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STRUCTURE AND THERMAL STABILITY OF THE Au(334) SURFACE AND Au(111) THIN FILMS IN AIR: A SCANNING TUNNELING MICROSCOPY STUDY

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November 1986

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Prepared for the U.S. Department of Energy
under Contract DE-AC03-76SF00098

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LBL-22389

STRUCTURE AND THERMAL STABILITY OF THE Au(334) SURFACE AND Au(111) THIN FILMS IN AIR: A SCANNING TUNNELING MICROSCOPY STUDY

by

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Applied Surface Science

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Abstract

A Au(334) surface cleaned and annealed under ultra high vacuum conditions was examined in air using a Scanning Tunneling Microscope. The STM images reveal a smooth surface with a plateau structure. On top of the plateaus parallel rows of monoatomic height steps can be observed. Annealing this surface in air to around 600°C results in segregation of impurities that form surface oxides. STM examination of this air annealed surface shows a structure where the plateaus have developed into large (111) facets. These facets are atomically smooth except for some steps near the edges. Au(111) films on mica, examined in air, were found to be atomically smooth over thousand of Angstroms, with the surface having occasional monatomic height steps. Several transient effects encountered in STM imaging in air are discussed.

1. Introduction

Scanning Tunneling Microscopy (STM) has shown great promise and potential in producing topographic and spectroscopic images at the atomic resolution level [1]. One of the exciting features of STM is that atomic imaging can be done not only under conditions of ultra high vacuum (UHV), but in air and liquid environments as well. While there have been several atomic resolution topographic images of surfaces in vacuum [1], so far only highly oriented pyrolitic graphite has been observed in air [2,3], and graphite, TaS_2 and $TaSe_2$ in liquid environments [4,5] with atomic resolution. It is thus of interest to find additional test surfaces in air where atomic imaging can be done. In this paper, we report atomic resolution STM images of Au(334), which is a stepped (111) surface, and of (111) oriented Au films on mica. We will also discuss what effect oxide segregation induced by annealing in air, has on the step structure. A short preliminary account of this work has been described previously [6].

2. Experimental

The experiments were carried out in two separate apparatus, one for sample cleaning and characterization, and one for sample imaging in air. A Au single crystal was prepared by standard metallographic techniques with its surface oriented parallel to the (334) plane by Laue x-ray back diffraction. The crystal was then cleaned and characterized in an ultra high vacuum (UHV) chamber by means of repeated cycles of Ar ion sputtering and annealing to near its melting point. This was done until

a clean and ordered surface was obtained as judged by Auger Electron Spectroscopy (AES) using a cylindrical mirror analyzer, and Low Energy Electron Diffraction (LEED). We also examined (111) oriented gold films that were prepared by evaporation in vacuum onto mica substrates. The thickness of these films is between 1,600 and 2,000 Å. These films were not characterized in our UHV chamber, but are known to be (111) oriented from grazing angle x-ray diffraction studies [7]. Both of these sample types were installed in the scanning tunneling microscope for imaging in air.

The scanning tunneling microscope was built with three piezoelectric transducers mounted in a tripod configuration [8] which support at their vertex the imaging tip. This is attached to a stainless steel block that also supports two micrometer screws for coarse and fine approach of the sample to the tip. This is accomplished by arranging their motion to bend a stainless steel beam that supports the sample. Vibration isolation was achieved by suspending the microscope assembly from three 7 inch long viton o-rings. Permanent magnets were used to provide eddy current damping. The entire microscope setup was mounted on a laser table that has a cut-off frequency of 3 Hz. Air cushioned legs supported this table. A glass bell jar was used to isolate the microscope from background sound noise. The tips used in this study were fabricated from 20 mil tungsten wire, and sharpened by electrochemical erosion in a saturated NaOH solution. Examination of the tips with a scanning electron microscope showed that the tip diameters obtained were on the order of a few hundred Angstroms.

The STM images were taken in the topographic mode [1], i.e. the tunnel current was kept at a constant value. The STM images are plots of the z-piezo feedback control voltage versus the x and y piezo voltages that were used to raster the tip across the sample surface. The feedback circuit consisted of an I-V converter preamp and then a comparator and an integrator to generate the feedback z piezo control voltage signal to keep the tunnel current at a constant value. In this first study the images were obtained by plotting the voltages directly on a chart recorder. A complete discussion of the mechanical design and the electronics will be described elsewhere [9].

As a check of instrument performance, atomic resolution images of graphite in air were obtained in the topographic mode with a noise level below 0.4 Å in the z direction (perpendicular to the surface). Thermal and piezo transducer drifts were present in different degrees with a typical figure of 0.3 Å/sec after approximately 20 minutes of stabilization. The x, y, and z piezo tansducers [10] were calibrated for voltages above 100 volts by using an inferometry microscope. One problem that was found was the hysteresis of the piezos that makes their response to the applied voltage a function of their past history. The z piezo was found to extend by amounts ranging from 13 to 18 Å/volt depending on previous polarizations, while the corresponding figures for the x and y piezos were between 15 and 20 Å/volt. For this reason our distance scales should only be considered as approximate (within 20%). To avoid the effect of the hysteresis, the STM traces were taken in one direction only. In short range scans, however, (a few hundred Å), the hysteresis effect is small, and images taken in both directions were

almost identical. Another undesirable effect was cross-talking between piezos (i.e. applying a voltage for movement in the x direction also causes movement in the z direction) that was responsible in part for the inclination of the traces in the topographic images. A typical figure for this effect in our system was 10% of the motion in the desired direction.

3. Results and Discussion

3.1 UHV Annealed Au(334)

The Au(334) crystal was prepared in UHV so that STM imaging could be done on an initially clean and ordered crystal. The crystal was subjected to several cycles of Ar ion bombardment and annealing. The Auger spectrum of the sample after this treatment (Figure 1a) indicates that the surface is clean to within the limits of the technique, i.e. approximately 1% of a monolayer. The corresponding LEED pattern is shown in Figure 3 and displays the hexagonal pattern with doublet spot splitting that is characteristic of stepped (111) surfaces [11]. The quality of the LEED pattern is such that it does not allow the determination of the average terrace width from the doublet separation, this being due to distortions and high background in the Figure. It is noticed that the background appears higher in the doublet direction which indicates small sizes for the domains where there are ordered steps.

To check whether an irreversible contamination of the surface would occur upon exposure to the atmosphere, the UHV chamber was brought up to air for a period of 10 minutes. After subsequent evacuation of the chamber, the Auger spectrum of Figure 1b was obtained. The only contaminant that was observed is carbon with a peak to peak height ratio of C(270)/Au(240) = 1.3. The surface coverage of carbon that this ratio corresponds to, can be estimated by comparison with carbon covered Pt surfaces. For an Auger peak height ratio of C(270)/Pt(237) = 3.2, it was determined that this corresponds to a surface coverage of one monolayer [12]. Since the Auger spectra of Au and Pt are very similar [13], the irreversible C contamination can be estimated to be roughly 0.3 monolayers. The LEED pattern for the air exposed surface had an increased background and additional blurring of the diffraction spots.

In spite of this carbon contamination after exposure to air, the Auger spectra still shows a dominant transition of 70 eV which corresponds to the main Au Auger peak. Since this peak is highly surface sensitive (a few monolayers would strongly attenuate it), it indicates that the Au surface stays essentially clean. The above evidence indicates that the carbon contamination is probably in the form of clustered patches on the surface rather than as a homogeneous overlayer film.

A large area STM scan in air of the Au(334) surface that was found to be clean and ordered in UHV is shown in Figure 2. It shows a sequence of images with increasing magnification, from 4000 x 4000 Å, down to 1000 x 1000 Å. These images could be reproduced several times and at various magnifications in spite of the slow but measurable drift. These images

were taken at a bias voltage of 240 mV (tip negative) and a constant tunnel current of 2nA. At the scale of a few thousand Angstroms the surface looks smoothly corrugated with extended plateaus of an average size of 500 Å on the xy plane and an average height of up to 50 Å in the z direction elongated preferentially along the [1$\bar{1}$0] direction. This coincides with the step orientation indicated by the LEED pattern obtained in UHV.

Examination of the top of one of these plateaus at higher magnification shows a multitude of steps running more or less parallel to its edges as shown in Figure 3. The images in this figure were taken at 300 mV bias and 10 nA tunneling current. The steps are of monatomic height (between 2 and 4 Å) and the terrace is found on the average to have a width of approximately 22 Å. This is to be compared with the 18 Å expected from a 7(111)x(001) gold surface. In the bottom image shown in Figure 3, it is observed that the terrace width changes from smaller values towards the left edge of the plateau (i.e. toward the (001) orientation of the [1$\bar{1}$0] zone) to higher values near the right edge (i.e. toward the (111) orientation). In other images of the same surface we have observed up to 12 parallel steps on a plateau.

3.2 <u>Air Annealed Au(334)</u>

The crystal was heated in air to around 600°C and an Auger spectrum after the chamber was again pumped down is shown in Figure 1c. Fe, O, Ca and C are the observed contaminants. The peak height ratio of Fe and Ca to the Au 240 eV peak was found to be roughly 0.7 and 0.5

respectively. In a recent study of iron oxide deposited on Pt(111) [14] the Fe(650)/Pt(237) Auger peak height ratio was found to be 1 at one monolayer. If again the Pt results are used to estimate the Au surface contamination levels, the indicated values correspond to a surface coverage of about 0.75 monolayers for Fe. The Ca coverage can be estimated to be of roughly 0.05 [13]. The small attenuation of the Au 70 eV peak again indicates that the segregated oxides are not uniformly distributed. To check that Fe and Ca segregated to the surface only in the presence of oxygen (air), the sample was heated in UHV to 600°C and then allowed to cool. The Auger spectrum shown in Figure 1d indicates that no contaminant segregated to the surface under these conditions. These Auger results indicate that annealing the surface in air results in the segregation of impurities that form oxides on the surface.

Large scale STM images of these air annealed surfaces reveal a topography that is dominated either by more or less rounded domains as shown in Figure 4, or by large rectangular domains or facets such as those seen in Figure 5. The average size and height of these domains is about the same as was found for the plateaus seen on the UHV annealed surface. At higher magnification the surface appears to be atomically smooth over a few hundred Angstroms near the center of the large domains, as seen in Figures 4 and 5. The step structure observed on the unannealed surface has thus vanished. Steps of up to a few atoms high are visible near the edge of the large terraces. An example of this is seen in Figure 5. If we measure the inclination of the facets relative to the average surface orientation, the angles are found to be between 6° and 10°. In comparison the angle between the (334) and the (111) surfaces is about 8°, indicating that most likely the large atomically smooth facets have (111) orientation and constitute the larger

component of the observed faceting which appears as the result of oxide segregation. The other facets that compose the domain structure are too small in size for a precise measurement of their orientation.

3.3 Au Films on Mica

Mica surfaces are classical templates for atomically smooth surfaces. It is therefore of interest to study evaporated thin films on mica with STM to see just how atomically smooth these thin films are. Figure 6 shows a STM image for Au/Mica obtained for a sample that had been annealed at 250°C for 24 hours in air. The imaging conditions were: bias voltage 3.94 volts (tip negative), tunneling current 4 nA. As can be seen in the figure, the surface is smooth to within a few Angstroms over regions thousands of Angstroms wide. Randomly scattered bumps some tens of Å high are also observed. We shall comment on these further below.

On closer examination with higher magnification we observe the occasional presence of monoatomic height steps as in the example shown in Figure 7 where two steps meet at an angle near the center of the image.

3.4 Transient Effects in STM Imaging in Air

In our imaging experiments transient effects of various types are frequently observed. Some of these are associated with instabilities or noise in well localized areas of the surface. Their location on the surface is fixed but not the pattern of noise observed. This is

illustrated in Figure 8 where two images (1 and 2) of the same area taken with 5 minutes interval are shown. The noisy area on the right hand part is reproduced but not its details. The frame on the top image indicates the position of the first one and illustrate also the drift present. These noisy areas might be associated with oxides or other non-conducting impurities that cause trapping of the tunneling electrons [15].

Other transient effects are related to the observation of more or less smooth bumps which appear and/or disappear in successive images. This is illustrated by the bump in the top left corner of the image in the same figure. In other occassions the bumps do not disappear abruptly but are smoothed in successive scans, like in the example shown in Figure 9.

We have shown above in the case of the Au(334) surface prepared in UHV, that the effect of air exposure is the appearance of carbon on the surface. It is thus tempting to associate these bumps to organic contaminants, in the form of large molecules, that are trapped on the surface and are subsequently displaced by the large electric field at the tip, or decomposed (smoothed), when immobilized on the surface, in successive scans. It would be interesting to pursue the study of the effects of the imaging process on organic material as it bears on the exciting possibility of the application of STM to biology.

4. Summary and Conclusions

1. A STM has been constructed and has been used to resolve atomic scale features of gold surfaces in air.

2. A clean and ordered Au(334) surface prepared in UHV has been shown to remain relatively clean and ordered after exposure to air. Carbon is the main contaminant and is probably inhomogeneously distributed on the surface. STM images of this surface in air show a smooth surface with a plateau structure elongated preferentially along the $[1\bar{1}0]$ direction. These plateaus are on average 500 Å wide and a few tens of Angstroms high. On top of these plateaus are domains of parallel monatomic height steps.

3. Annealing of the Au(334) surface in air to around 600°C results in the segregation of impurities that form surface oxides. The total amount of segregated material is on the order of a monolayer. STM images of these surfaces show structures that are either rounded or rectangular composed of large flat facets. These facets appear atomically smooth in general, except for steps near the edges. Their orientation relative to the (334) surface is that expected for the (111) surface, within the experimental accuracy.

4. Gold films epitaxily grown on mica are found by STM imaging in air to be atomically smooth over thousands of Angstroms. These films contain occasional steps of atomic height that are found to cross the length of the surface.

5. Transient effects are observed in STM images in air. These effects include localized noise, bumps that disappear completely in successive scans, and structures that are smoothed out in successive scans.

Acknowledgement

We gratefully thank J. Katz for his work on the STM electronics. D. Coulomb and W. Wong for their work on the STM assembly. We also thank J. Sass (Fritz-Haber Institute, Berlin), for supplying the samples of Au films on mica.

This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Materials Science Division of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.

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Figure Captions

1. Auger spectrum from the Au(334) surface.

   (a) Clean surface.

   (b) After exposure to air.

   (c) After annealing to 550°C in air.

   (d) After heating in UHV to 600°C.

2. Large scale STM images of a Au(334) surface in air. Plateaus elongated along the [1$\bar{1}$0] direction can be easily observed. The frames in the two upper images correspond to the area of the magnified imaged shown below.

3. STM images of a Au(334) surface in air. The sequence of images from top left to bottom right illustrate the surface topography at various scales from 1000 Å to 200 Å. The monoatomic height step structure (indicated by segments) starts to be visible in the x2.5 image along the [1$\bar{1}$0] direction, and is fully visible in the higher magnification image. The frames indicate the area that is shown magnified in the next image. The vertical scale is only indicated in this last image but scales up as indicated by the multiplying factors. The LEED pattern at 70 eV on the left reveals the doublet structure characteristic of stepped (111) surfaces. The surface is oriented in the same way (±10°) as in the STM images.

4. Large scale STM scan of a Au(334) surface that has been annealed in air to around 600°C. Flat, atomically smooth facets are observed at high magnification.

5. Large scan STM image of an air annealed Au(334) surface (630°C). Large, rectangular shaped facets, tile the surface with other smaller facets separating the large flat areas. The right hand side figure is the same as the one on the left with lines drawn to more clearly show the facets. The large facets appear atomically smooth, except near the edges (bottom image) where mono and multiple atomic height steps can be observed.

6. STM images of a thin film of Au (1600 to 2000 Å) on mica, after annealing in air to 250°C. Large (A) and small (B) scan areas showing an atomically smooth surface with occassional bumps, a few tens of Angstroms high.

7. A close, STM scan of an area of 400 x 400 Å. Two monoatomic height steps meet at an angle near the center of the image.

8. Consecutive STM images of a 1000 x 1000 Å area of Au film on mica. The time elapsed between the two images is approximately 5 minutes. The frame indicates the corresponding areas in the two images. Notice the noisy area on the right and the bump near the top left that is not present in the first image.

9. Smoothening of a surface structure after repetitive scans over the same area.

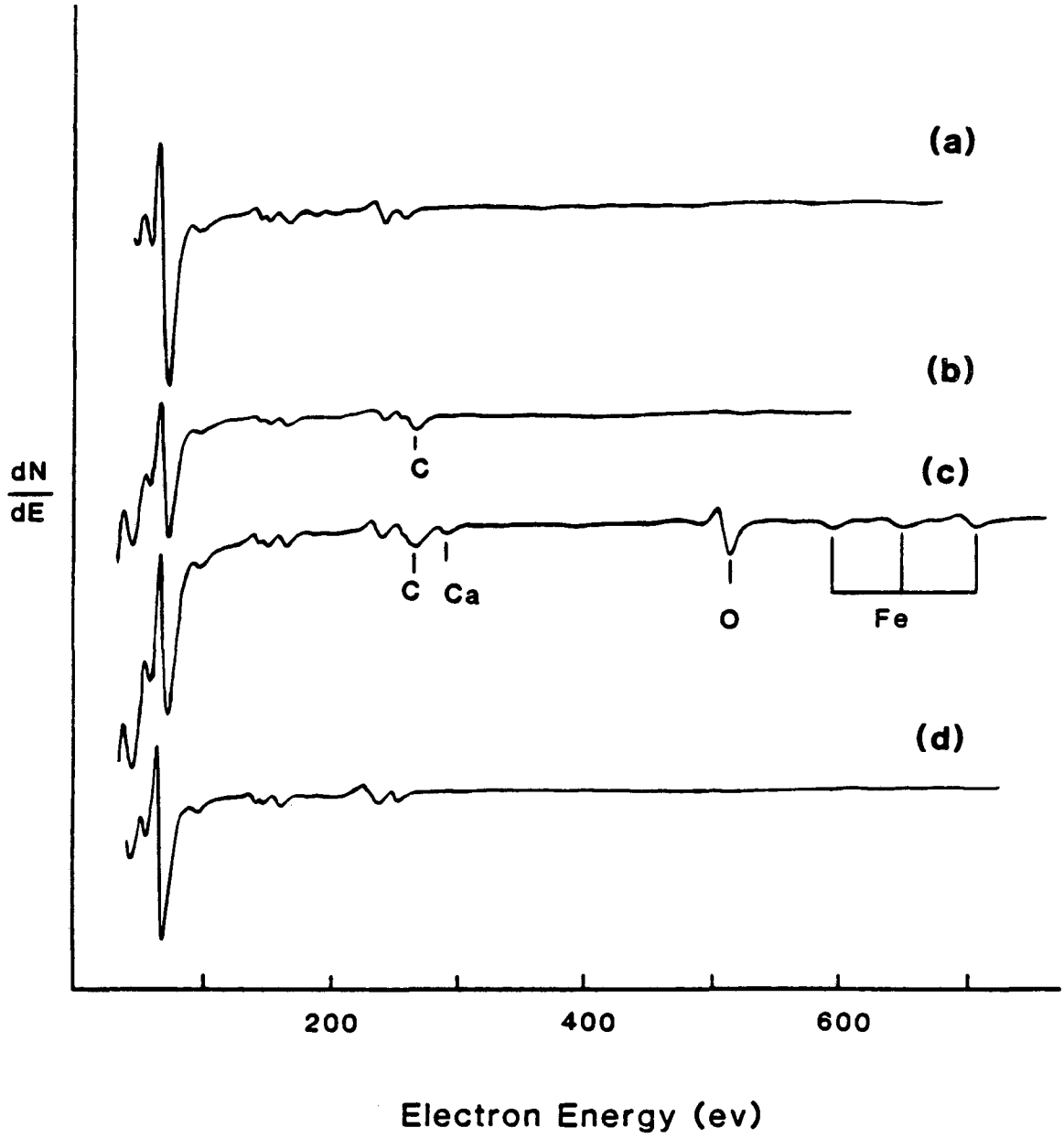

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Figure 1

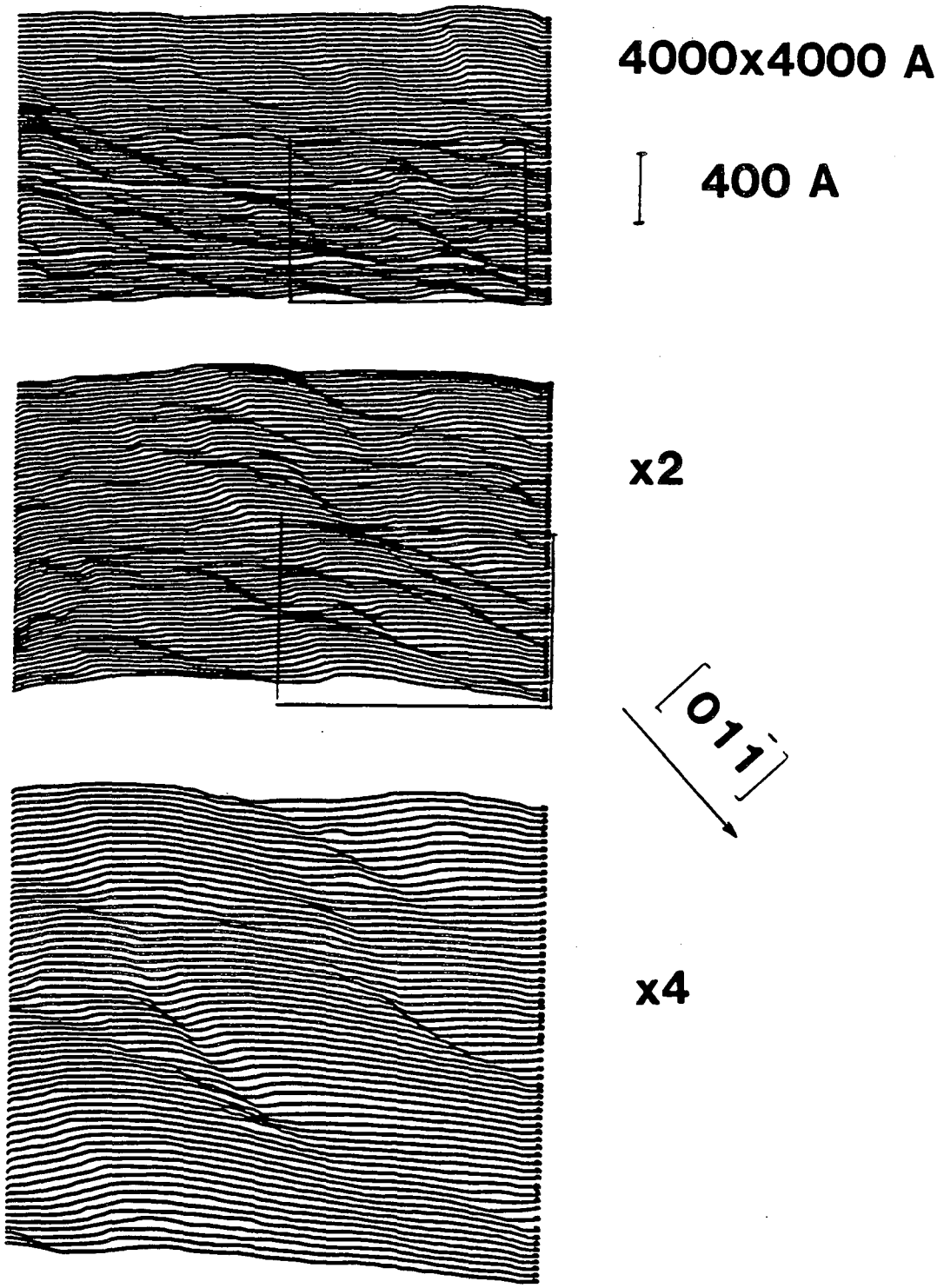

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Figure 2

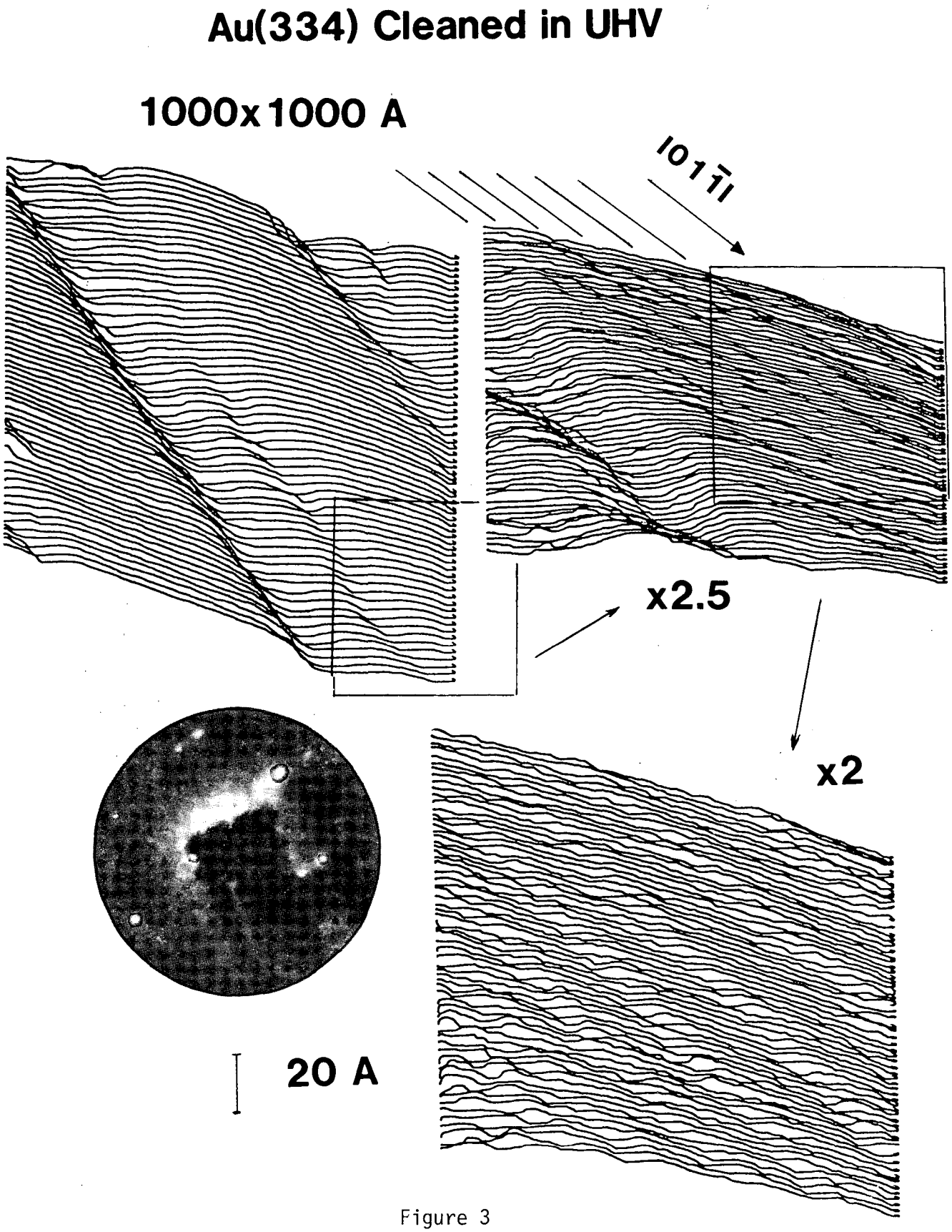

Figure 3

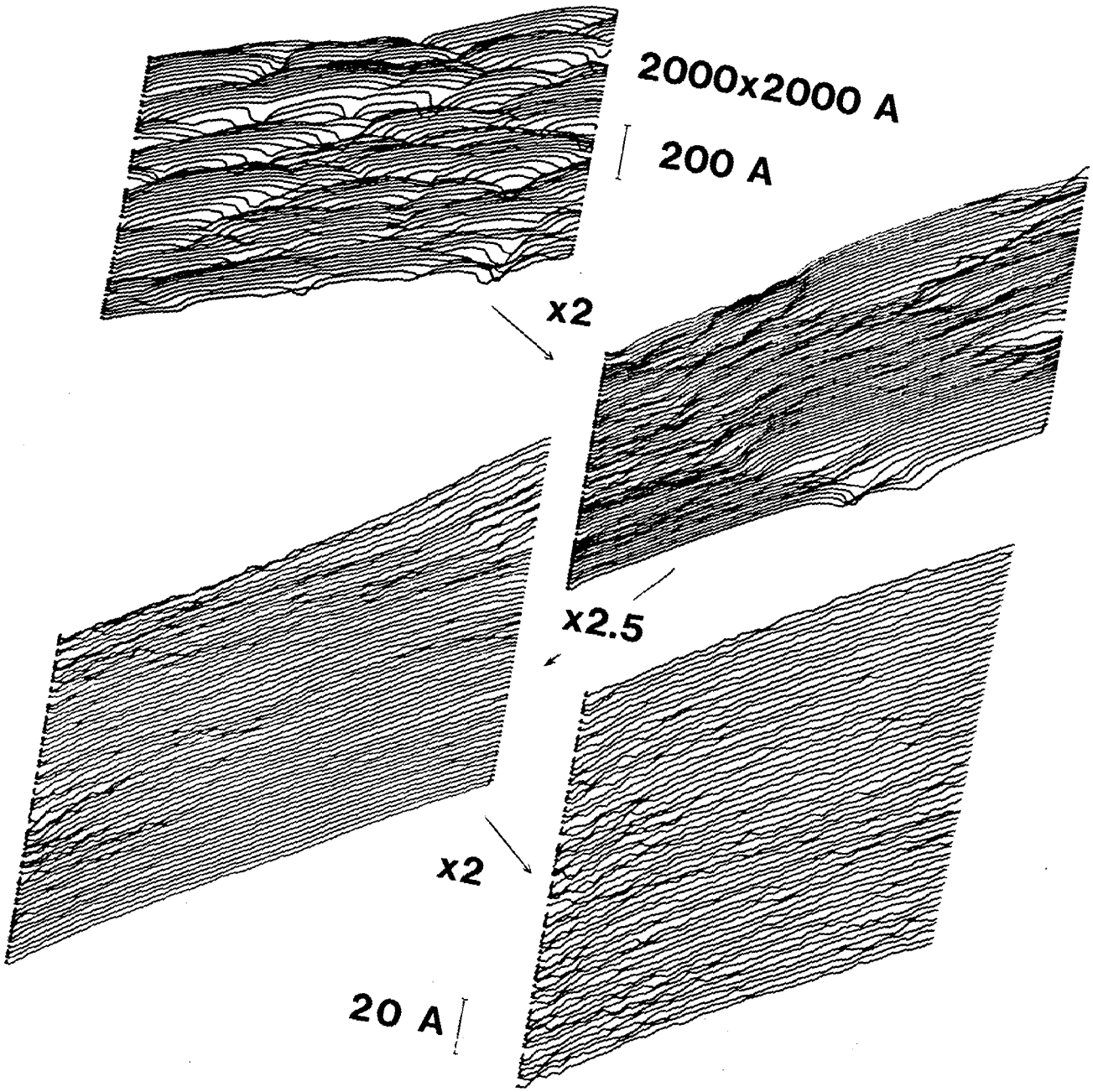

Figure 4

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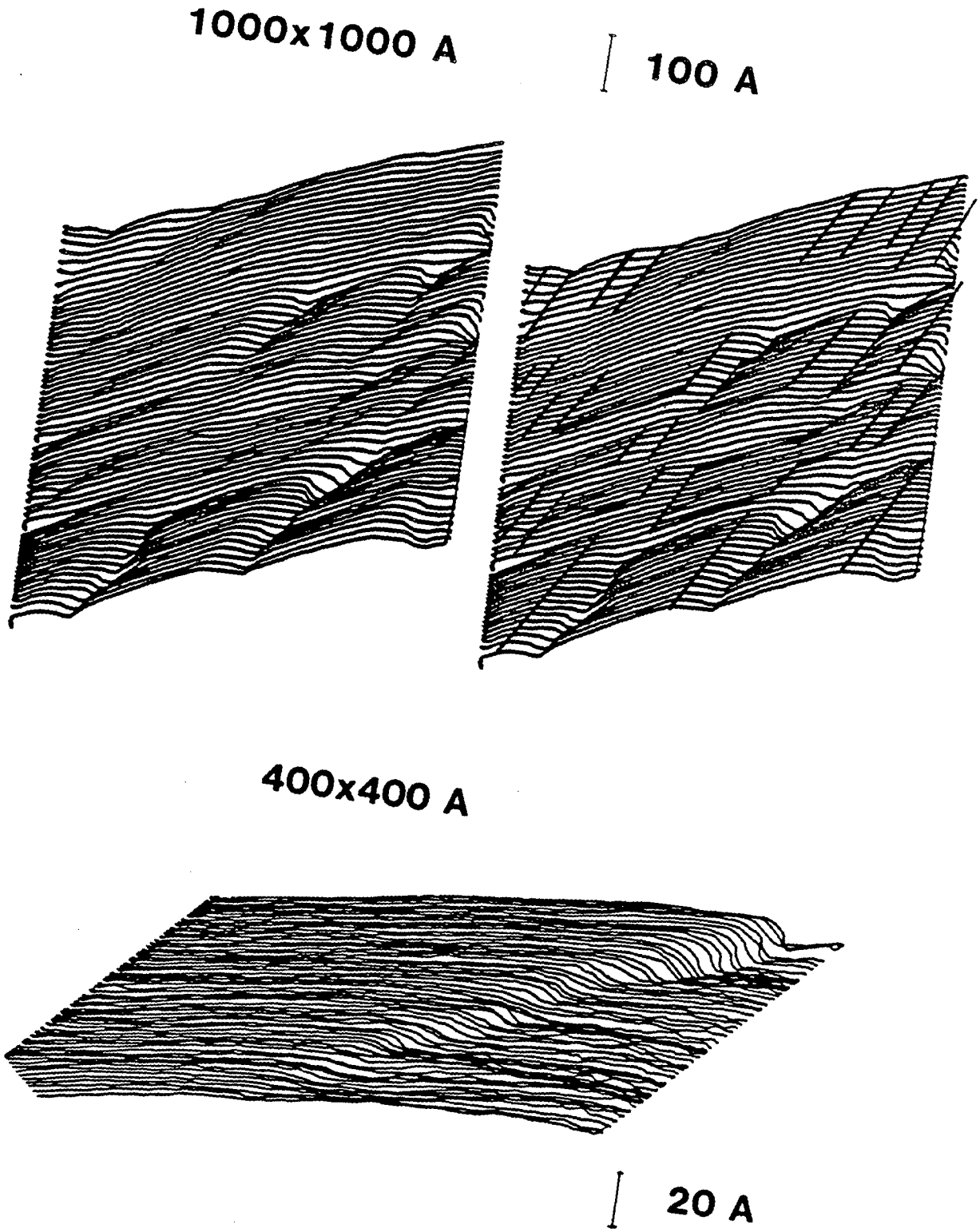

Figure 5

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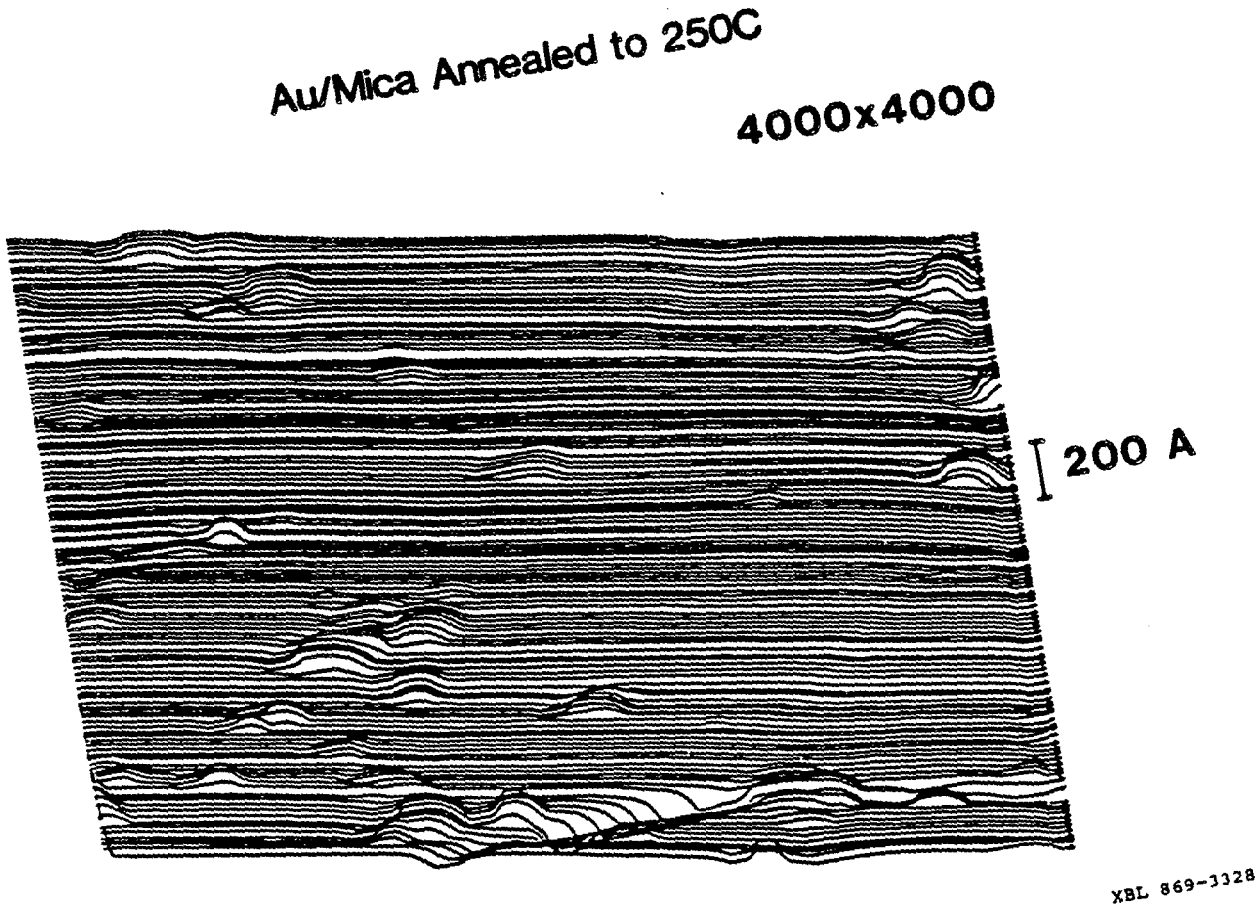

(A)

Figure 6A

Au/Mica Annealed to 250C

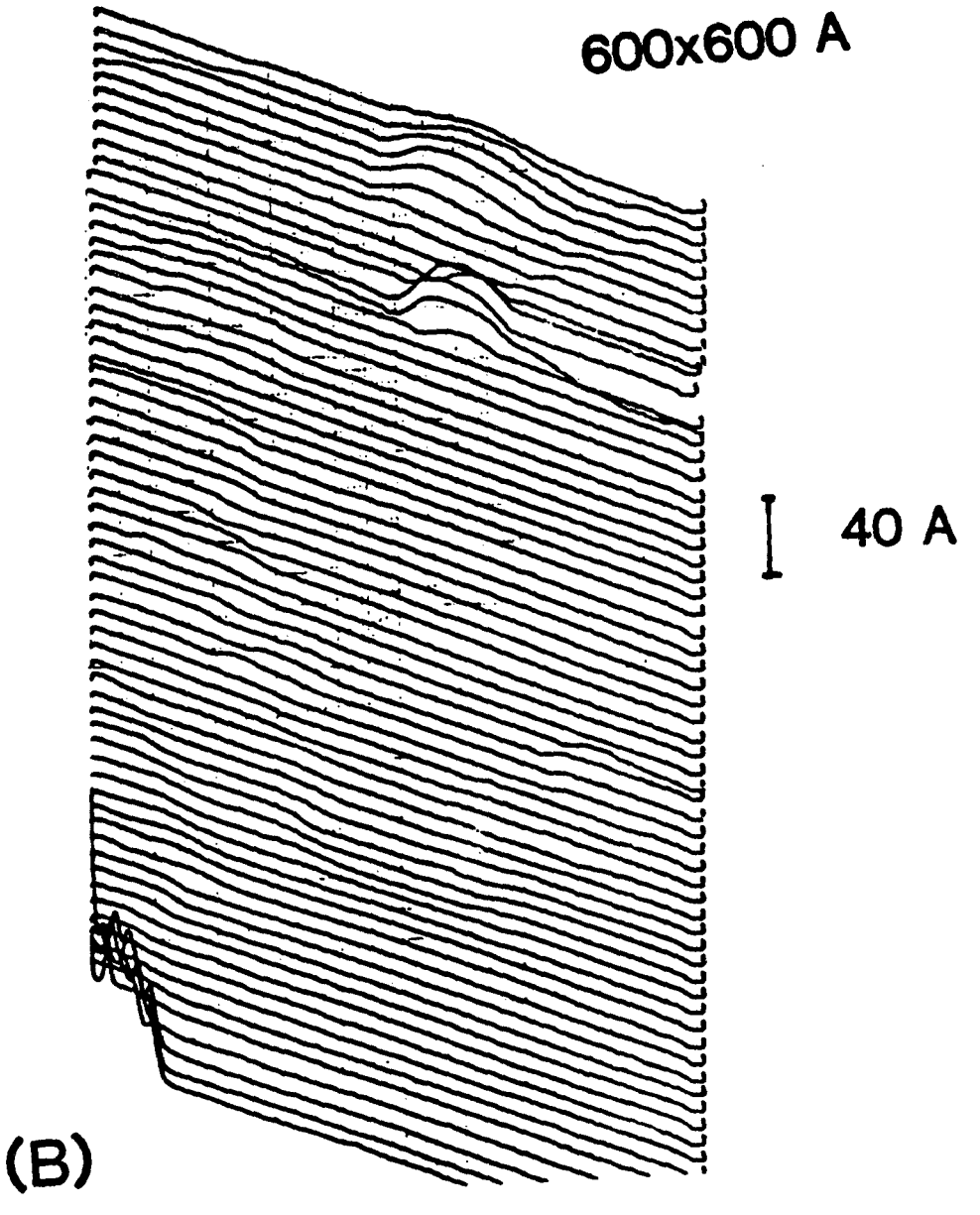

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Figure 6B

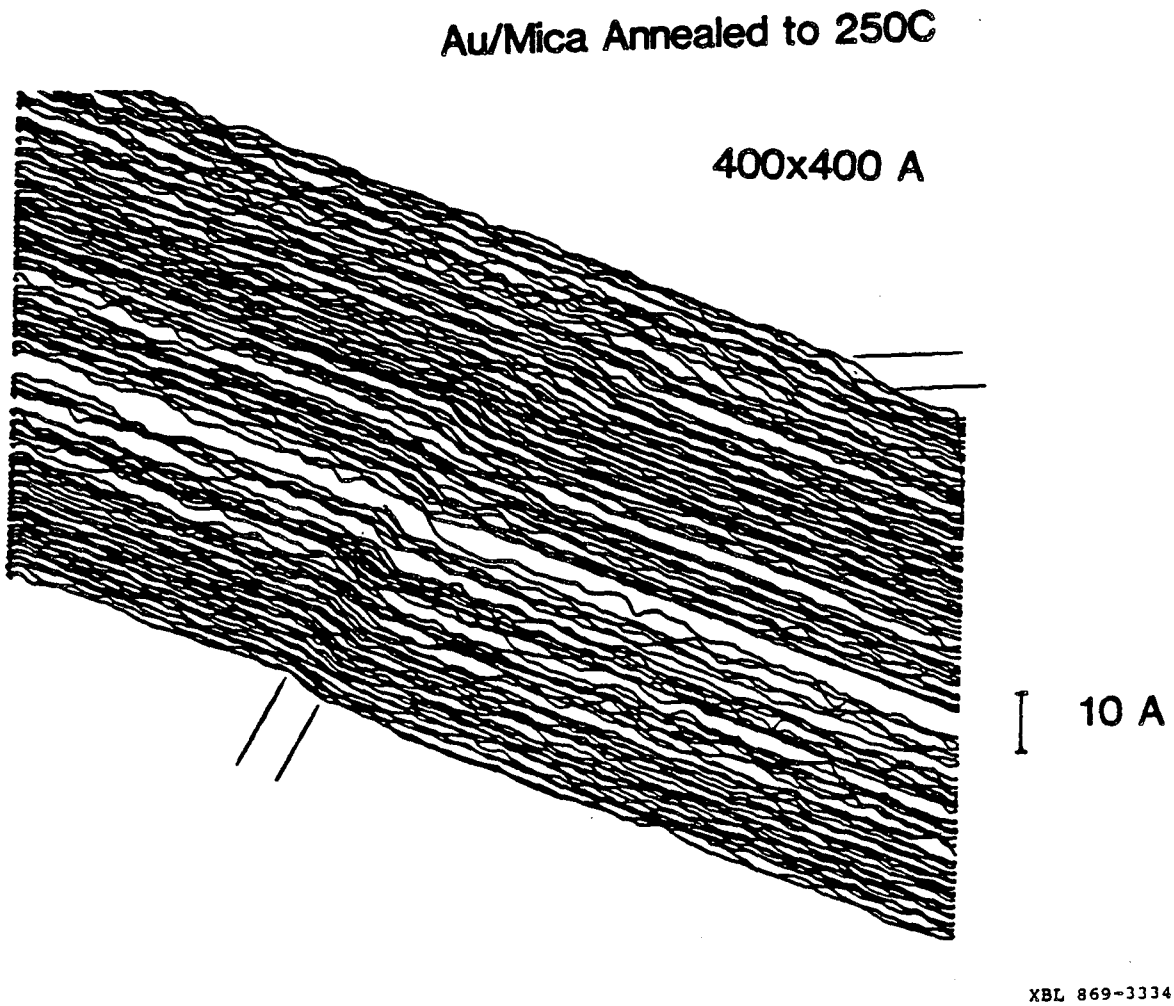
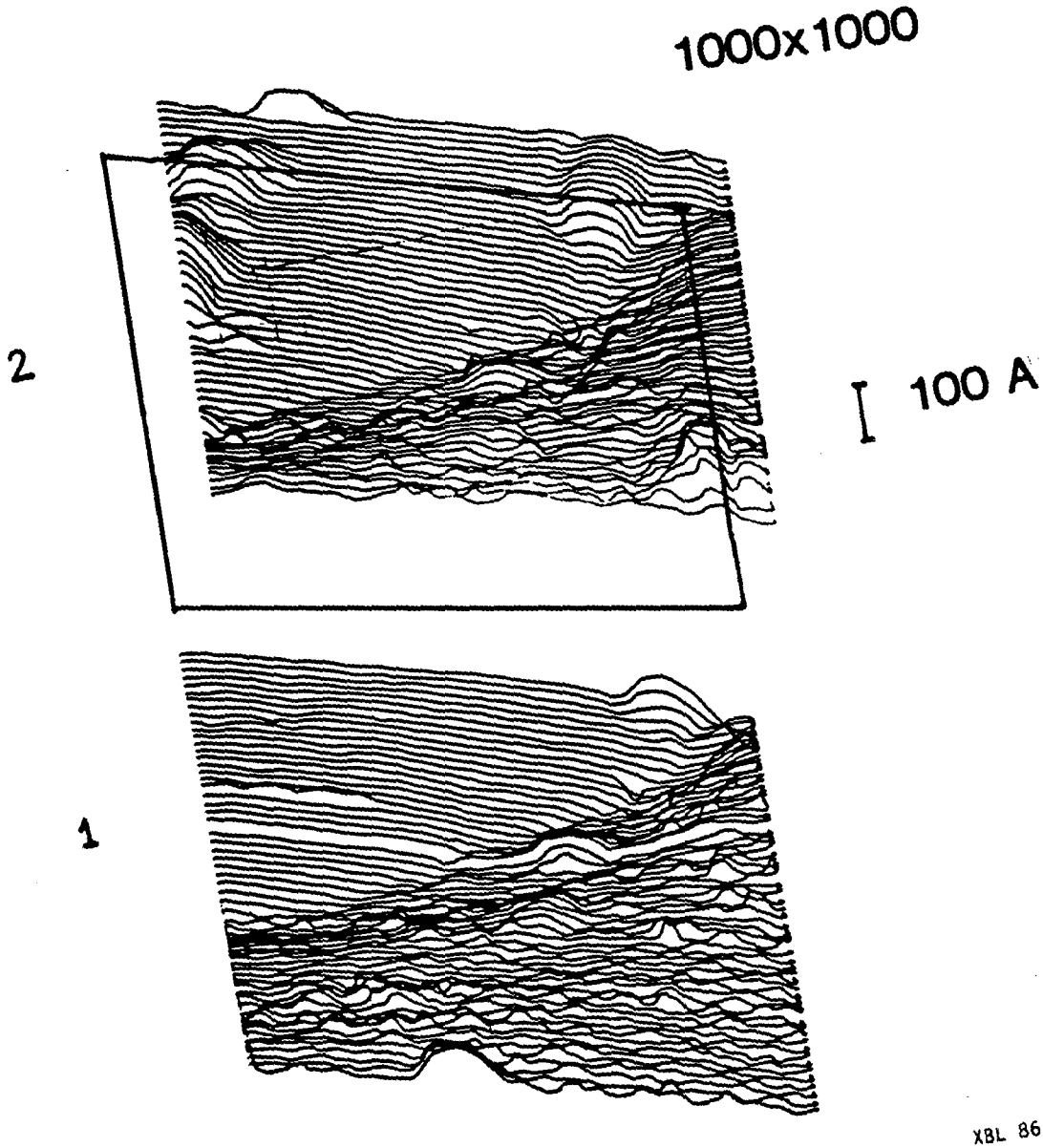


Figure 7

Au/Mica annealed to 250c



XBL 8610-3653

Figure 8

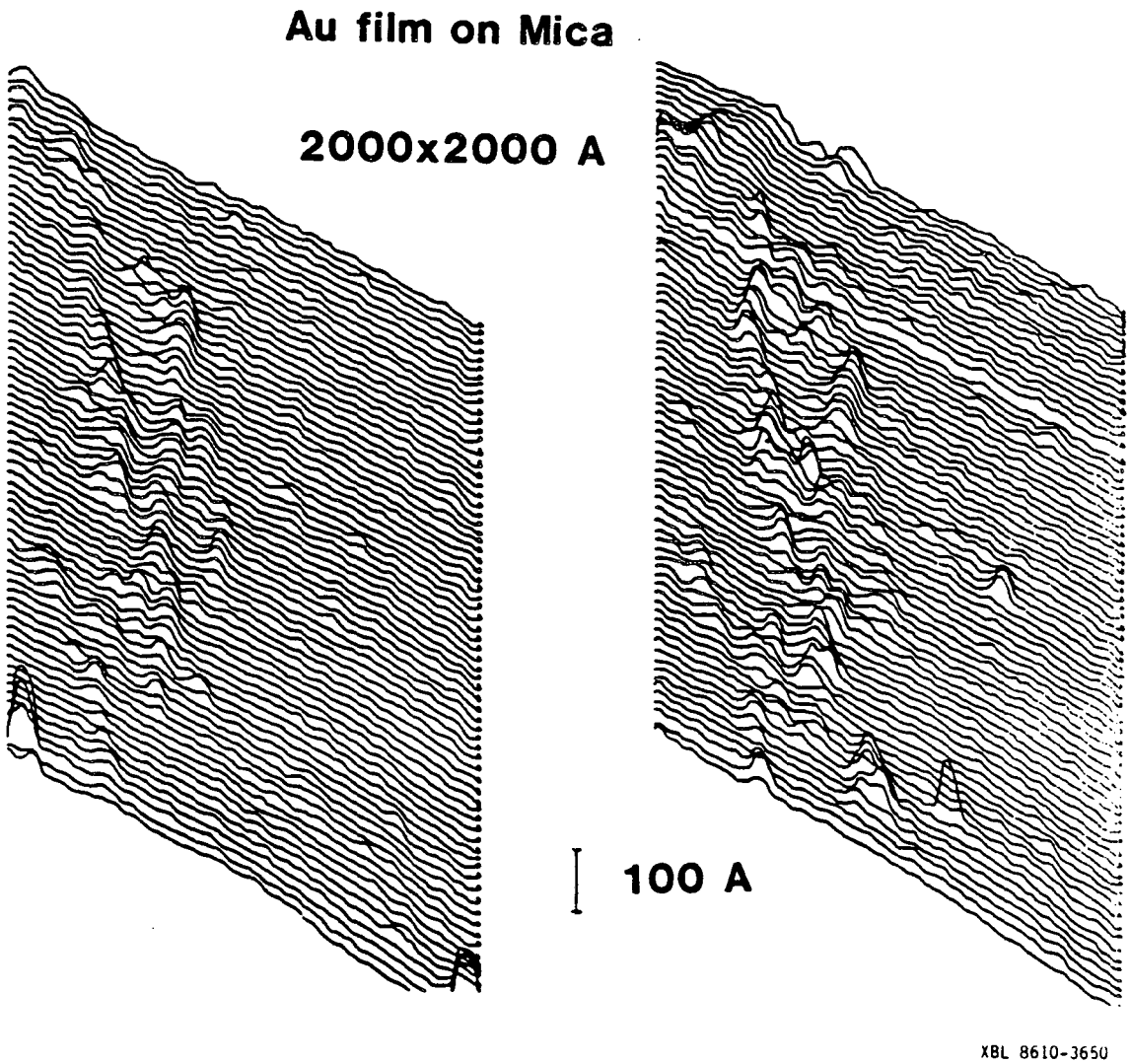


Figure 9

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