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Atomic Relaxation at Ordered Electrochemical Surfaces Probed by
Scanning Tunneling Microscopy: Au(111) in Aqueous Solution
Compared with Ultrahigh-Vacuum Environments

by

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| Detailed surface atomic rearrangements at the ordered Au(111)-aqueous interface triggered by negative electrode charges are examined by in-situ scanning tunneling microscopy (STM). Not only the ($\sqrt{3} \times 22$) atomic reconstruction, but also the longer-range superstructures, formed at this electrochemical interface are seen to be remarkably similar to those observed previously by STM on clean Au(111) in ultrahigh vacuum. | | | |
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ABSTRACT

Detailed surface atomic rearrangements at the ordered Au(111)-aqueous interface triggered by negative electrode charges are examined by in-situ scanning tunneling microscopy (STM). Not only the ($\sqrt{3} \times 22$) atomic reconstruction, but also the longer-range superstructures, formed at this electrochemical interface are seen to be remarkably similar to those observed previously by STM on clean Au(111) in ultrahigh vacuum.

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Understanding the atomic structures formed at ordered monocrystalline metal surfaces by reconstruction, both in the absence and presence of adsorbates or other means of modifying the surface environment, constitutes a centrally important topic in surface science. Almost all the experimental information on surface reconstruction gathered so far refers to metal-ultrahigh vacuum (uhv) interfaces, where electron diffraction and related techniques can be employed. Similar phenomena are anticipated at metal-solution (i.e., electrochemical) interfaces, where the electrode potential offers a powerful additional means of altering the chemical and electrostatic surface state. Evidence that surface reconstruction occurs at lower potentials on low-index gold electrodes has been obtained by examining emersed surfaces in uhv.¹ The acquisition of more reliable potential-dependent information on electrochemical surface reconstruction, however, requires in-situ measurements; these have been limited severely by the paucity of suitable techniques. Nevertheless, the emergence of scanning tunneling microscopy (STM) as a means of obtaining atomic structural information for metal surfaces in electrochemical²⁻⁵ as well as uhv environments is currently altering this situation substantially. We have recently obtained in-situ atomic-resolution STM images for several aqueous electrochemical systems, including CO adlayers on Rh(111),⁴ and for clean Au(100) and Au(110).⁵ The latter systems exhibit marked surface reconstructions which are sensitive to the applied electrode potential.

We report here in-situ (STM) images at ordered Au(111)-aqueous interfaces that indicate the subtle yet striking degree of atomic relaxation that can be engendered by electrochemical means on this hexagonal close-packed metal surface. By comparison with the unusually detailed STM images obtained recently for clean Au(111) in uhv,^{6,7} the present results demonstrate how atomic-level information on both local and long-range surface relaxation can be obtained for in-situ

electrochemical interfaces with the same degree of comprehensiveness that is beginning to be achieved in uhv environments.

Gold is of particular interest to electrochemists because of its inertness and the wide polarizable potential ranges accessible even in aqueous media. Moreover, ordered monocrystalline surfaces can readily be prepared by flame annealing in ambient environments.⁸ Gold is also unique among face-centered cubic (fcc) metals in exhibiting a reconstruction even of the hexagonal close-packed (111) surface in uhv. Low-energy electron diffraction (LEED)⁹ and other diffraction or scattering techniques¹⁰ indicate an apparent (1 x 23) surface reconstruction on clean Au(111). In addition to providing a real-space representation of these corrugations on Au(111), recent uhv STM measurements have revealed beautifully the atomic domain patterns, and particularly how the long-range lattice superstructure is influenced by terrace edges and surface defects.⁶

Experimental procedures for the present electrochemical STM measurements are largely as described elsewhere.^{3,4,11} The microscope is a commercial Nanoscope II (Digital Instruments) with a bipotentiostat for electrochemical STM. The STM tips were 0.01in tungsten wire etched electrochemically in 1 M KOH. Most STM images were recorded using the "current mode", i.e., constant-height mode (see figure captions for specific conditions). The Au(111) crystal (hemisphere, 5 mm diameter) was prepared in LEI-CNRS; the nominal orientation is $\pm 0.25^\circ$. It was flame annealed, cooled in ultrapure water, and transferred to the STM cell protected by a drop of water. Electrode potentials were measured versus an oxidized gold wire, but are quoted here versus the saturated calomel electrode (SCE).

Figure 1 shows a typical unfiltered STM image of a (70 x 70Å) terrace region, obtained at 0.1 V in 0.1 M HClO₄; similar images could be obtained over the potential range ca 0 to 0.3 V.¹² A hexagonal close-packed structure, with

interatomic distances ($2.9 \pm 0.1\text{\AA}$) close to the Au hard-sphere diameter (2.89\AA), is clearly evident, diagnostic of a (1 x 1) (i.e., unreconstructed) surface. Altering the potential to lower (negative) values, however, yielded marked changes in the surface atomic structure. Figure 2A is a typical atomic-resolution STM image obtained for a $150 \times 150\text{\AA}$ terrace region under these conditions, at -0.3V . Overlaid onto the hexagonal pattern of gold atoms are corrugations appearing as parallel pairs of broad "lines" (regions of higher tunneling current) running in a $[11\bar{2}]$ direction, i.e., at an angle midway between a pair of intersecting close-packed atomic rows. The distance across the corrugated pairs (in the $[1\bar{1}0]$ direction) is $63(\pm 3)\text{\AA}$: 23 gold atoms are observed in this unit cell dimension, instead of 22 for the unreconstructed surface; hence a (1 x 22) unit cell is evident. [This structure as deduced from STM is consistent with the usual (1 x 23) designation made from diffraction, given the uncertainties inherent in the latter for large unit cell directions.] The occurrence of surface reconstruction on Au(111) in aqueous perchloric acid at potentials below ca 0.3 V has also been inferred by means of second harmonic generation;¹³ however, few structural details can be extracted by this means.

Essentially the same surface atomic arrangement has been observed by STM for clean Au(111) in uhv.¹ A comparable structure can also be inferred from recent STM data for Au(111) in air and in organic polar solvents.¹⁴ Closer inspection of the present images provides further detailed information on the nature of the surface relaxation. Figure 2B shows a magnified portion of the image in Fig. 2A, including the region between the row pairs. The atomic rows in the $[1\bar{1}0]$ direction are seen to be displaced sideways by distances up to ca 1.0\AA in the channels between the row pairs. This is consistent with an alteration from fcc to hcp stacking¹⁵ within this region, thereby yielding strictly a ($\sqrt{3} \times 22$) unit cell designation.^{6,7b} Again, the form of this atomic

relaxation is identical to that seen in uhv.⁶ The appearance of the ($\sqrt{3} \times 22$) reconstruction is relatively slow, requiring ca 5-10 mins after altering the potential negative, and appears to be triggered preferentially in regions close to terrace edges. This observation suggests that an important source of the additional ca 4.5% surface atoms required for the reconstruction is gold atoms from such domain boundaries. Indeed, some surface regions away from terrace edges remain as (1 x 1) domains under these conditions. Nevertheless, the reconstruction patterns reported here were found consistently reproducible in many replicate experiments.

Figures 3A-C give examples of the myriad of longer-range superstructures formed under these conditions. Figure 3A shows regions close to terrace edges (discerned by dark shadowed lines), including a screw dislocation. The long-range (ca 100-200Å) influence of the terrace edges in altering the corrugated structure into a more complex mosaic is evident, as is the appearance of ($\sqrt{3} \times 22$) segments running at 60° to the prevalent corrugations. The image in Fig. 3B, obtained in air, provides a clear example of a commonly observed pattern, consisting of strings of corrugations extending even across terrace edges and other defects, yet featuring periodic 60° shifts in direction (cf ref. 6). The expected appearance of three distinct rotational domains, two of which are seen in both Figs. 3A and B, is indeed observed in some images. Figure 3C is an unfiltered "height mode" (i.e., constant current) image of a 900 x 900Å region of a uniform terrace, i.e., containing no terrace edges. Nevertheless, several distinct corrugation domains are again observed. Some domains terminate in "U" shaped connections enclosing an hcp reconstructed region, similar to those observed in uhv.⁶ Several "Y" shaped faults are also observed, comparable to those discerned on Au(111) films by means of transmission electron microscopy.¹⁶ Such "height mode" images, as in Fig. 3C, also enable the amplitude of the

($\sqrt{3} \times 22$) corrugations to be estimated from the tip z-displacements. The amplitude, 0.1–0.2 Å, observed in this manner is comparable to that observed in uhv.⁶

Altering the potential back to positive values, above ca 0.5 V for 5–10 mins, yielded removal of most corrugated domains and reappearance of the prevalent (1 x 1) structure. The surface relaxation is therefore largely reversible. The shape of the terrace edges, however, tends to be altered, suggesting that the additional atoms required for the reconstruction migrate back to such sites. Cycling the potential through the anodic oxide region, above 1.0 V in 0.1 M HClO₄, produced darker blotches (apparently hollows) averaging 30 Å diameter, on the STM images (cf ref. 17). At least in ultrapure 0.1 M HClO₄, these imperfections are not removed entirely after returning to negative potentials (cf ref. 17b). Most facets of the ($\sqrt{3} \times 22$) reconstruction nevertheless return, except in the immediate vicinity of the hollows.

Given that the potential of zero charge (pzc) of Au(111) in perchloric acid is about 0.25 V,¹⁸ it is apparent that the occurrence of extensive ($\sqrt{3} \times 22$) reconstruction, yielding identical structures to clean Au(111) in uhv, requires the imposition of significantly negative surface electronic charges (ca -10 to -15 $\mu\text{C cm}^{-2}$). The lack of extensive reconstruction at the pzc, where the metal surface is uncharged as in uhv, may be due to the influence of the inner-layer water dipoles.¹⁹ Nevertheless, the deduction that excess electronic charge can provide a substantial driving force for reconstruction is in harmony with theoretical predictions for low-index noble metal surfaces.²⁰

It might be asked why the present STM images on Au(111) are apparently not affected more directly by the presence of the aqueous double-layer environment, or by adventitious impurities. While interfacial solvent and diffuse-layer (if not specifically adsorbed) ions are obviously present, these are not expected to

be imaged by STM since they should exhibit high mobility. (Only especially immobile adsorbates, such as compressed CO adlayers,⁴ should yield STM images at ambient temperatures given the long timescale, $\geq 0.1s$, of the technique.) Also, while the presence of aqueous dielectric may alter the detailed surface-tip electron-tunneling characteristics, the basic physics should be unchanged compared with short-range (elastic) tunneling through vacuum (contrast ref. 14).

Overall, then, the present findings provide clear evidence that in-situ STM measurements at ordered metal-solution interfaces can yield detailed atomic-level information on surface reconstruction on a par with that currently being achieved in uhv environments. In addition, it is apparent that such electrochemical interfaces offer a unique and powerful means of triggering and controlling surface atomic transformations at ambient temperatures. The demonstrated equivalence of such charge-induced reconstruction at the Au(111)-aqueous interface with the "clean" uhv surface as discerned here encourages the intriguing prospect of utilizing in-situ electrochemical STM as a real-time dynamical probe of atomic structural perturbations. Detailed results along these lines will be forthcoming from our laboratory.

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FIGURE CAPTIONSFig. 1

Unfiltered atomic-resolution STM image obtained for an unreconstructed Au(111) terrace region in 0.1 M HClO₄, at 0.1 V vs SCE. Tunneling conditions: set-point current (i_t) = 26 nA, bias voltage (V_b) = -11.5 mV.

Fig. 2

A) Atomic-resolution STM image for reconstructed Au(111) terrace region in 0.1 M HClO₄, at -0.3 V vs SCE. Tunneling conditions: i_t = 11 nA, V_b = -16 mV;
B) Magnified portion of Fig. 2A.

Fig. 3

Examples of longer-range superstructures formed by reconstruction on Au(111). A). In 0.1 M HClO₄ at -0.3 V, i_t = 2.7 nA, V_b = -24 mV; B). In air; i_t = 12 nA, V_b = 55 mV; C). In 0.1 M HClO₄ at -0.3V; "height-mode" image, i_t = 3.0 nA, V_b = -47 mV.

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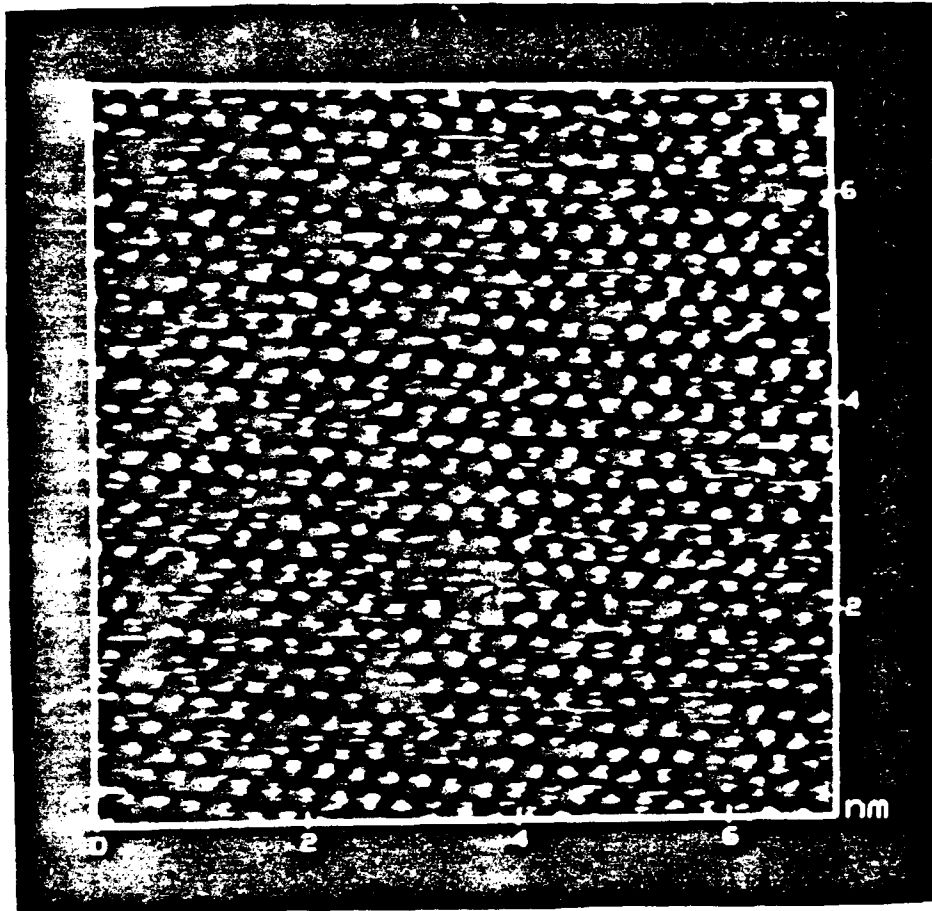


Fig.1

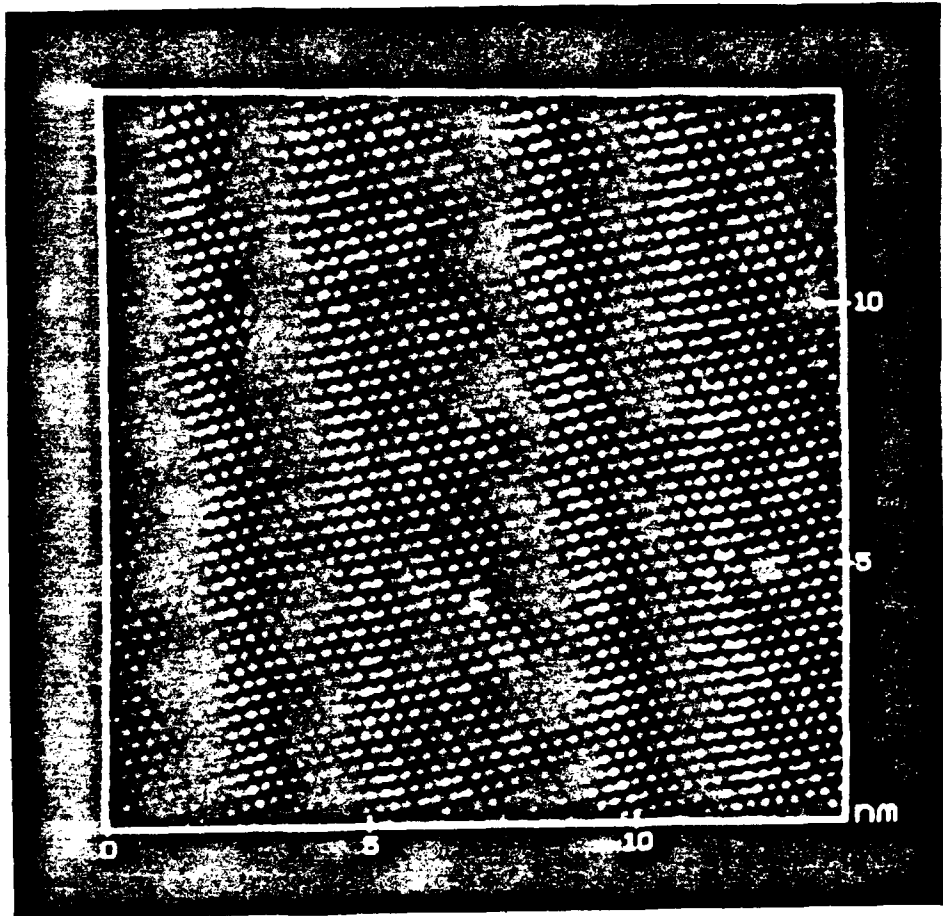


Fig.2A

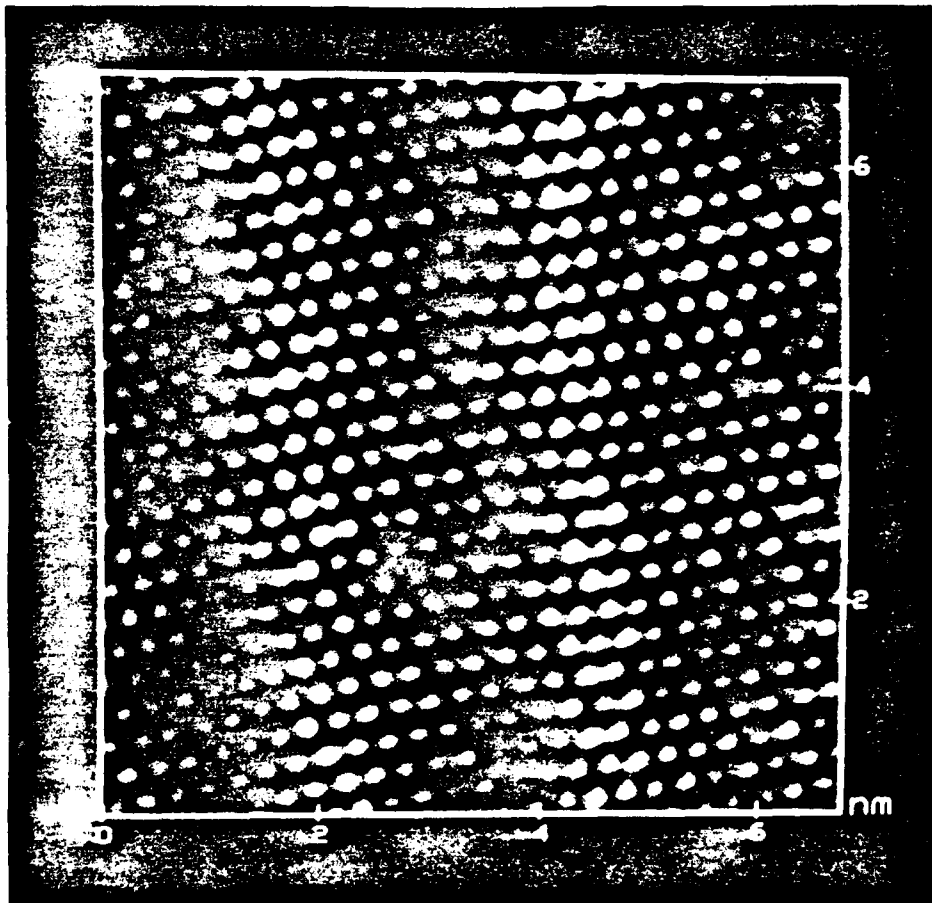


Fig.2B

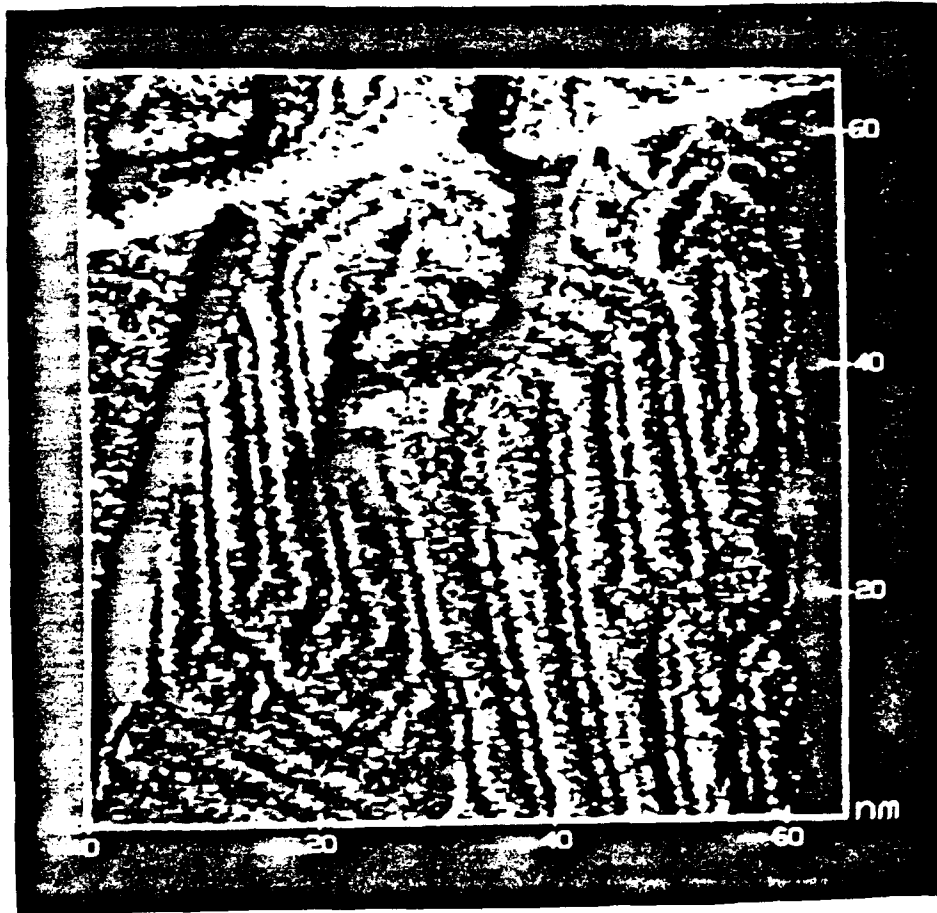


Fig.3A

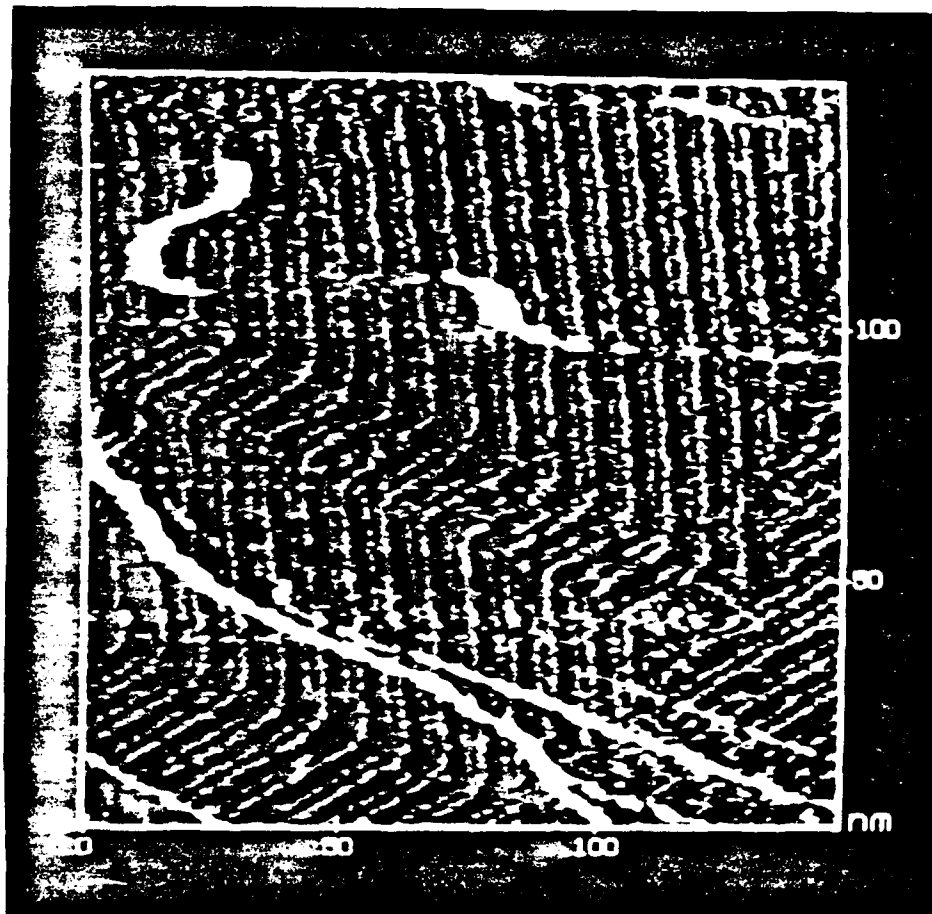


Fig.3B

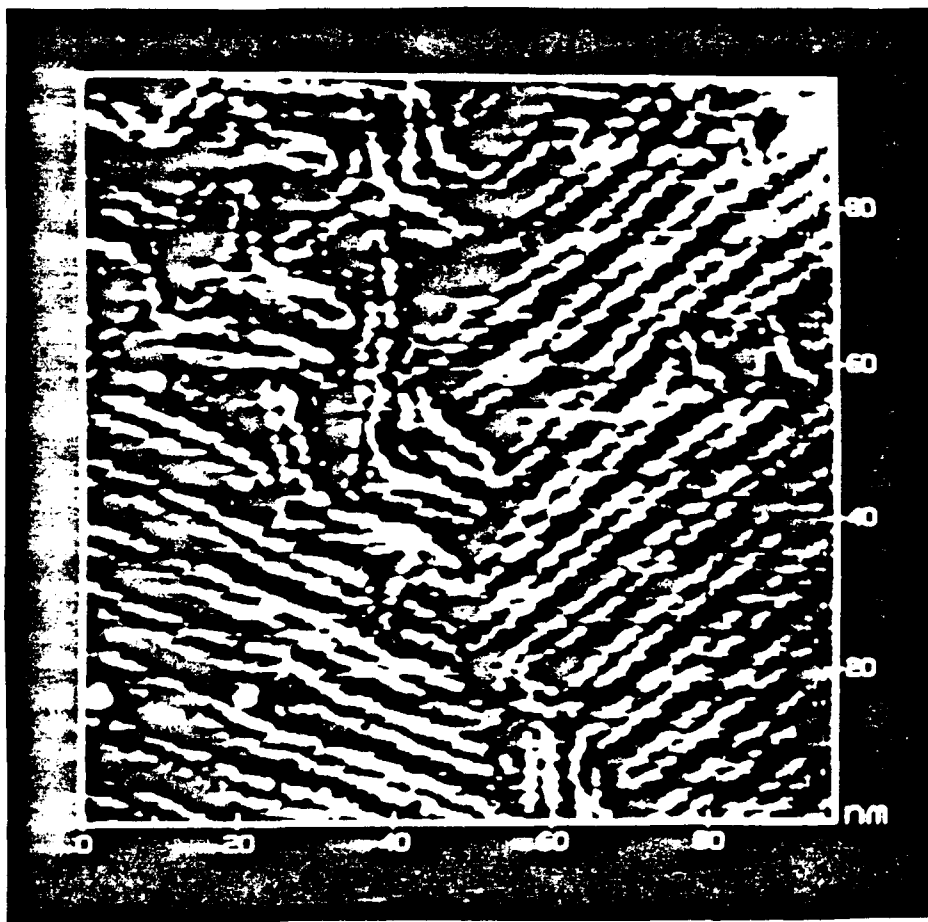


Fig.3C