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A New Type of Long-Range Restructuring of Ordered Metal Surfaces Induced by Lateral Adsorbate Interactions: Iodide on Au(110) Electrodes

by

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ABSTRACT

A new form of long-range surface restructuring of Au(110) is reported, specifically for Au(110) in aqueous iodide electrolyte at high electrode potentials where an ordered iodide adlayer is present. In-situ scanning tunneling microscopy reveals the formation of periodic terrace strips paralleling the (1$\bar{1}$0) direction with widths, ca 25–40 Å, that diminish as the surface potential is increased. The (1 × 1) substrate unit cell, however, remains unaffected. The restructuring is postulated to be due to dipole-dipole repulsive interactions destabilizing terrace sites distant from steps, and hence limiting the size of the substrate-adlayer domains.

Understanding the nature of substrate atomic arrangements at ordered metal surfaces is of central importance in surface physics and chemistry. The emergence of scanning tunneling microscopy (STM) as a powerful new means of obtaining local structural information down to the atomic level for in-situ electrochemical as well as vacuum-based metal interfaces[1] is offering substantial new opportunities along these lines. The importance of the former interfacial systems in this context lies in the additional dimension of control of the surface composition and electrostatic properties afforded by the electrode potential. This capability has recently been exploited, for example, to examine structural and dynamic aspects of potential-induced surface reconstructions[1-3] and adsorbate phase transitions[4]. In addition to relaxations and reconstructions, atomic restructuring of metal surfaces can be envisaged that involves nanoscale or even longer-range structural alterations[5]. However, both information on, and understanding of, such phenomena is at present only sketchy[6,7].

We describe here the first observation by means of STM of an apparently new type of surface restructuring, specifically for Au(110) in aqueous iodide electrolyte, involving the *retention* of the original atomic-scale unit cell *yet* featuring the creation of remarkably ordered longer-range (30-50 Å) terrace/step periodicities. The restructuring, which is triggered in the presence of close-packed iodide adsorption at suitably high electrode potentials, can be reversed by returning to lower potentials. It is postulated to arise from a subtle interplay between longer-range repulsive dipolar forces involving the adsorbate and the metal-metal cohesive energy.

The experimental details for in-situ STM are described elsewhere[2]. The microscope is a Nanoscope II (Digital Instruments) with a bipotentiostat for electrochemical STM. The Au(110) single crystal (hemisphere, 5 mm diameter) was flame annealed, cooled partly in air and then in ultrapure water, and transferred immediately to the STM cell. The STM tip was an electrochemically etched tungsten wire. All electrode potentials are reported here versus the saturated calomel electrode (SCE).

Figure 1A-E shows a representative sequence of potential-dependent in-situ STM images for a large (150 nm square) region of Au(110) in aqueous 5 m$\underline{M}$ KI. The first image (A) obtained at 0.1 V, exhibits several large terraces separated by monoatomic steps. The direction of the (110) gold rows is evident in the atomic-resolution image of a uniform terrace, shown in Fig. 2A, obtained at -0.4 V in the same experiment. The (1 × 1) substrate arises from the presence of sufficient (albeit mobile) iodide adsorption to lift the (1 × n) reconstruction that is otherwise observed[8]. At the higher potential where Fig. 1A is obtained, however, an ordered chemisorbed iodide adlayer having (3 × 2) symmetry (coverage = 0.67), is imaged instead of the substrate, with the iodide arranged in parallel close-packed rows in between the gold (110) rows[4b]. The relatively straight terrace edges, seen in Fig. 1A, running at about 30° from the $(1\bar{1}0)$ direction, also differ from those observed beforehand at potentials below -0.4 V, which tend to be curved or even semicircular.

Altering the potential, E, to more positive values yields more remarkable changes in the substrate morphology. Figure 1B is an image taken 2 min after increasing E to 0.25 V. Appearing are a number of bright straight "ad-rows" running along the terraces. We believe these threads to be composed of iodine atoms based on the interatomic distances; a closeup (atomic-resolution) image of a pair of such strings overlaid on the (3 × 2)-I structure is given in Fig. 2B. Another, perhaps more significant, change apparent from Fig. 1A to B is a "sharpening" of the terrace-edge extremities, whereby the inward- and outward-jutting corners become decidedly indented and extended, respectively, preferentially along directions tending towards [1$\bar{1}$0]. These latter structural alterations become more pronounced after increasing the potential to 0.3 V, as shown in Fig. 1C, where the indentations take on an appearance increasingly similar to ditches along with a lengthening of the protrusions extending from the sharp terrace corners. In addition, the strings formed along terrace regions become lengthened and broadened. Figure 1D shows the situation about 9 min later, after altering E to 0.35 V. The originally sharp terrace domains have now been largely dissipated, being replaced by increasingly uniform arrays of long islands and channels, about 40 Å and 15 Å wide, respectively, running roughly parallel to each other along the (1$\bar{1}$0) direction. A further increase in potential, to 0.4 V, yields still more uniform strings, now only 25-30 Å wide, as shown in Fig. 1E. A similar structural evolution occurs upon holding the potential at 0.35 V for 10-15 min. (Note also that the faradaic electrooxidation of iodide to polyiodide commences at slightly higher potentials, ca 0.45 V.)

The z-corrugation between adjacent island strings and channels is about 2 Å, indicating the presence of monoatomic steps. Also evident from Fig. 1D and E are regions containing pairs of adjacent (upward or downward) monoatomic steps between strings, located close to terrace edges prior to the restructuring. Significantly, however, the atomic structure of the iodide adlayer, and hence the underlying substrate, located within the island strings and intervening channels (i.e. both the upper and lower z-corrugation regions) remains essentially the same as that observed prior to restructuring, i.e. an approximately (3x2)-I (θ=2/3) adlayer is still present, as can be discerned in the atomic-resolution image shown in Fig. 2C. Consequently, then, the restructuring involves *only* the production of longer-range (20-40 Å) periodicities in the form of extended step edges running preferentially in the (1$\bar{1}$0) direction.

Figures 1A-E show clearly that an important growth mode of the restructuring involves terrace edges and especially corners. Within large terraces, an alternative growth mechanism can be discerned, involving the concerted formation of island strings and nearby channels, both featuring a ca 2 Å (i.e one atom) corrugation with respect to the initial terrace. This is illustrated in Fig. 1F, obtained at 0.32 V: the 100 nm square region in the lower-right side was initially a single flat terrace.

Despite the drastic alterations in surface morphology caused by restructuring, these changes can largely be reversed upon returning the electrode potential to the original less positive values. As an example, Fig. 2D shows the same surface region as Fig. 2C, but 1 min. after lowering the potential to 0.2 V. The trio of strings seen in the former have become largely combined into a single terrace in the latter image. More generally, large (up to ca 50 nm) (1 × 1) substrate terraces are seen to be reformed in this manner within 1-2 min. Moreover, altering the potential to more negative values, say -0.4 V, also regenerates the original *curved* form of the terrace edges (vide supra).

Similar potential-induced restructuring as seen in Figs. 1 A-F could also be obtained for Au(110) surfaces coated with *irreversibly* adsorbed (3 × 2) iodide adlayers formed by emersion and transfer into iodide-free electrolyte. (This circumstance eliminates the occurrence of solution iodide electrooxidation and its possible influence upon the restructuring.) As an example, Fig. 2E shows a Au(110) surface with a (3 × 2)-I adlayer in 0.1 M $HClO_4$ at 0.2 V, and Fig. 2F shows the changes incurred 1 min. after stepping to 0.4 V, respectively. While such higher potentials were necessary to induce the restructuring, the latter image shows clearly the "sharpening" of terrace corners and initial growth of indentations and protrusions characteristic of this process. A further increase in potential, to 0.6 V, yielded arrays of island strings similar to Figs. 1D and

E. Note, however, that no iodine "ad-row" growth on the terraces can be discerned (contrast with Figs. 1 B, C).

A qualitative explanation for this remarkable potential-induced long-range restructuring of the Au(110) surfaces can be offered. In general, one can distinguish between the average surface energy of a gold atom within a (110) terrace and at a monoatomic step (edge) site. The difference between these energies, ($E_e - E_t$), can be thought of as the "surface tension" γ_s of the particular (two-dimensional) terrace domain. At least at potentials where the surface charge (including the adsorbate charge) is small, one expects that γ_s will be positive, since the terrace site is stabilized relative to the edge site by the additional cohesive bonding energy, ϵ_b, arising from the greater metal surface coordination number. The terrace edges should therefore tend to be circular under these conditions so to minimize their length, as observed (vide supra). As the Au(110) surface is charged by increasing the electrode potential, triggering more extensive iodide adsorption, the energy difference γ_s between terrace and edge sites is anticipated to diminish since the former will face increasing electrostatic repulsion[9] with surrounding sites to a greater extent than will the latter. As γ_s becomes small (and eventually negative), the terrace domains will become unstable, terrace edges become much more abundant, and the surface will restructure. The particular form of restructuring observed here can be accommodated simply in this picture by noting that the average electrostatic repulsive energy per site, ϵ_r, which acts to destabilize terrace sites involves forces that are inherently more long-range in nature than those that control ϵ_b. One therefore anticipates that terraces that are smaller along at least one direction than the characteristic distance over which ϵ_r forces operate should be stabilized relative to larger terraces, i.e. ϵ_t and hence E_t will decrease.

Thus for rows of hexagonally packed adsorbate dipoles arranged in strips

N atoms wide, the value of ϵ_r will be smaller than for an infinitely wide terrace by the approximate factor $[1 - 0.67\ N^{-1} \sum_{n=1}^{N} n^{-1}]$. Integration shows that $\epsilon_r(N)$ approaches $\epsilon_r(N \to \infty)$ only slowly: thus when $N = 7$, for example, (corresponding to a 30 Å wide strip, as in Fig. 2C), the former is only 75% of the latter.

Offsetting this anticipated energy stabilization when forming such nanoscale terraces, of course, will be the greater density of edge sites thereby produced, since these offer smaller ϵ_r. This energy cost, however, should be the smallest for terrace edges which parallel the $(1\bar{1}0)$ direction since the gold-gold surface cohesion coordination is clearly weaker across, rather than along, these metal "rails." One can therefore rationalize the observed formation of the restructured ribbons in the $(1\bar{1}0)$ direction, with perpendicular terrace widths diminished to the dimensions, 25-40 Å, required to relieve lateral electrostatic repulsions within the adlayer-covered terraces. This model can also account for the observed diminution in the restructured terrace widths as the electrode potential is increased, since the magnitude of ϵ_r should be enhanced under these conditions.

Having accounted at least qualitatively for the surface energetics, it remains to consider the mechanisms by which the restructuring can occur. Figure 3 is a cartoon representation suggested by the STM results. The two gold atoms labeled a and b on the Au(110) terrace shown in A have similar ϵ_b values, yet the former is anticipated by the above arguments to be less stable since the surrounding terrace dipoles should engender greater lateral repulsion than is the case for the more "outlying" site b. (Part B of the figure illustrates that such dipole repulsion should be more effective within a single terrace plane than across steps.) One can therefore envisage gold atoms migrating from a to b, or to and from related sites, so to carve out indentations and grow nearby protrusions. This is precisely what is observed in Figs. 1A-C, and Figs. 2E and

F. The dynamics of this process necessarily require a suitably high surface mobility of the gold atoms. We have recently noted the ability of adsorbed iodide to engender remarkably rapid surface mass transport of gold atoms on Au(100), associated with potential-induced hexagonal reconstruction[10]. This "terrace-edge" mechanism appears to be the major mode of restructuring, although island strings can also form on top of terraces, as seen in Fig. 1C.

A long-range self-organization of oxygen domains on Cu(110) to form periodic strips has been reported recently[6]. Although the nature of the forces are not fully understood, longer-range adsorbate repulsions of the type considered here may partly account for the observations in ref. 6. The present type of surface restructuring, involving ordered periodic fracturing, may be anticipated more generally, although the high surface mobility of gold along with the anistropy of the (110) surface make the present system perhaps an exceptional case. Nonetheless, the present observation that dramatic changes in the terrace-edge superstructure can be induced by altering the surface charge has broader implications in surface science.

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FIGURE CAPTIONS

Figure 1

A-E: Sequence of potential-dependent STM images for 150 nm square region of Au(110) in aqueous 5 m$\underline{M}$ KI. A, 0.1 V vs. SCE; B, 2 min. after increasing potential to 0.25 V. C, 2 min. later, at 0.3 V; D, 9 min. later, at 0.35 V. E, 3 min. later, at 0.4 V. F: largely single terrace surface region, 3 min. after increasing from 0.2 to 0.32 V. Tip-substrate bias voltage ≈ -0.08 V; tunneling current ≈ 10 nA.

Figure 2

A: unfiltered atomic-resolution image of Au(110) substrate in aqueous 5 m$\underline{M}$ KI at -0.4 V. B: atomic-resolution image of (3 × 2)-I adlayer with iodine "ad-rows", 2 min. after stepping to 0.25 V. C: Atomic-resolution image of restructured strings/channels, at 0.35 V. D: Same region as C, but 1 min. after returning to 0.2 V. E, F: various terrace regions with irreversible adsorbed (3 × 2)I adlayer in 0.1 $\underline{M}$ $HClO_4$, obtained at 0.2 V (E), and 1 min. after stepping to 0.4 V.

Figure 3

Schematic picture illustrating differences in site stability engendered by dipole repulsion, and possible restructuring mechanisms (see text).

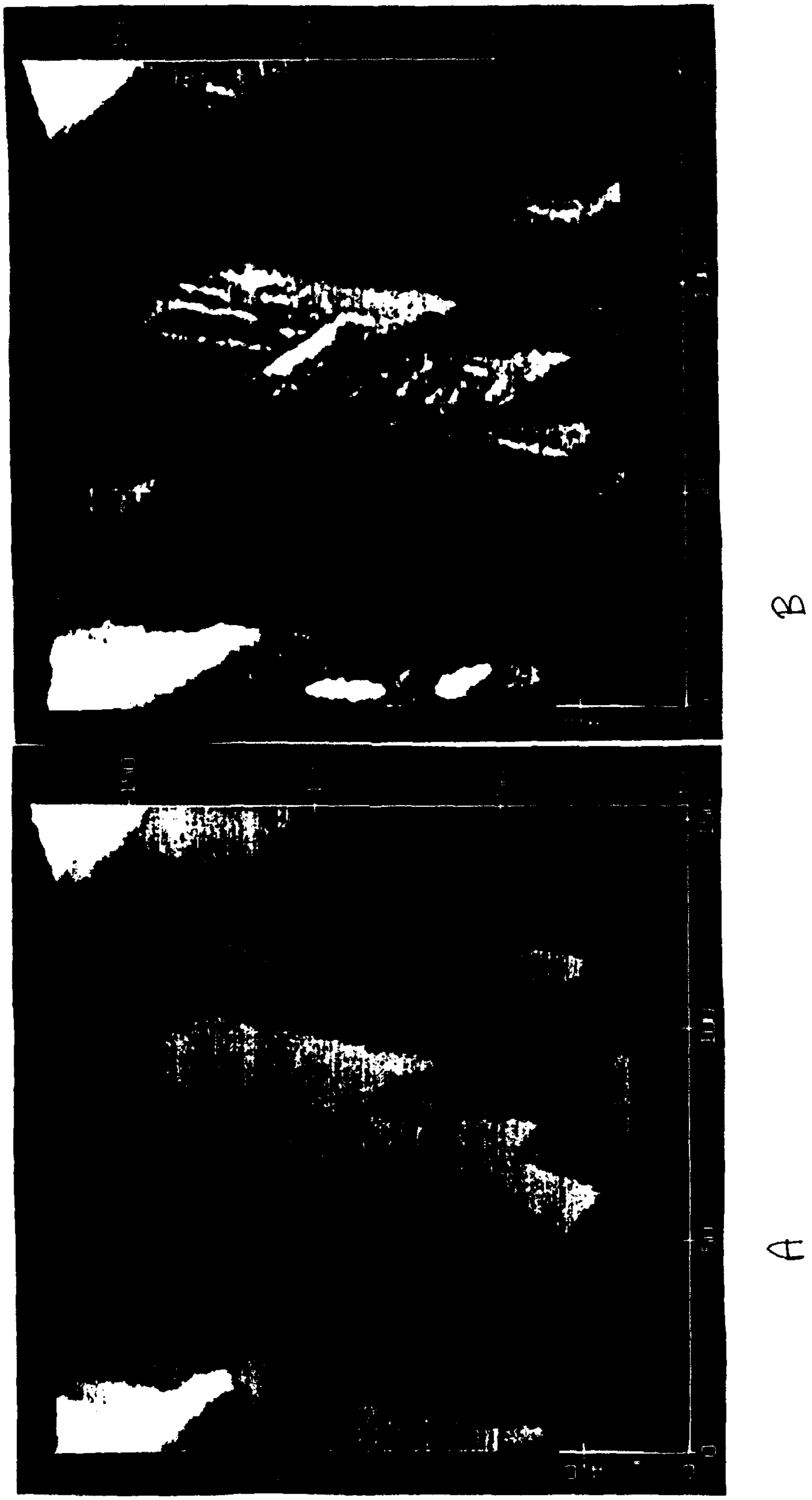
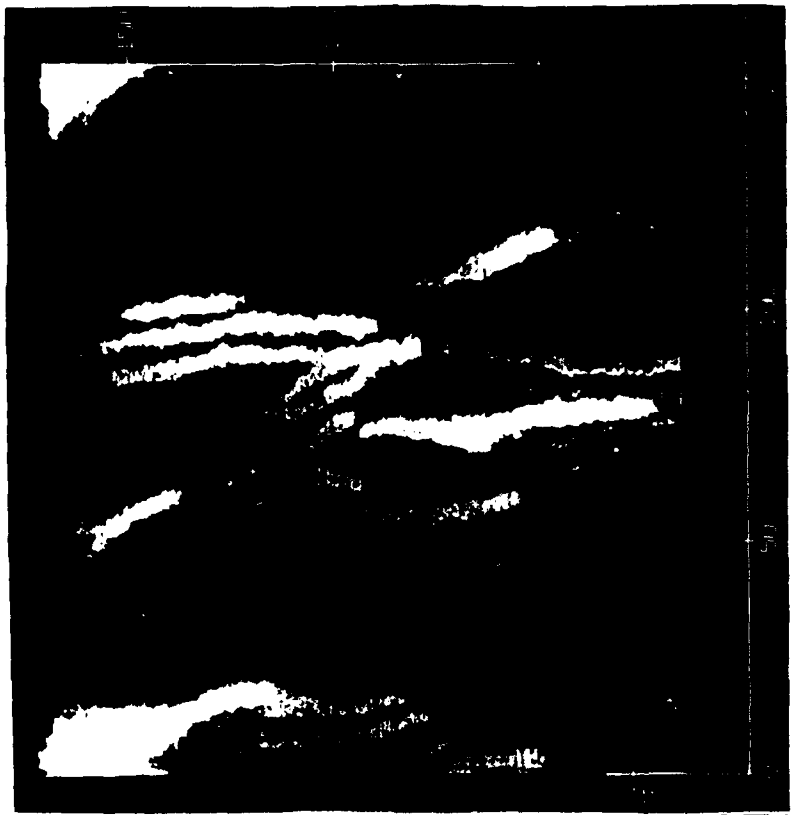


FIG 1



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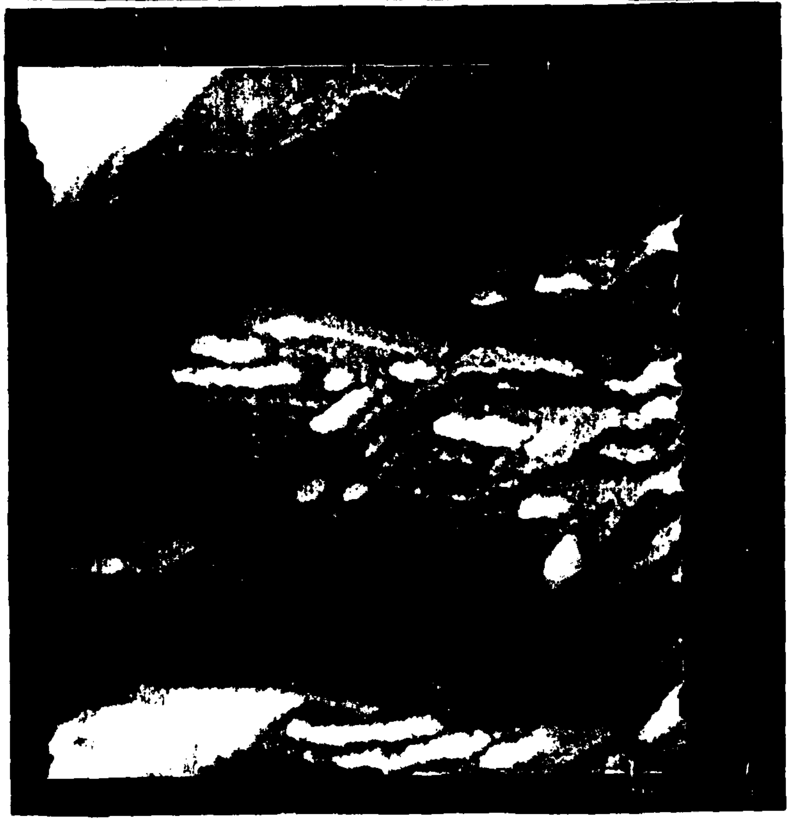
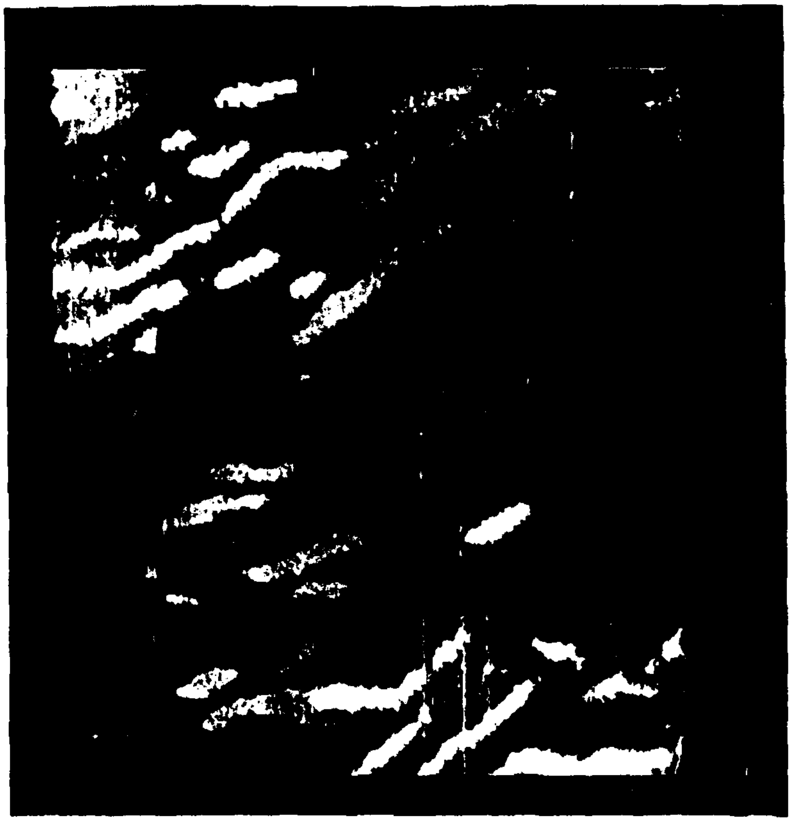


C

FIG 1 (CONTD.)



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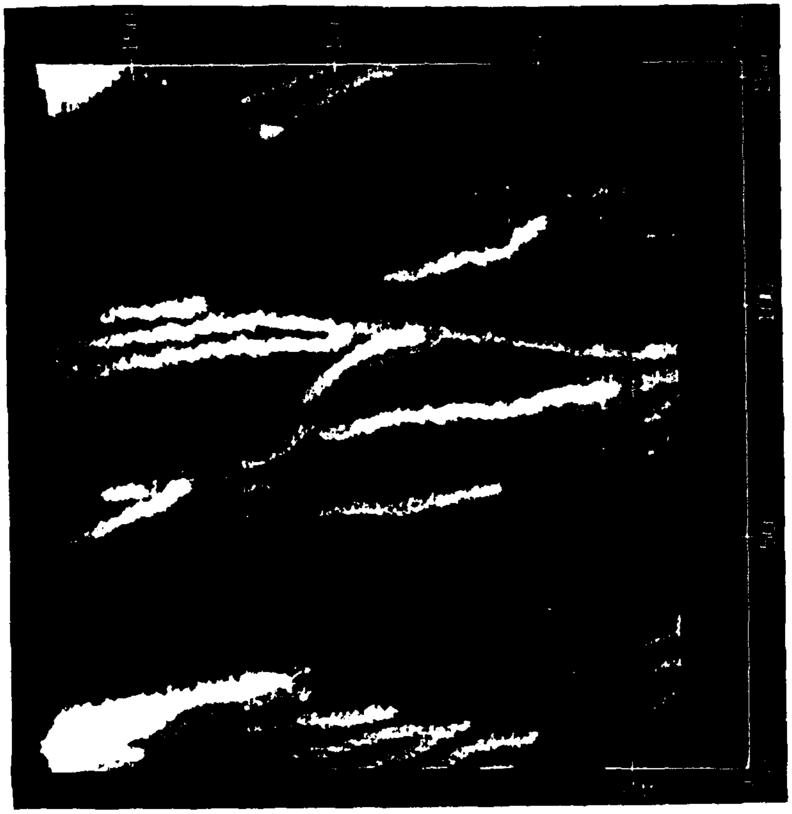


E

FIG 1 (CONTD.)

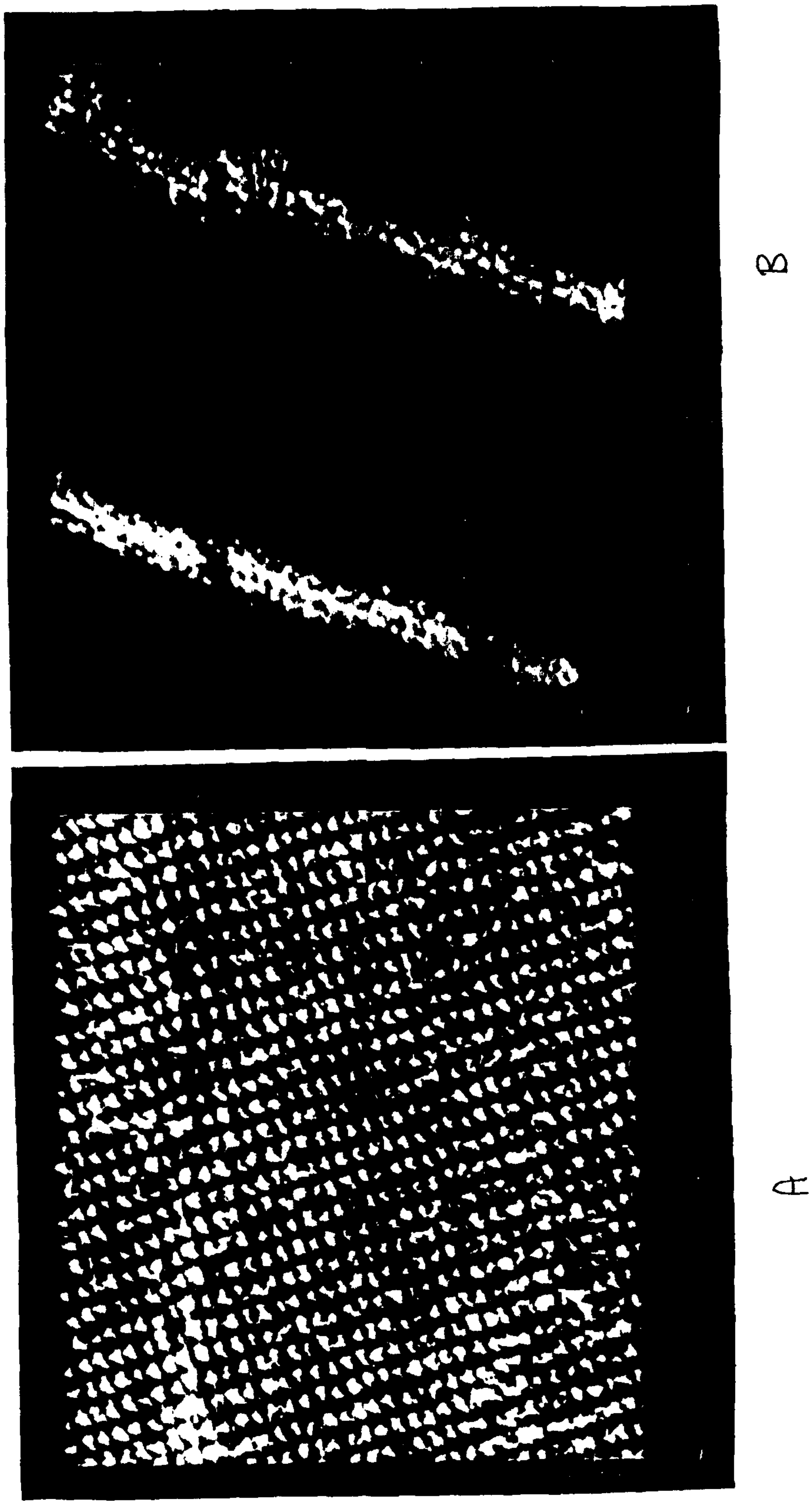
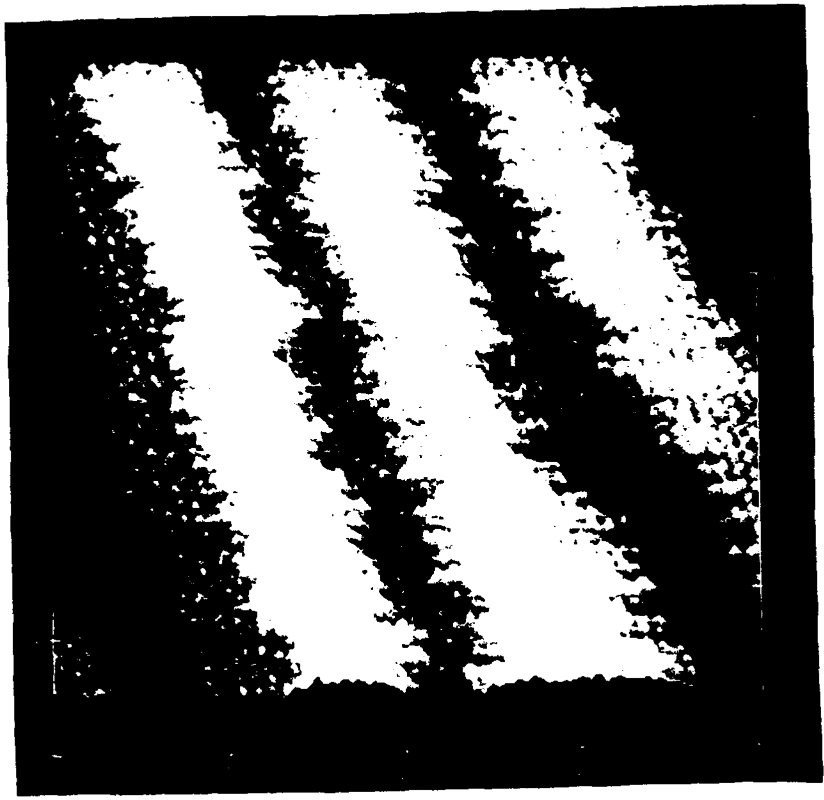


FIG 2



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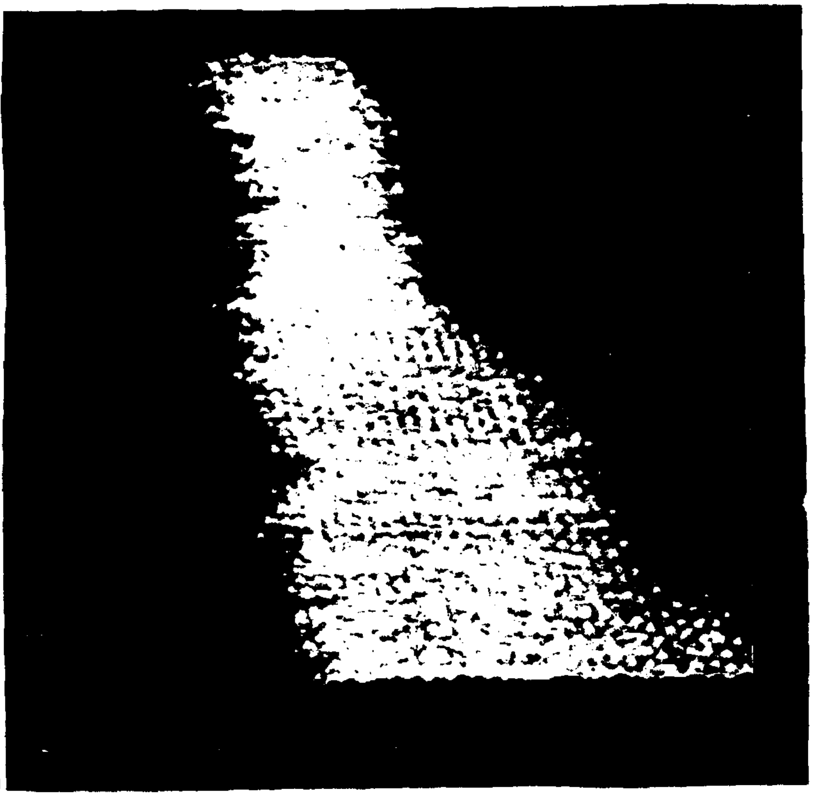
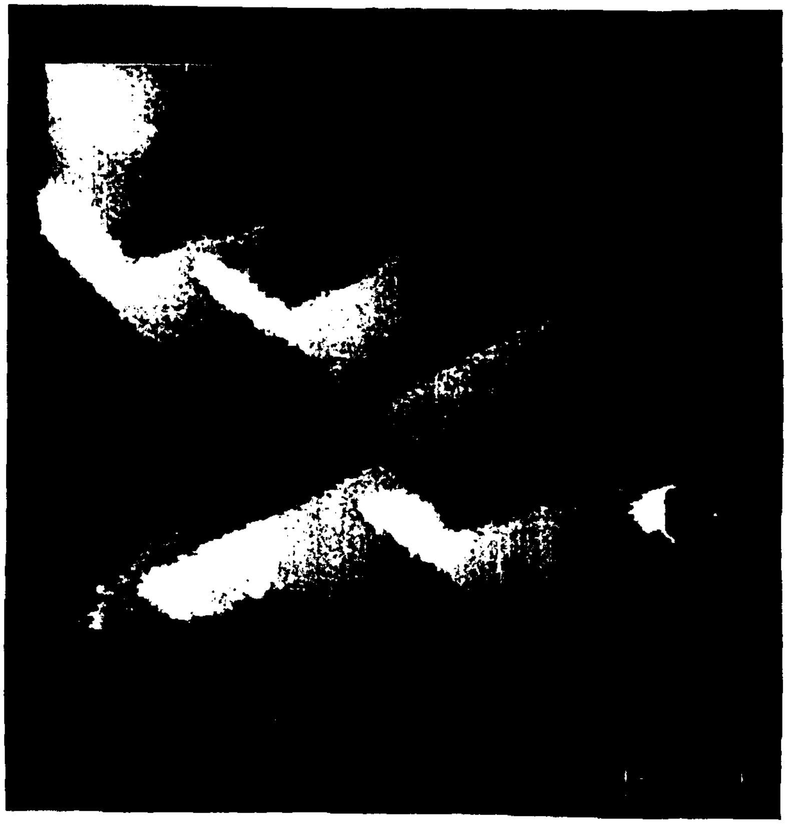


D

FIG 2 (CONTD.)



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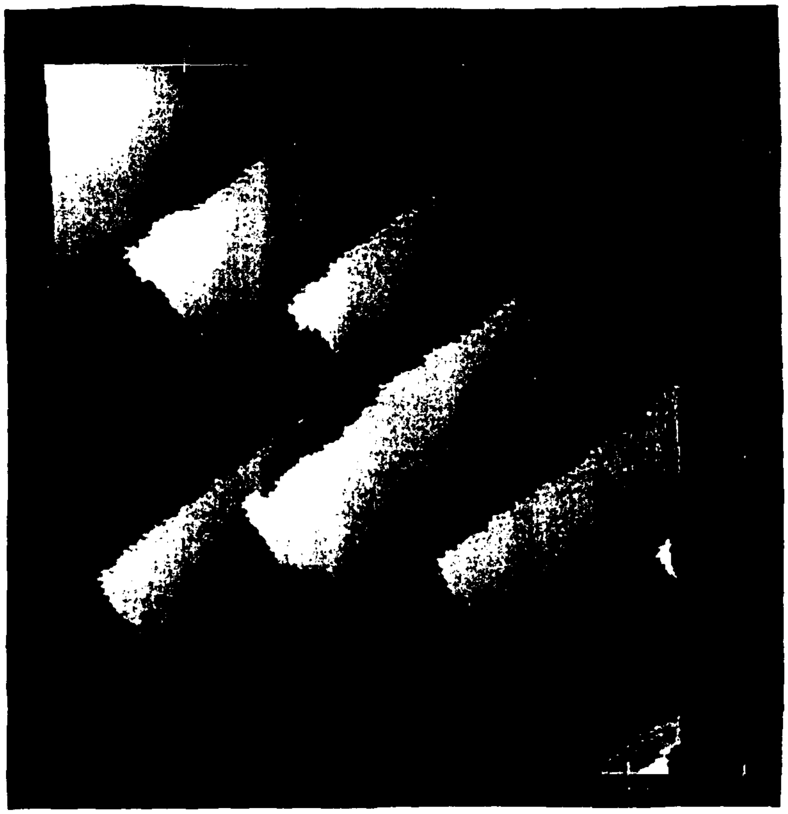

E

FIG 2 (CONTD.)

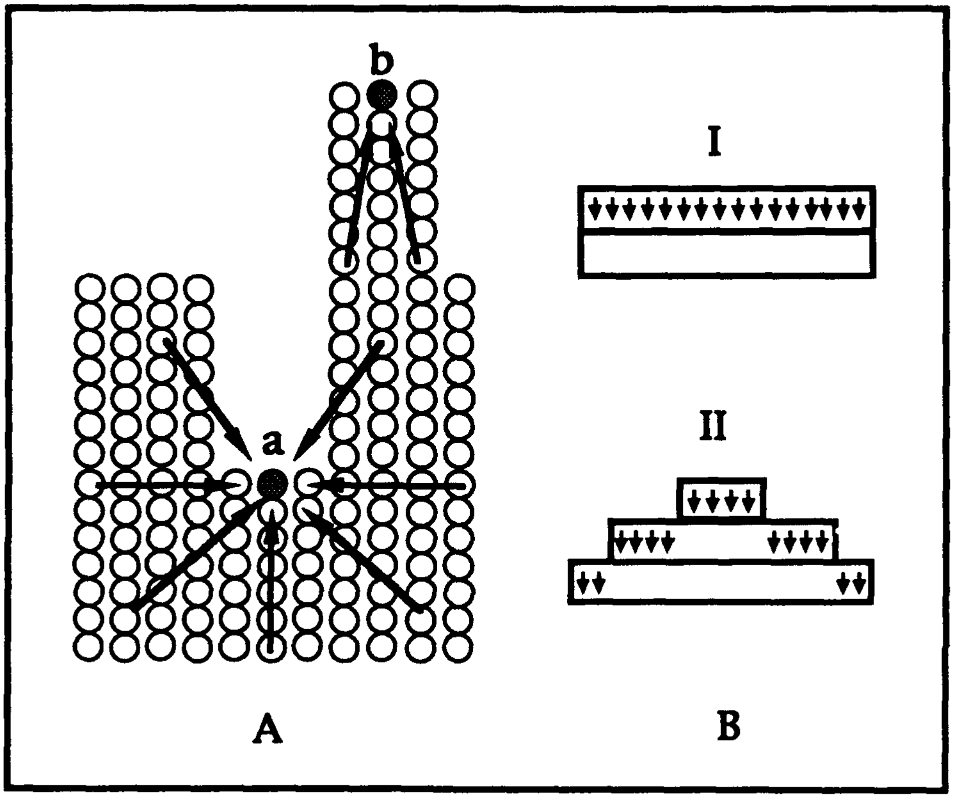

Fig. 3