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Scanning Tunneling Microscopy Studies of Self-Assembled Monolayers of Alkanethiols on Gold

by

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SCANNING TUNNELING MICROSCOPY STUDIES OF SELF-ASSEMBLED MONOLAYERS OF ALKANETHIOLS ON GOLD

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Abstract

We have used scanning tunneling microscopy to probe the molecular scale structures of pure and mixed composition self-assembled monolayers of $CH_3(CH_2)_{15}SH$ and $CH_3O_2C(CH_2)_{15}SH$ on gold. A predominant defect structure is found for both films and is assigned as a void defect in the thiolate overlayer. The mixed composition films are observed to phase segregate into domains of the pure component thiolates. Time-lapse series of scanning tunneling microscope images reveal kink-driven motion at step edges and exchange of thiolate molecules on terraces.

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Introduction

Self–assembled monolayers (SAMs) are of great current interest because of potential applications in electronics, surface treatment and passivation, adhesion, and nanotechnology. These films are being used in attempts to create complex, multifunctional surface architectures such as artificial receptor sites[1] and controlled–size transport channels on electrodes.[2] For all these applications the structure, motion, and defects of these films on the nanometer scale are critically important. We have conducted a series of experiments focused on elucidating the nanometer scale structure and dynamics of SAMs of substituted alkanethiols on gold surfaces.[3–5]

In this paper we discuss mechanisms by which thiolate moieties move within SAMs of alkanethiols on gold. Two observations have led us to look for this motion. First, we observed phase segregation in mixed composition SAMs of two similar non–hydrogen bonding alkanethiols of identical alkyl chain length.[3] Second, we observed that void defects appeared to be essentially absent on narrow terraces on the Au{111} surface.[4] Both of these effects can be attributed to motion within the self–assembled film.

Experimental

Substrates were prepared by resistive evaporation of gold (99.999%) onto the surface of freshly cleaved mica which was preheated in vacuum to ~340°C.[6] The base pressure in the chamber during evaporation was $\leq 6 \times 10^{-7}$ torr. After ~100 nm of gold was deposited, the substrate temperature was returned to <40°C while still under vacuum, then the chamber was back–filled with purified nitrogen, the substrates removed, and immersed immediately in the thiol solutions. Companion substrates were prepared by evaporating ~9 nm of chromium, followed by ~200 nm gold onto cleaned surfaces of polished, native oxide–covered single crystal Si(100) wafers according to a previously reported procedure.[7] The silicon wafer surfaces were pre–cleaned by immersing the samples in a 1:4 mixture of H_2O_2/H_2SO_4 at 110°C for 10–15 minutes, followed by rinses in deionized purified water[8] and absolute ethanol. The freshly prepared $Au/Cr/SiO_2/Si$ samples were immediately characterized using single wavelength ellipsometry and then immersed directly

(maximum ambient exposure of 5 minutes) into ethanolic solutions of $CH_3(CH_2)_{15}SH$ and $CH_3O_2C(CH_2)_{15}SH$ at 1mM total thiol concentration. Five solutions were used: one pure solution of each thiol and three mixed solutions using 1:3, 1:1, and 3:1 molar ratios of the two thiols. At these concentrations, both thiols are soluble in ethanol, and readily form homogeneous solutions. The substrates were kept immersed in the solutions for 4 days at room temperature, after which the samples were withdrawn, rinsed in ethanol, and dried under a stream of nitrogen. Mica–supported samples were analyzed using STM.[9] The companion samples were then characterized by X–ray photoelectron spectroscopy (XPS), ellipsometry, and infrared spectroscopy (IRS) to verify the quality, thickness and composition of the assembled films.[10,11]

STM experiments were conducted in air using a very stable microwave–frequency–compatible, beetle–style STM,[4,12,13] but the samples were sufficiently conductive to allow use of the dc tunneling current to control the tip–sample separation.[14] The passive drift rate of this microscope is <1Å/min, which allows recording series of images of the same area for hours without drift correction. Images were recorded in constant tunneling current mode using Pt–Ir STM tips, and are shown unfiltered.

Results and Discussion

Fig. 1 shows an image of a pure composition SAM of $CH_3O_2C(CH_2)_{15}SH$ on gold when the large terraces are examined. A number of depressions in the image of the surface are found randomly distributed in this and many other images recorded. These depressions have a characteristic shape and size; they are 18–25Å in diameter and *ca.* 1Å deep. A cross section through one such depression is shown in Fig. 2. We interpret these depressions as defects in the thiolate layer on the basis of the following reasoning. Missing adsorbate defects should display definite depth characteristics as a function of the number of missing chains. In the simplest model, the chains are approximated as rigid rods tilted at 26–30° and occupying $\sim 21.6Å^2$ per chain (nearest neighbor spacing of 5.0Å on a hexagonal lattice).[10,11,17] In this model, a single missing chain would produce a narrow, deep, tilted hole in the film which would have a vertical component about 12–15Å deep (depending upon the tilt

azimuth relative to the setting planes in the unit sub–cell) with an exposed chain at the bottom. Removing any adjacent chains would expose the substrate. However, at ambient temperature, because thermal energies are significant compared to the CH_2–CH_2 rotational barriers, chains would be expected to relax conformationally into the void spaces, thereby increasing the defect span while diminishing the depth. Since the alkanethiolate layer is packed hexagonally ($(\sqrt{3}x\sqrt{3})R30^\circ$ for Au{111}), there will be six nearest neighbor and six next nearest neighbor chains around each void. If these neighbors conformationally relax to an assembly having a slightly lower (liquid–like) density, we estimate this would result in a 20Å diameter hole of 2Å depth. In reasonable agreement with this, experimentally we find that the smallest and most common defects are ~1Å deep and 20–25Å full width half minimum in the STM images. The STM does not measure topography, but rather constant contours of the local density of states, so we do not interpret this as a 1Å depression in the film surface.[18] We speculate that the smallest observed defects, as shown in Figs. 1 and 2 are due to conformational relaxation of no more than a small number of neighboring chains to fill the void left by a single missing chain. This assignment is a topic of current debate[16,20] and will be the topic of a future paper. Among the other interpretations put forward is that the defects are in the underlying Au substrate,[20] but this appears to be inconsistent with the preparation dependence of the defect morphology. When our samples are prepared with shorter incubation periods in the thiol solution, larger defects are found using STM, such as have been seen by Kim and Bard for their short incubation films.[21] An exception to the random distribution of these defects is that on narrow terraces of the Au{111} surface, *i.e.* less than 100Å wide, there appear to be far fewer void defects.[3,4]

By comparing the total areas of domains in STM images of the 1:3, 1:1, and 3:1 mixed composition SAMs, we have found that we can distinguish between phase segregated domains of the two alkanethiolates by their topographic height differences.[22] The surface density of each of the molecules is the same as the fraction of the surface covered by film that appears with a particular height. We have also verified that the film composition reflects the solution composition by reflectance infrared spectroscopy and by X–ray Photoelectron Spectroscopy.[3] In Figs. 3a–c, we

show three STM images of a 500Åx500Å area of a 1:1 mixed composition SAM of $CH_3(CH_2)_{15}SH$ and $CH_3O_2C(CH_2)_{15}SH$ on gold. Phase segregated domains are apparent in the images as regions with a 1Å height difference with the $CH_3O_2C(CH_2)_{15}SH$ domains appearing higher.[18] Two monatomic height steps in the underlying Au{111} substrate are imaged through the thiolate monolayer. We find a substantially lower density of void defects for these mixed composition monolayers than for the single component films. In addition, we find features smaller in diameter than the void defects (and than any features observed for the pure composition films) which we attribute to molecular domains as small as single molecules.[3]

Because the mixed composition SAMs phase segregate, these monolayers obviously do not represent the limiting case of an ideal solution which might otherwise be inferred from the approximate correspondence of the solution compositions and the film compositions found in macroscopic measurements.[3] Instead, we infer that the self–interaction energies of each component are larger than the cross–interaction. This would drive the phase segregation and also have the effect of creating an interface energy resulting in an "edge tension" (interface line tension) in these domains. Our observations of domain formation require that *some* fraction of the thermodynamic equilibrium character be reflected in the film formation process. Therefore, the true equilibrium structure must consist of discrete molecular domains on *some* size scale.[23]

Extensive time–lapse imaging shows that motion occurs in these films at room temperature and that two types of motion are apparent. Both of these types of motion can be found in Figs. 3a–c. First, the separated domains indicated with an arrow between them in Fig. 3a, are found to have coalesced by the time that Fig. 3b was recorded 6 minutes later, and further changes have occurred by the time that Fig. 3c was recorded 41 minutes later. Second, the Au step edges imaged through the thiolate layer are found to change shape in between images. Two changes are highlighted in the step regions circled in the images shown in Figs. 3b and 3c. The reorganization of the step edges shows that the gold surface has not entirely lost the mobility that the bare surface has in air and

solution.[4,24–26] The coalescence of the phase segregated domains is indicative of intermolecular exchange within the SAM.[3] Each of these types of motion are discussed below.

We observe that Au{111} step edges, imaged through the thiolate layer, change position and shape over periods of minutes to hours.[4] From this we infer that integral complexes of Au atoms with alkanethiolate molecules move as units along step edges. This is the kink–driven type of step flow motion discussed for bare Au{111},[25,26] and for other surfaces.[27] This process may account for a large part of the surface diffusion contribution for phase segregation mentioned above.[3]

Results on large thiolate–covered Au{111} terraces show that individual molecules within the monolayer can move. The arrow in Fig. 3a indicates regions where exchange has taken place between the time that Figs. 3a and 3b were recorded. This is inferred from the data because regions indicated by the arrow change from being at the topographic height of $CH_3O_2C(CH_2)_{15}SH$ domains to that of $CH_3(CH_2)_{15}SH$ domains, and in so doing coalesce previously isolated domains of $CH_3(CH_2)_{15}SH$. We have never observed the reverse process in which a single domain of one thiolate breaks up into two or more domains.

We draw two conclusions from the observations of this thiolate exchange and coalescence. First, since the process is proceeding unidirectionally with the domains growing by coalescence, we infer that the structure is not yet near local equilibrium, a state composed of larger and fewer domains of the two thiolate components. Second, the thiolate molecules are able to move within the densely packed monolayer. While the motion of individual molecules would be driven by thermal fluctuations, we speculate that the overall flow governing domain redistribution would be driven by the thermodynamics of the edge tension of the quasi–two–dimensional domains. Most of the observed exchanges occur at points of high curvature within the domains, lending further credence to this argument. We note that the curvature of the domain boundaries decreases and the domain sizes increase over time periods of hours. The above mechanism for diffusion of individual adsorbate species would likely be due to site hopping hindered by the surrounding monolayer. This hopping process would be governed primarily by an activation energy related to the gold–thiolate potential energy surface.[28] The observed rates of exchange are much slower than the rates at which

step edges rearrange and flow via kink and step adatom motion on the thiolate covered surfaces. The rates of motion at step edges are in turn much lower than analogous rates on bare gold surfaces in air (or halide covered surfaces in solution). We have proposed that the reduced diffusion rates are due to attractive interactions of the alkyl chains to which the Au atoms are tethered by the Au–thiolate bonds.[4]

Conclusions

Scanning tunneling microscopy has been used to image self–assembled monolayers of alkanethiols on gold, and several important observations result. First, motion of the films is observed at step edges. Second, a nearly singular type of defect has been observed and is assigned to missing chain voids filled in by conformational relaxation of molecules in neighbor and next nearest neighbor sites. Third, phase segregation and molecular exchange is observed to occur within the film in mixed composition SAMs of two similar non–hydrogen bonding alkanethiols.

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22. We can further distinguish these domains from the void defects which have a characteristic shape and size, and can occasionally be found within single component domains of the mixed composition SAMs.[3]
23. These assumptions have been tested using two–dimensional Monte Carlo simulations which show phase segregation of species A from species B when the identical A–A and B–B interactions (4kT) are larger than the A–B interactions (various values in the range 0–3.4kT).
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FIGURE CAPTIONS

1. A scanning tunneling microscope image of a 600Åx600Å area of a self–assembled monolayer of $CH_3O_2C(CH_2)_{15}SH$ on Au. The image was recorded in constant current mode at a tunneling current of 2 nA and a tip bias of $^{-}$2V. A number of features which have been assigned as void defects appear as depressions in the image of the surface.

2. A cross section through a void defect shows the typical *ca.* 20Å full width half minimum depression.

3. Scanning tunneling microscope images of a 500Åx500Å area of a mixed composition self–assembled monolayer of $CH_3O_2C(CH_2)_{15}SH$ and $CH_3(CH_2)_{15}SH$ on Au recorded at the times shown in *hours:minutes*. The images were recorded in constant current mode at a tunneling current of 2 nA and a tip bias of $^{-}$2V. Phase segregated domains are apparent in the images as regions with a 1Å height difference with the $CH_3O_2C(CH_2)_{15}SH$ regions appearing higher. An arrow highlights domains which coalesce from image a) to image b), indicating molecular exchange within the film. Examples of regions where Au{111} step edges rearrange are circled in images b) and c).

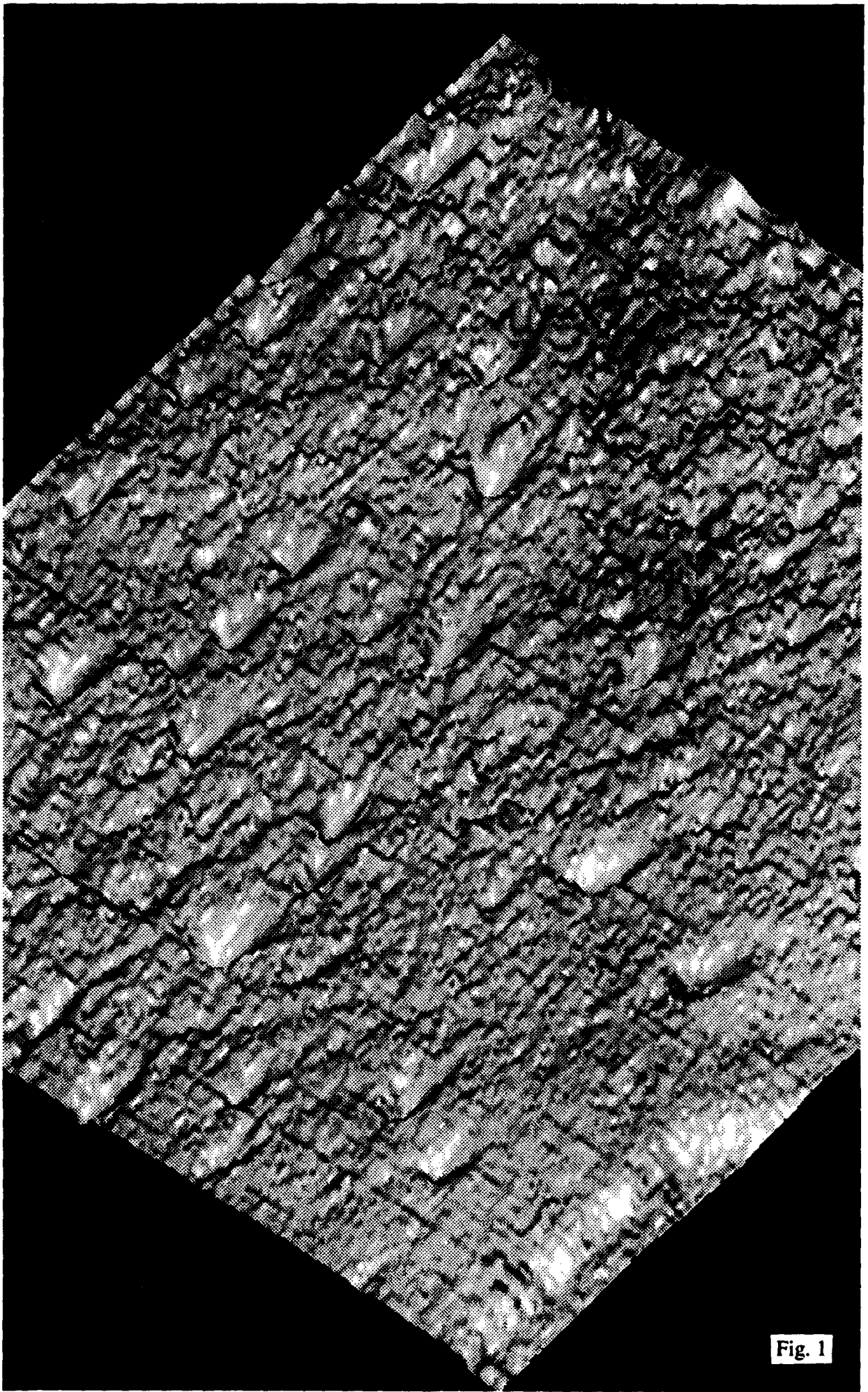

Fig. 1

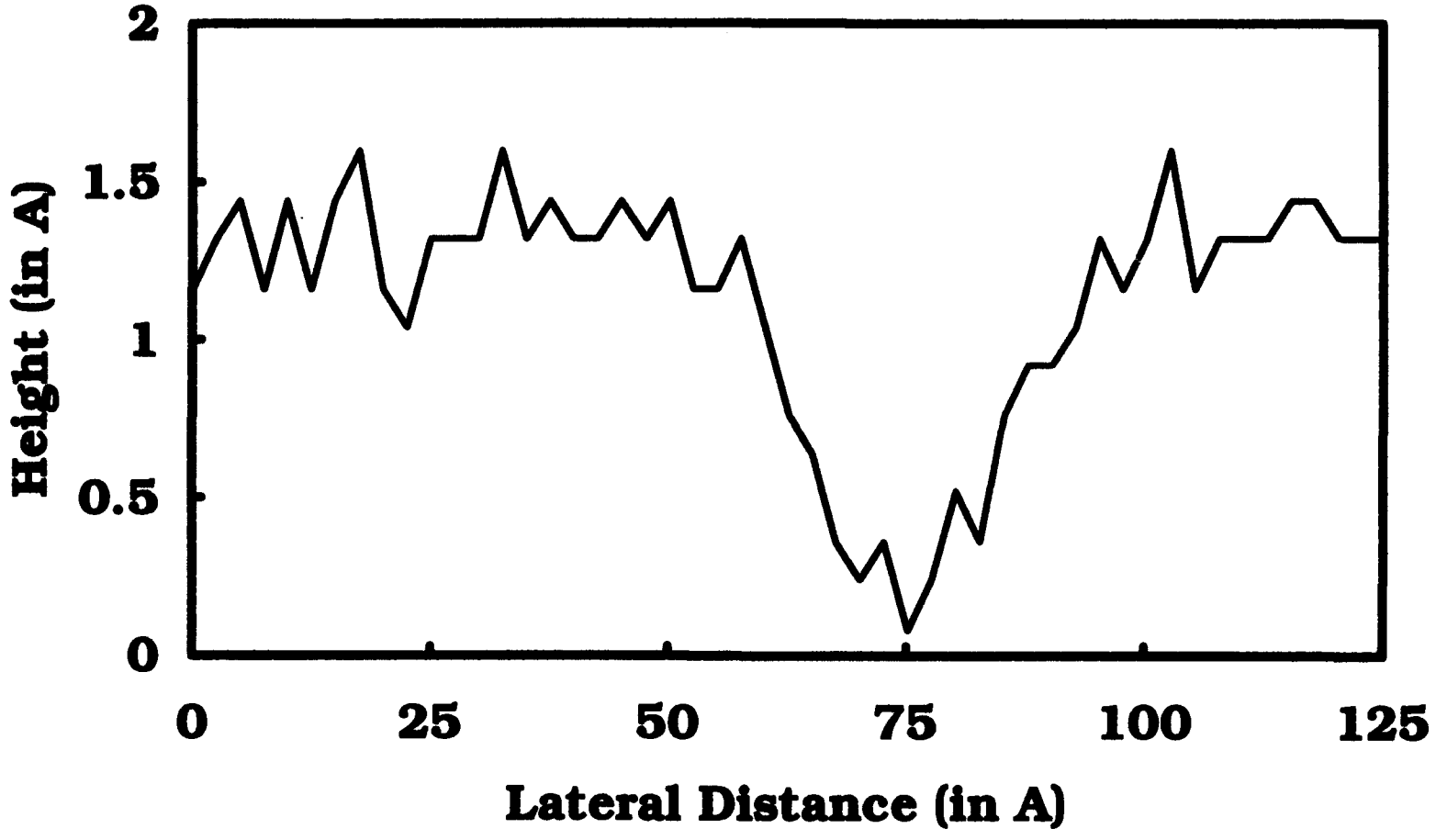

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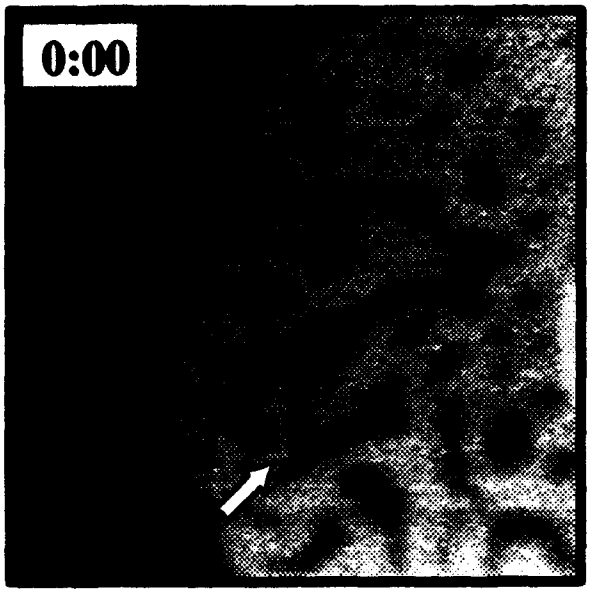
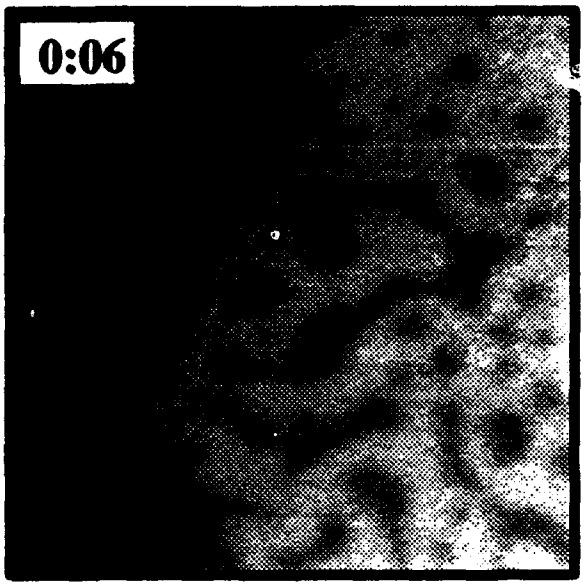
Fig. 2





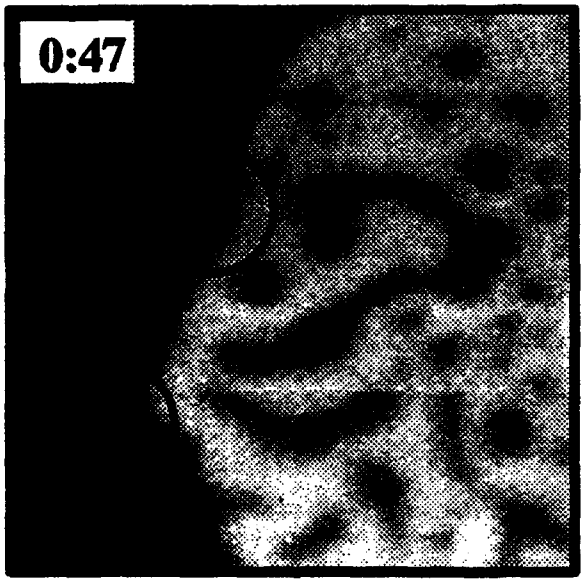


Fig. 3