II from Digital Instruments). The force sensors were commercial micro-fabricated Si_3N_4 cantilevers (force constant $K \# 0.12 \text{ N.m}^{-1}$, resonance frequency $\omega_r \# 100 \text{ kHz}$). All AFM experiments were performed in air under ambient conditions (air-conditioned, $T = 20 \pm 1 \text{ }^\circ\text{C}$, relative humidity $30 \pm 5 \%$).

The samples were scanned at constant force in the range 10^{-8} – 10^{-9} N . Scan rates were usually in the 5–20 Hz range, depending on the sample and scale of observation.

Molecular modelling

In order to obtain estimates for the dimensions of the grafted hydrocarbon groups, we undertook some computer simulations. The surface of glass was represented by clusters of 4 SiO_4 tetrahedrons sharing oxygen atoms at apices. The central Si-O was taken site. The peripheral dangling bonds were saturated by hydrogen atoms. An example of such a model for the case of $-\text{Si}(\text{CH}_3)_3$ grafted groups is shown in figure 1.

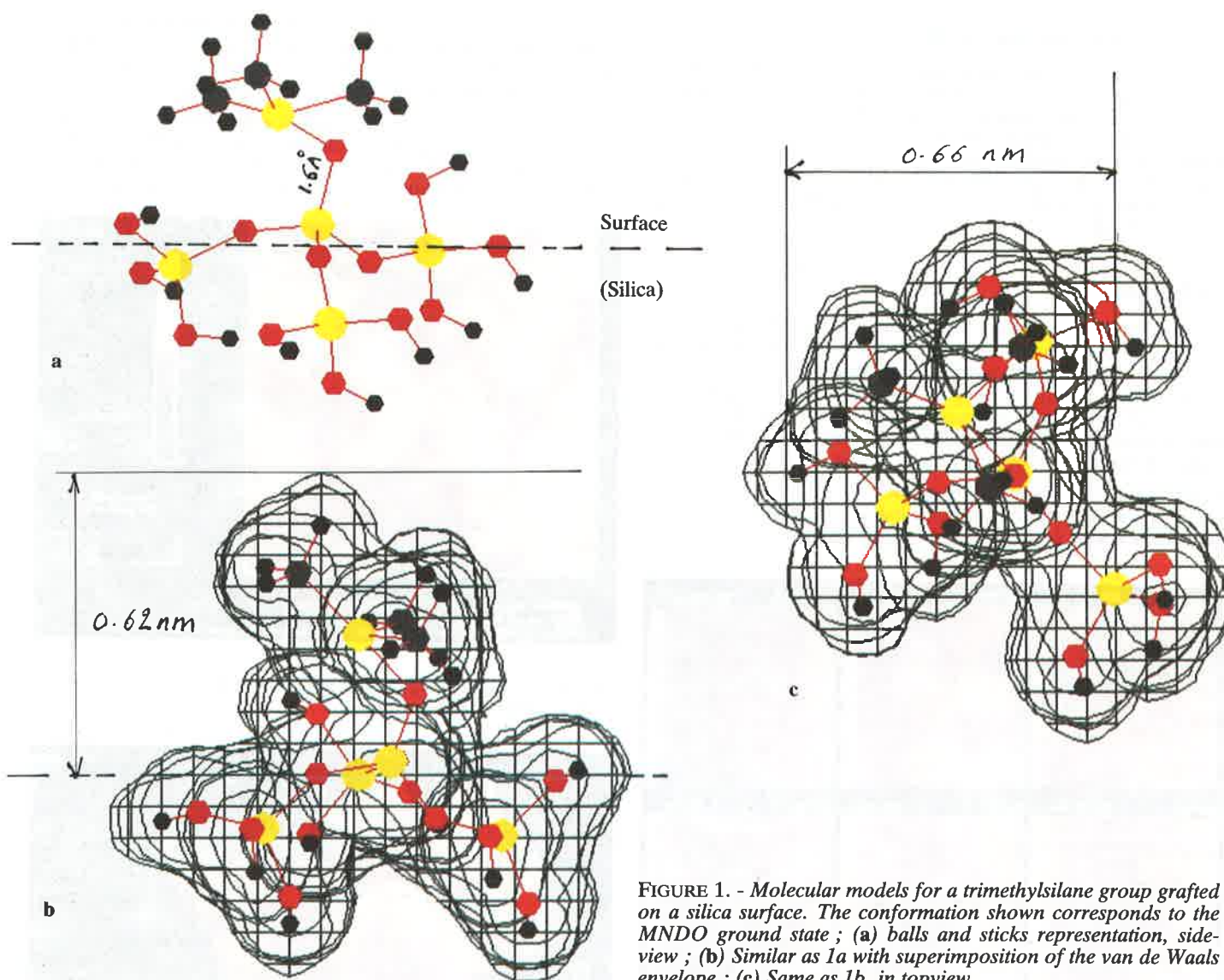


FIGURE 1. - Molecular models for a trimethylsilane group grafted on a silica surface. The conformation shown corresponds to the MNDO ground state ; (a) balls and sticks representation, side-view ; (b) Similar as 1a with superimposition of the van de Waals envelope ; (c) Same as 1b, in topview.

In order to determine the geometries at the minimum total energy and ground state (0 K), and the corresponding van der Waals envelopes, semi-empirical self-consistent-field quantum mechanics calculations were performed on such model clusters. For that purpose we chose the MNDO method [5], as implemented in the Mopac package [6], QCPE 455 version 4.1. The molecular editing, structure representations, preparation of quantum mechanics files, and mapping, were done in the Chem-X environment [7]. All calculations were performed on a VAX 3520 workstation.

Results

Wettabilities

The contact angles were measured on freshly prepared samples and after exposure to short wavelength UV light for 2 hours under a gentle flow of air. The ozone (O_3) formed in these conditions in the proximity of the surface is able to oxidise completely all organic materials in the adsorbed layer. The contact angle results are presented in table I.

TABLE I. - Contact angle results for the glass and silanated glass samples. The bracketed figures are the observed standard deviations on the angle. The contact angles are measured with water, under *n*-heptane.

Sample	As prepared	UV/ O_3 treated
Glass	47 (3)	21 (3)
AA	70 (1)	20 (1)
AAHMDS	125 (4)	15 (5)

The AA sample appears surprisingly less hydrophilic than the original glass. After UV/ O_3 both glass and AA give the same relatively low contact angle in water : this treatment has standardized the glass wettability.

The silanated glass show, as expected, a high contact angle in water. However, there is still partial wetting by water.

The UV/ O_3 oxidised AA HMDS sample wettability can be compared to that of the oxidised glass and AA glass. It is slightly more hydrophilic on average, but with a higher standard deviation, which indicates some degree of heterogeneity of the surface's wettability, possibly some hysteresis of wetting.

Molecular modeling results

All the results of interest for the present study have been summarized in figure 1. Figure 1a shows a sideview of the optimized configuration of the trimethyl group grafted on the SiO_2 cluster. Figure 1b shows a similar sideview, with the calculated van der Waals envelope superimposed. Figure 1c is a topview, with the van der Waals envelope. The van der Waals envelope was calculated assuming standard tabulated van der Waals radii for all atoms involved.

AFM results

Figure 2 shows unfiltered data obtained on AAHMDS on zooming down from 300 nm to 2 nm. Figure 3 concentrates on the aspect of AAHMDS at very small scales (10, 5, 2 nm from left to right). The three images of the top row are unfiltered, while a passband filter has been applied to the data of the bottom row, in order to cut off wavelengths shorter than 0.05 nm and supposed without physical meaning.

Figure 2 and 3 reveal at scales smaller than 20 nm a carpet-like aspect which is consistent with the expected surface topography for a surface with grafted trimethylsilane groups.

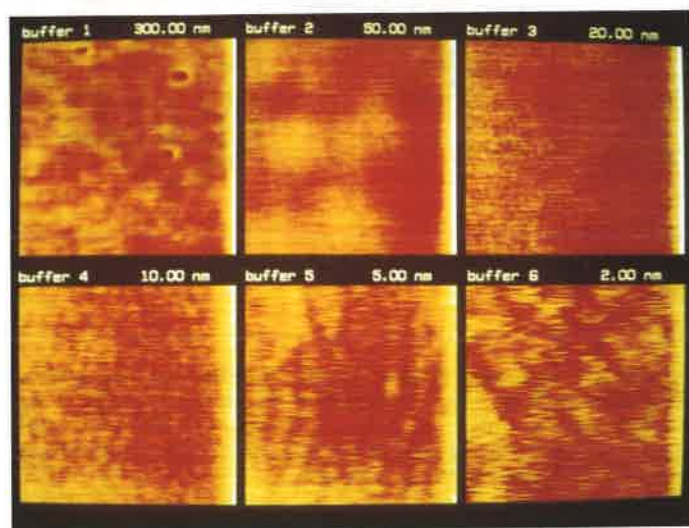


FIGURE 2. - AFM images obtained on AAHMDS at various scale. Unfiltered data.

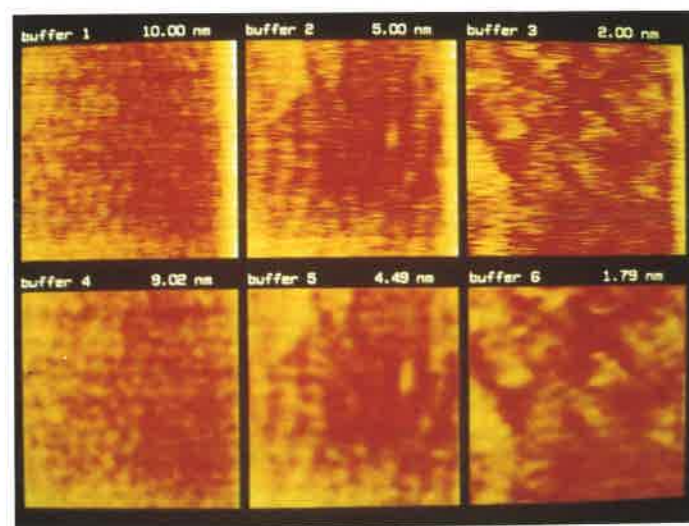


FIGURE 3. - AFM images obtained on AAHMDS at small scales. Top row, unfiltered data. Bottom row, filtered data (see text).

Each one of the fuzzy yellow domains, approximately 0.5 nm in diameter, which can be distinguished on the pictures as individual "hairs" of a brush, would thus correspond to such an organic surface group, directly observed for the first time.

Figure 4 and 5 present a topview and a perspective view of the same filtered data respectively, showing the $-\text{O}-\text{Si}(\text{CH}_3)_3$ surface groups in a square of sides 1.8 nm at the AA HMDS sample's surface. This assignment will be discussed in the next section.

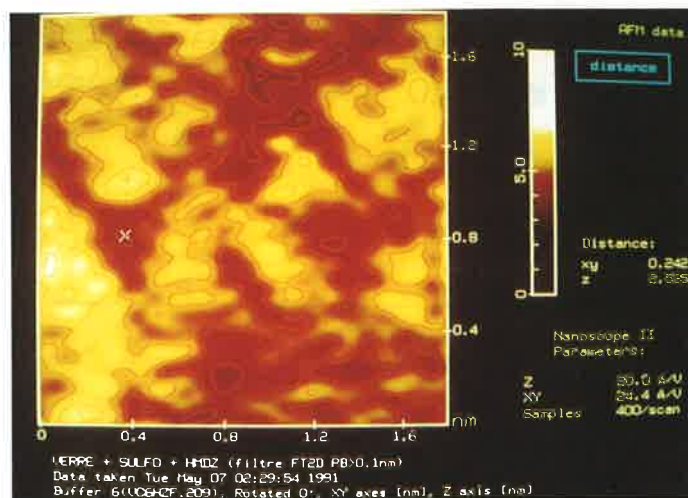


FIGURE 4. - AFM image obtained on AAHMDS at the nanometer scale. Topview. Filtered data.

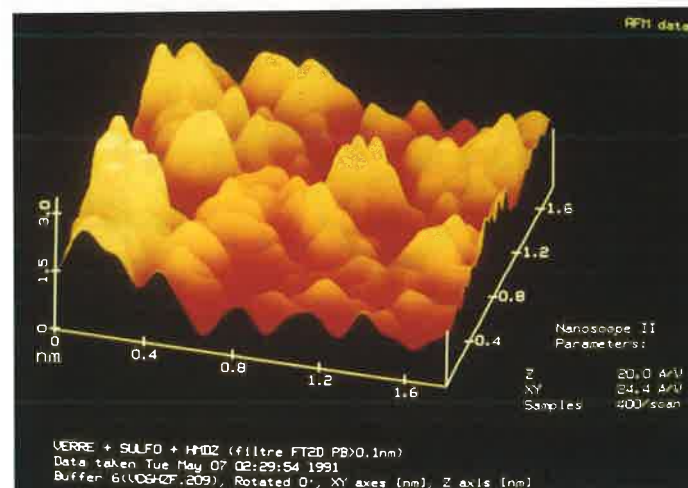


FIGURE 5. - AFM image obtained on AAHMDS at the nanometer scale. Filtered data. View in perspective.

Figure 6 presents a section analysis of the apparent topography at the 9×9 nm scale. The Fourier spectrum of the section profile shows a distinct peak corresponding to the wavelength 0.69 nm.

Figure 7 is a bearing curve analysis of the same 9×9 nm area. The average apparent height of surface features is 1.9 nm.

Discussion of results

On counting the "hills" (yellow dots) in Figures 3 and 4, and dividing by the respective areas of scanning, one finds an average density value of 3 per square nanometer. This density is consistent with the typical Figure usually reported for $-\text{OH}$ groups surface densities in the case of silicas [4]. Because HDMS is mono-functional, it is expected that each surface $-\text{OH}$ has reacted with one $-\text{Si}(\text{CH}_3)_3$, and thus, the expected density for the grafted groups is also 3 nm^{-2} .

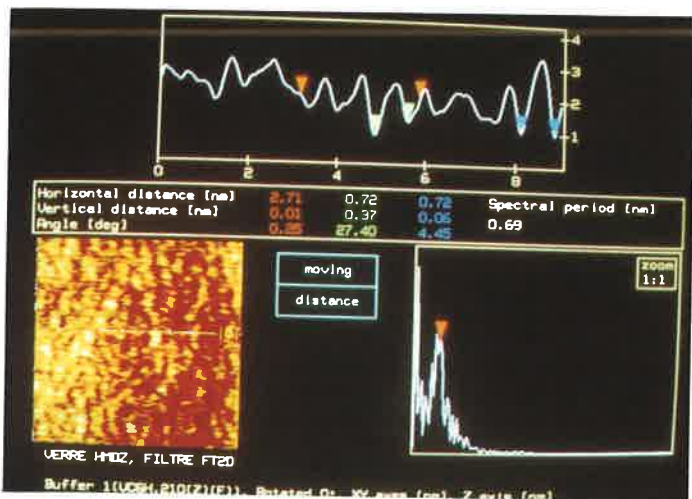


FIGURE 6. - AFM image obtained on AAHMDS at the scale 10×10 nm. Unfiltered data. Section analysis.

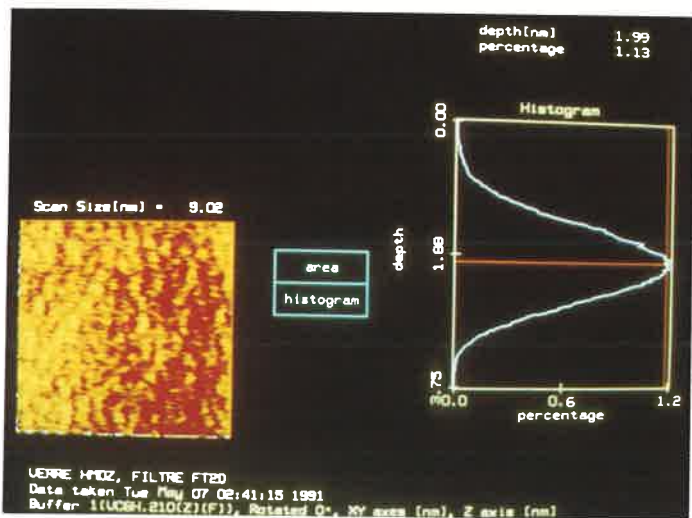


FIGURE 7. - AFM image obtained on AAHMDS at the scale 10×10 nm. Unfiltered data. Bearing area analysis.

According to our MNDO calculations, the equivalent diameter, in topview, of the van der Waals envelope of one grafted group should be close to 0.7 nm (see figure 1c). This dimension corresponds very well to the average size of our AFM "hills", as shown for instance by the occurrence of a peak at wavelength 0.69 nm in the Fourier spectrum of Z profiles from the images (figure 6).

However, the calculated height of the grafted group VdW envelope is around 0.6 nm, whereas our AFM results give an average peak to valley amplitude of 1.9 nm (see figure 7). We have therefore a discrepancy of a factor 3.2. In other terms, the aspect ratio of the presumed grafted group is different than expected.

We propose that the origin of this discrepancy is in the heterogeneity of surface energy at the molecular scale on that sample, where $-\text{Si}(\text{CH}_3)_3$ groups are not densely packed, but on the contrary allow the tip to probe the underlying glass surface in the intervals.

We can try to rationalize this idea as follows :

We used Si_3N_4 cantilevers furnished by Digital Instruments. In air, a very thin oxidation layer covers Si_3N_4 , which has consequently the same surface properties as silica : it is hydrophilic [8].

As the tip scans over the glass surface, the tip-sample interaction is attractive, and the tip-sample distance is regulated by the loop in order to maintain the preset deviation of the cantilever. As the tip scans over a hydrophobic trimethyl surface group, it will become less attracted and will tend to disengage. In order to recover the prescribed cantilever deflection, the piezo will have to pull off the sample up to the point where the other adhesive components of the attractive interaction (wetting forces induced by the adsorbed fluid layer) will have compensated for the local hydrophobicity. This change of the tip sample distance will proceed in the same direction as the change induced by a local hill on the surface, and consequently will be recorded as a hill, but without topographical meaning. The concept is illustrated in figure 8.

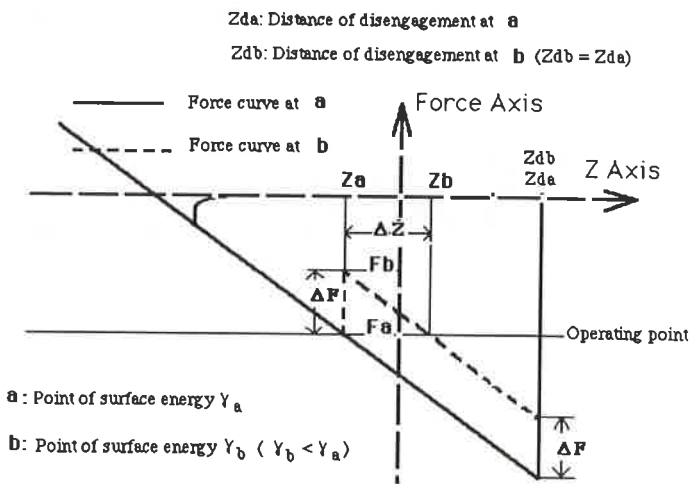


FIGURE 8. - Force-distance relationships in case of a sample with a local heterogeneity of surface energy.

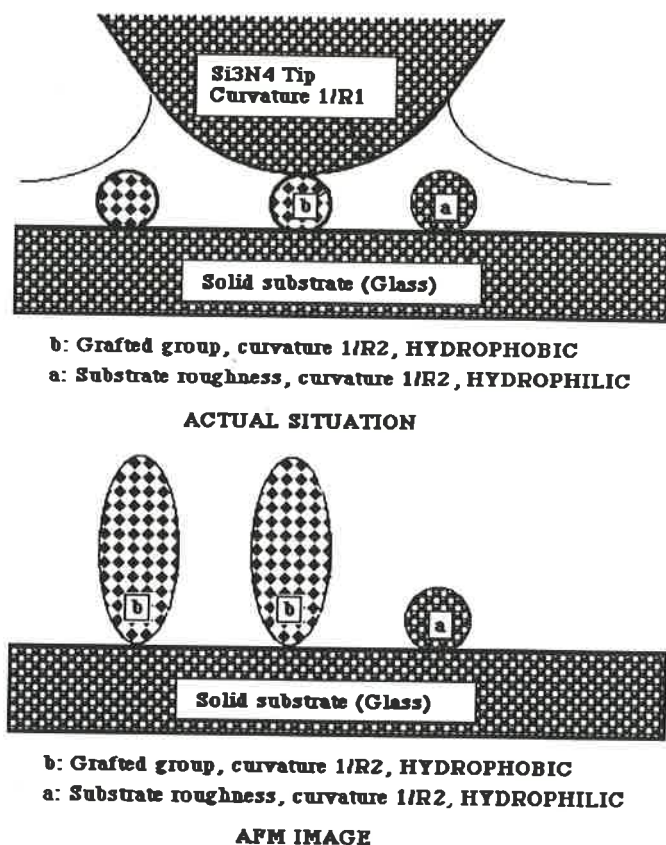


FIGURE 9. - Effect of a local heterogeneity of surface energy of the solid on the AFM image in attractive contact mode.

Conclusions

Silanated glass surfaces have been imaged at the nanometer scale by atomic force microscopy.

With hexamethyl-disilazane as silanating agent, each hydroxyl surface group was expected to have reacted, giving a few grafted $-\text{Si}(\text{CH}_3)_3$ groups per square nanometer. According to our MNDO calculations, the van der Waals envelope of such groups was expected to be approximately spherical, with a diameter of 0.6-0.7 nm.

The AFM results were consistent with these expectations except for the apparent height of the surface features believed to correspond to the grafted trimethyl groups.

We interpret this discrepancy in terms of an effect of the surface energy heterogeneity displayed by our samples at the sub-nanometer scale.

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