Hierarchy of adhesion forces in patterns of photoreactive surface layers

Gregor Hlawacek,[1] Quan Shen,[1] Christian Teichert,[1,a)] Alexandra Lex,[2,b)] Gregor Trimmel,[2] and Wolfgang Kern[3]
[1]*Institute of Physics, University of Leoben, 8700 Leoben, Austria*
[2]*Institute for Chemistry and Technology of Materials, Graz University of Technology, 8010 Graz, Austria*
[3]*Institute of Chemistry of Polymeric Materials, University of Leoben, 8700 Leoben, Austria*

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Precise control of surface properties including electrical characteristics, wettability, and friction is a prerequisite for manufacturing modern organic electronic devices. The successful combination of bottom up approaches for aligning and orienting the molecules and top down techniques to structure the substrate on the nano- and micrometer scale allows the cost efficient fabrication and integration of future organic light emitting diodes and organic thin film transistors. One possibility for the top down patterning of a surface is to utilize different surface free energies or wetting properties of a functional group. Here, we used friction force microscopy (FFM) to reveal chemical patterns inscribed by a photolithographic process into a photosensitive surface layer. FFM allowed the simultaneous visualization of at least three different chemical surface terminations. The underlying mechanism is related to changes in the chemical interaction between probe and film surface. *© 2009 American Institute of Physics*. [DOI: 10.1063/1.3062841]

I. INTRODUCTION

Modern low cost devices are increasingly based on organic semiconductors. This important class of materials allows to achieve well-priced thin film transistors and optical components such as light emitting diodes. An important intermediate step in this technology is the possibility to control the growth behavior of active organic materials in terms of orientation and structure on short length scales. To do so patterned thin surface layers or self-assembled monolayers can be used. The patterning of such films can be achieved in various ways including but not limited to soft lithography,[1,2] scanning probe techniques (dip pen lithography,[3] nanografting,[4,5] etc.), energetic beams (UV-light,[6] electrons,[7,8] etc.), and many more.[9]

Here, we present a friction force microscopy (FFM) study of thin surface layers of a photosensitive thiocyanate-functionalized trialkoxysilane on silicon oxide (SiO_x). These films can be reliably prepared on this technological important surface with a high degree of control over the final film thickness. However, more important is the fact that these films can easily be modified by UV-light and subsequently functionalized.[10]

As different end groups of the molecule will have different interactions with the probe of the atomic force microscope (AFM), FFM (Ref. 11) allows to differentiate between them. Although FFM is an AFM technique performed in contact mode it has also been successfully applied to soft samples[12] and especially to the characterization of thin surface layers and self-assembled monolayers.[13–15] Using this technique, four different terminations could be distinguished on a sample that has been subsequently irradiated twice using line masks with different feature spacings. As a result the different terminations could be hierarchically ordered by their interaction strength with the AFM probe.

II. EXPERIMENTAL

For the preparative work of the organic thin surface layers, hazardous chemicals and solvents are used (ammonium thiocyanate, methanol, propylamine, 2,2,2-trifluoroethylamine, and piranha solution). In addition, piranha solution is explosive, and its preparation is highly exothermic (up to 120 °C). Therefore, reactions must be carried out in a fume hood, and protective clothes and goggles must be used! UV irradiation causes severe eye and skin burns. Precautions (UV protective goggles and gloves) must be taken!

The photoreactive surface layers were prepared by immersion of pretreated (by piranha solution) boron doped silicon wafers into a solution of trimethoxy[4-(thiocyanatomethyl)phenyl]silane (Si-SCN) in toluene. X-ray reflectivity measurements revealed a film thickness of 6 nm for these films. It has to be emphasized here that obviously this is not a monolayer but an oligolayer with a thickness corresponding to five or six individual layers (assuming upright standing molecules). The formation of oligolayers is attributed to cross-linking of the trimethoxysilane groups in the presence of water.[16] In a subsequent step, the samples were illuminated with UV-light under inert gas to avoid photo-oxidation (254 nm, 80 mJ/cm^2). The illumination leads to an isomerization of the benzyl thiocyanate (Si-SCN) group to the corresponding benzyl isothiocyanate (Si-NCS). This illumination step was done by utilizing a contact mask with equidistant lines and spaces to create a pattern on the surface, which consists of alternating stripes of Si-SCN and Si-NCS. For selected samples, an additional posi-

a)Electronic mail: teichert@unileoben.ac.at. URL: http://www.unileoben.ac.at/~spmgroup.
b)Present address: Institute of Physical Chemistry, University of Münster, 48149 Münster, Germany.

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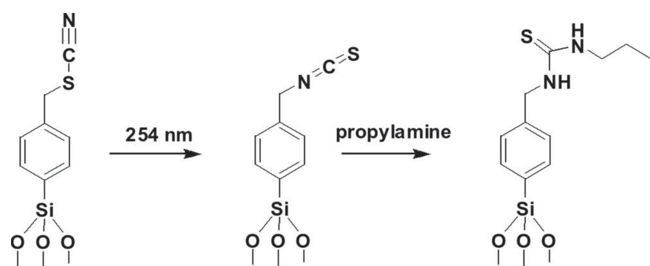

FIG. 1. Reaction pathway and products investigated by FFM.

somerization modification was performed by exposing the surface to vapors of propylamine. In this process the isothiocyanate group reacts to the corresponding thiourea group (Si-PA). The sequence of the reaction steps together with the respective molecular structure is shown in Fig. 1. A detailed description of the film preparation has already been given elsewhere.[10]

The AFM results were obtained with a Digital Instruments Multimode IIIa AFM. To reduce damage to the film, the topographic images were recorded in intermittant contact mode, eliminating effectively lateral forces between the tip and the sample surface. For intermittant mode conventional Si probes with a typical resonance frequency of 300 kHz were used. For roughness characterization, the rms-roughness σ, the lateral correlation length ξ, and the Hurst parameter α were calculated from the images using the height-height correlation function.[17] All roughness parameters have been obtained by analyzing at least three independent 5 μm images. FFM (also called lateral force microscopy or chemical force microscopy)[11,18] is a special type of contact mode AFM. Lateral forces acting on the tip will twist the cantilever, when scanned perpendicular to its long axis, leading to a deflection of the laser on the four-quadrant photodiode in lateral direction. The twist of the cantilever depends on the friction between the tip and the sample surface. As cantilevers, specially designed FFM rectangular beam type cantilevers made from silicon are used. The cantilevers have a nominal length of 225 μm and a force constant of typical 0.2 N/m.

The lateral force acting on the tip is influenced by the friction coefficient between tip and sample surface. This coefficient depends on the interaction between the tip and the terminating group of the molecules forming the thin film.[19] For a clearer contrast, FFM images are calculated from trace and retrace images obtained simultaneously with the topographic image.[20] This effectively reduces false FFM contrast originating from the surface morphology. The presented images are therefore always calculated from (trace-retrace)/2. For the presented FFM images no scale is given as no force calibration was performed prior to the measurement. Thus, information that can be obtained is purely qualitative; however, it bears sufficient accuracy allowing to establish a hierarchy of adhesion forces.

III. RESULTS

Figure 2 presents AFM topography images demonstrating the effect of film preparation on surface roughness. Homogeneous films of Si-SCN [Fig. 2(b)], and propylamine modified Si-NCS (Si-PA) films [Fig. 2(c)] were prepared and compared to the surface of the bare substrate [Fig. 2(a)].

The surface of the substrate [Fig. 2(a)] shows a uniform featureless topography as expected for a silicon oxide surface. The root mean square (rms) roughness of $\sigma=0.2$ nm, the lateral correlation length $\xi=30$ nm, and the Hurst parameter $\alpha=0.5$ confirm the qualitative observation. Investigations of polished silicon wafers report a much larger correlation length.[21] We address the smaller values given here to the limited AFM scan length applied for the roughness analysis and to differences in sample preparation (plasma etching).[10] Deposition of a thin layer of Si-SCN and subsequent illumination with 254 nm UV-light for 20 min [resulting in a Si-NCS film shown in Fig. 2(b)] leads to an increase in the rms-roughness: $\sigma=0.3$ nm, $\xi=30$ nm, and $\alpha=0.5$. As mentioned above, X-ray reflectivity measurements revealed a film thickness of 6 nm for this layer.[10] Modifying the surface with vapors of propylamine [Fig. 2(c)] leads to a further increase in rms-roughness ($\sigma=0.4$ nm, $\xi=20$ nm, and $\alpha=0.5$). The increase in the vertical roughness and the change in ξ can be mainly attributed to contamination of the sample surface due to handling and residue from the chemical compounds used during modifications and cleaning.

In the following, FFM data of the patterned films are presented. Figure 3 compares the topographic image (a) obtained on a Si-SCN layer that was illuminated through a stripe mask with 10 μm lines and 10 μm spaces to the simultaneously recorded FFM image (b). Whereas in the topography image no stripe pattern is visible, a stripe pattern with a 10 μm pitch appears in the FFM image. In all FFM images presented, bright areas mean higher friction and dark ones correspond to lower friction. It will be demonstrated below that the high friction areas correspond to the illumi-

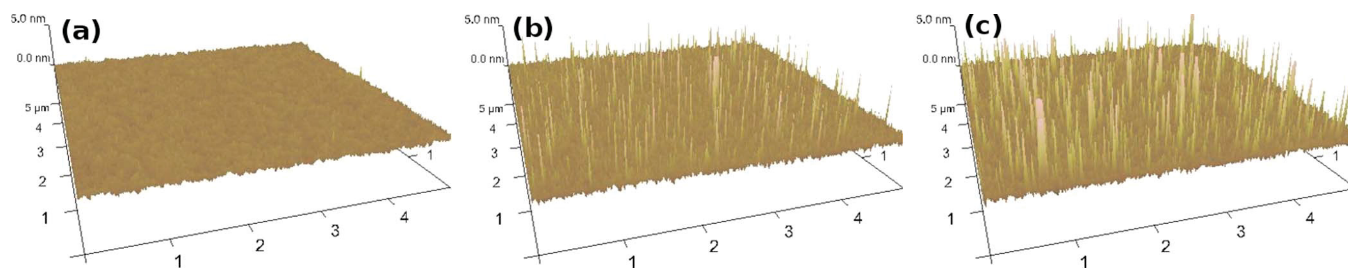

FIG. 2. (Color online) AFM topography images recorded in intermittant mode of (a) the SiO_2 substrate, (b) the film after Si-SCN deposition and subsequent flood illumination with 254 nm UV-light, and (c) modification with propylamine. (z-scale in all images is 5 nm.)

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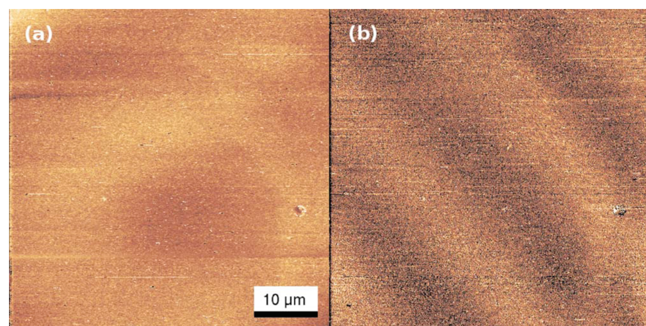

FIG. 3. (Color online) Topographic (z-scale: 10 nm) (a) and corresponding friction force images (b) from a Si-SCN film patterned with 254 nm UV-light through a 10 μm mask. In the FFM image (b) bright areas correspond to Si-NCS terminated areas showing high friction. The dark stripes are the nonilluminated Si-SCN areas.

nated Si-NCS stripes and the low friction areas are the pristine Si-SCN stripes covered by the mask during illumination.

Figure 4 shows AFM images obtained after the patterned sample described above has been exposed to vapors of propylamine. While the topographic image presented in Fig. 4(a) shows a weak stripe pattern with the expected spacing, the corresponding FFM image in Fig. 4(b) allows a clear identification of the line pattern created by contact lithography and of errors in the masking process (lower right corner). From the combined cross section in Fig. 4(c) the height difference of 0.5 nm between the modified Si-PA and the pristine Si-SCN stripes is clearly discernible. The addition of an alkyl group to the molecule will result in an increase in the film thickness. The 6 nm thick films of Si-SCN (and also after illumination—the Si-NCS films) are cross-linked. Thus, it is difficult to predict the theoretical increase in film thickness after reaction of the NCS units with gaseous propylamine. Assuming that all Si-SCN units present in the polymer photoisomerize to Si-NCS and, if the postexposure reaction with propylamine (to give thiourea units) proceeds at 100% yield, a total increase in volume (and thickness) by 30%–40% can be expected. This is deduced from the molecular structure of the compounds. However, from earlier studies,[10,22] it is known that the yield of the photoreaction (from SCN to NCS) is approximately 30%, but the reaction of NCS with propylamine is almost quantitative. From the discussion above, an increase in layer thickness by about 10% or 0.6 nm for the modified part (Si-PA) is reasonable and meets our expectations. However, as these reactions proceed in a cross-linked network, the calculation remains somewhat speculative. These propylamin modified areas show a lower friction signal. Areas of lower height correspond to nonilluminated (and unmodified) zones of the layer containing Si-SCN structures, which give a higher friction than the Si-PA structure.

In a further experiment, the surface has been exposed twice to illumination using crossed masks with an intermediate propylamine reaction step. The whole sample preparation process is sketched in Fig. 5(a). In a first step, a mask with 5 μm lines and spaces was employed during UV illumination. After the Si-SCN film has been exposed to vapors of propylamine, a surface layer made up of alternating 5 μm stripes of Si-SCN and Si-PA is created. The resulting pattern is similar to the one presented in Fig. 4. This modified film was now illuminated for a second time through a mask with 10 μm lines and spaces oriented perpendicular to the first mask pattern. During this step both stripes, Si-PA as well as Si-SCN, are illuminated partly. It can be expected that the Si-PA surface will not change significantly during this process. However, the remaining Si-SCN stripes will be converted into alternating 10 μm patches of Si-SCN and Si-NCS. The resulting surface morphology and the friction image are presented in Figs. 5(b) and 5(c). As in the previous case, the main features in the topographic image [Fig. 5(b)] are not related to the mask process but result from contamination and small long range undulations in the SiO_x surface of the wafer. However, the FFM image shows a clear pattern of regular 5×10 μm^2 patches of four different shadings, i.e., of four friction levels. One might argue that there is a slight change in the overall level of friction across the presented image. The observed shift in total friction might be attributed to deposits of film material on the tip apex due to minimal wear of the film. This can result in a slight change in the tip sample interaction while measuring. In addition, it is the nature of the multistage patterning process that small and random changes in the actual film homogeneity and

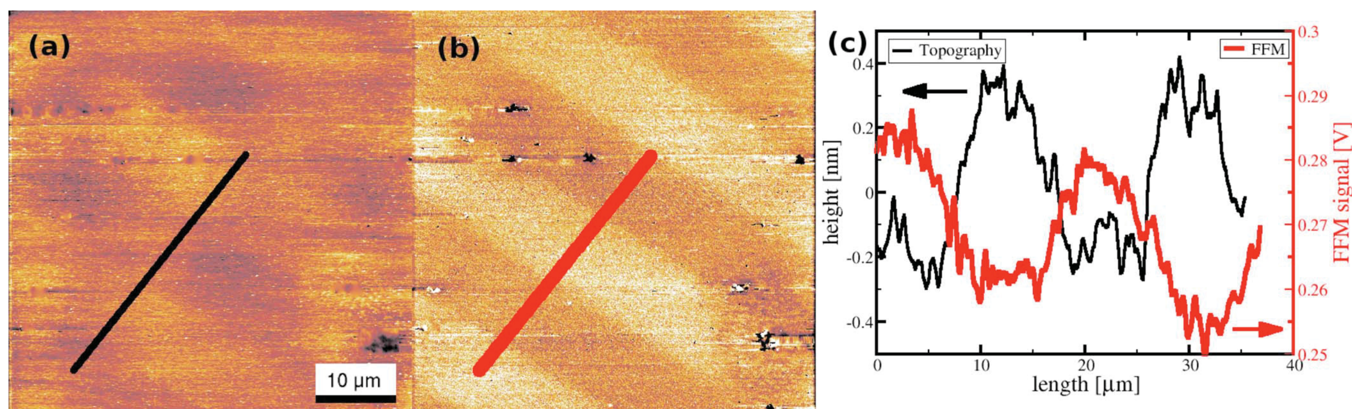

FIG. 4. (Color online) 50 μm topographic (z-scale: 5 nm) (a) and FFM (b) images from a patterned Si-SCN/Si-PA film. The pattering has been done through a contact mask with a 10 μm pitch. (c) Indicated cross sections reveal the expected 10 μm pitch in both topography and friction contrast. The Si-PA stripes are roughly 0.6 nm higher than the Si-SCN stripes.

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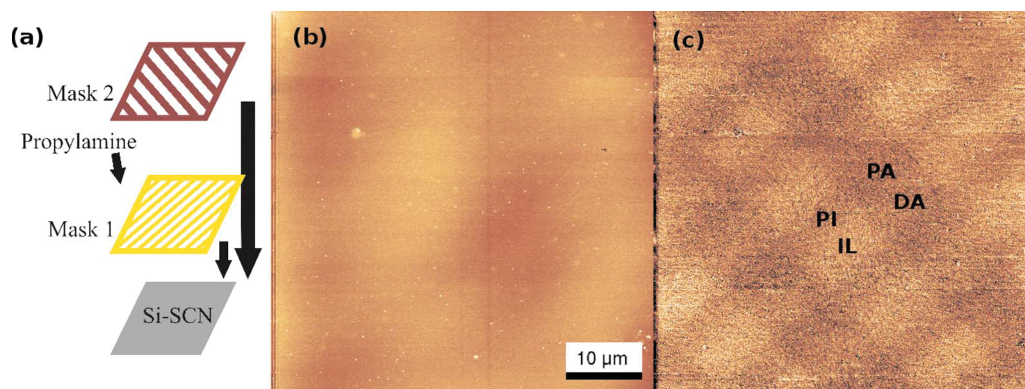

FIG. 5. (Color online) (a) Scheme of sample preparation: Illumination of Si-SCN through a 5 μm mask (mask 1); exposure to propylamine; second illumination through a 10 μm mask (mask 2). (b) Resulting topographic (z-scale: 10 nm) and (c) corresponding FFM images from the double patterned Si-SCN/Si-PA/Si-NCS film. The respective materials are indicated in the FFM image (see text).

roughness may occur, leading to the fact that the lower left corner of Fig. 5(c) shows a higher overall friction than the rest of the image. Thus we are confident that the friction data essentially show only four different levels of interaction in agreement with the four different terminations in the pattern.

We can identify the four areas using the information on the friction contrast obtained from the patterned samples described above. The dark areas in Fig. 5(b) are the Si-PA areas (labeled PA) created in the first illumination step. The neighboring brighter patches (PI) in the 5 μm stripe are the Si-PA areas that were subsequently illuminated a second time. In the neighboring 5 μm stripes (shadowed during the first illumination) one patch has been protected by the mask in both illumination steps (DA) while the other one has been exposed to UV-light a single time during the second illumination (IL). The last two areas are comparable to those shown in Fig. 3 and therefore allow the identification of the stripes in Fig. 3(b). The areas marked PA and DA are comparable to the combination shown in Fig. 4.

The observed friction contrast can therefore be ordered in the following way: The highest tip-film interaction and therefore the largest friction are observed for Si-NCS (IL) followed by Si-SCN (DA) and the two propylamine modified surfaces [PI and PA in Fig. 5(b)].

A possible explanation for this sequence can be given by the different polarity of the individual end groups at the surface [thiocyanate (Si-SCN), isothiocyanate (Si-NCS), and propyl (CH_2-CH_2-CH_3, Si-PA)] and by the stiffness of the molecular end groups.

Comparing data on the dipole moment of ethyl isothiocyanate (3.67 D) and ethyl thiocyanate (3.33 D) as well as on the surface tension γ (at 20 °C) of these compounds (ethyl isothiocyanate: γ=36.0 mN/m and ethyl thiocyanate: γ=34.8 mN/m) it is found that isothiocyanates are of higher polarity than the corresponding thiocyanates.[23] Assuming that the friction force between the surface and the silicon tip (which is covered with a native oxide layer) increases with the polarity of the surface, for the UV illuminated regions (containing NCS units at the surface) a higher friction force will be recorded than for the nonilluminated regions bearing SCN units. From the above presented values it becomes immediately clear why the contrast in Fig. 3(b) is rather poor compared to Fig. 4(b). The difference in surface free energy between the two terminations compared in Fig. 3 is only 1.2 mN/m.

After reaction of the photogenerated NCS groups with propylamine (PA), the surface is terminated with nonpolar alkyl groups. It is therefore not surprising that the postexposure derivatization with propylamine will result in a lower friction force. Also the stiffness of the molecule is reported to influence the resulting friction coefficient.[14,24] The flexible alkyl group that terminates Si-PA will therefore also reduce the observed friction by bending under the applied normal load. In contrast, the shorter and stiffer thiocyanate and isothiocyanate groups (Si-NCS has two double bonds between sulfur, carbon, and nitrogen; Si-SCN has a triple bond between carbon and nitrogen while the sulfur is linked by two single bonds) cannot bend under the applied load.

The intermediate friction contrast observed for areas that were illuminated and modified with propylamine and then illuminated for a second time can also be explained that way. During the second illumination, residual SCN units—which have remained unreacted in the first illumination step—are converted into NCS groups leading to an increased interaction between the surface and the AFM tip. NCS groups, which have reacted with propylamine (to yield propylthiourea units), are expected to remain unchanged during the second illumination step since N,N'-dialkyl substituted thiourea groups are stable under UV-light. Especially from the last sample, the hierarchy in the interaction forces (Si-NCS $>$Si-SCN$>$Si-PA) between the individual terminating groups becomes evident.

IV. CONCLUSION

For lithographically patterned photoreactive surface layers we demonstrated that FFM is not only able to distinguish between different head groups, but also that this can be done simultaneously for at least three different terminations. The method is able to detect minute changes in the molecular end group. The case of the thiocyanate (Si-SCN) and isothiocyanate (Si-NCS) head groups is especially relevant since these are educts and products of an isomerization reaction. With proper measurement parameters, FFM is able to discern the

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two terminations, although, only the sequence of the terminating three atoms is altered. However, the resulting change in polarity of the terminating molecular groups is large enough to be detected by FFM as slightly different friction levels. In addition, the postisomerization modification with propylamine could be clearly visualized with FFM. In this case, a further reduction in polarity together with a change in the stiffness of the molecule leads to the lowest friction observed in the investigated system.

Currently, contact angle measurements are underway to obtain an independent confirmation of the observed hierarchy. The next step in future work will be to quantify the adhesive and frictional forces responsible for the qualitative results presented here. For this task a well known but time consuming and delicate approach suggested in literature will be used to calibrate the AFM probes with sufficient accuracy.[25] These studies shall include the use of functionalized tips to fine-tune the probe sample interaction.[26]

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