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Formation of Striped Surface Phases by Short-Range Forces

by

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# FORMATION OF STRIPED SURFACE PHASES BY SHORT-RANGE FORCES

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## Abstract

Anisotropic Cu-O islands form striped periodic supergratings upon annealing an oxygen-exposed Cu(110) surface. While the formation of these striped phases has been attributed to long-range repulsive forces between stripes, we show using the one-dimensional Ising model and Monte Carlo simulations that short range adsorbate-adsorbate interactions are capable of producing striped phases. In these systems there are (at least) two time scales of importance: the time required for the formation of Cu-O strings and the time required for the formation of stripes. It is demonstrated that the latter process can be extremely slow at room temperature and that approximately evenly spaced stripes are formed upon annealing by employing only short range interactions.

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## I. Introduction

Striped phases are observed in nature for diverse systems from sorted stone stripes to clouds [1]. Kern *et al.* observed that when oxygen is adsorbed on Cu(110) and annealed, anisotropic Cu-O islands form striped periodic supergratings [2]. The observed spacings between Cu-O islands depended upon the coverage and temperature, and were studied using scanning tunneling microscopy (STM) and He diffraction [2,3]. The unannealed O/Cu(110) surface has been the subject of a number of earlier STM studies, and displays disordered "strings" of adsorbates along the  $\langle 001 \rangle$  direction which are one atom wide in the  $\langle 1\bar{1}0 \rangle$  direction [4-6], or islands of condensed strings [5,7]. These "added row" strings are found on a number of O and S covered fcc(110) surfaces [8,9]. Kern *et al.* found that annealing causes several strings to condense together forming "stripes" of quite uniform width and spacing in the  $\langle 001 \rangle$  direction. These interesting results have been interpreted as being the result of long range forces due to surface stresses [2,10]. However, such forces alone are unable to account for the narrow distributions of stripe widths and spacings found experimentally [10-12].

In this paper we use a one-dimensional approximation and two-dimensional simulations to explore the roles of short range forces and interface entropy (or the so-called "entropic repulsion" [13,14]) on the formation of superstructures. In the limit of a highly asymmetric interaction, a two-dimensional lattice can be approximated by a one-dimensional lattice. Given the strong Cu-O interaction in the  $\langle 001 \rangle$  direction, we use the one-dimensional Ising model to approximate the O/Cu(110) system in the  $\langle 1\bar{1}0 \rangle$  direction. For this simple and well known model we show that evenly spaced islands are the most likely configuration. Additionally, we have performed a Monte Carlo study of the two-dimensional system. The experimental coverage dependence on stripe spacing for O/Cu(110) are reproduced in both cases.

## II. One-Dimensional Ising Model

For simplicity, the one-dimensional Ising model is discussed in terms of the micro-canonical ensemble; that is, there are  $N$  atoms on  $M$  sites with  $N_{11}$  nearest neighbors [15]. The energy, which is

set equal to the expectation value of the energy for the corresponding canonical system, can be expressed as

$$E = J(N - N_{01}/2) \quad (1)$$

where  $N_{01}$  is the number of nearest neighbor pairs with one site full and one site empty and  $J$  is the interaction energy. Thus, the energy is only dependent on the number of islands. The most likely distribution of atoms among the islands is the one with the highest degeneracy. The number of ways of arranging the atoms into the islands so that there are  $n_1$  in the first island,  $n_2$  in the second, etc. is given by

$$g = \frac{N'!}{n_1!n_2!n_3!\dots n_{N_{01}}!} \quad (2)$$

(where  $N' = N - N_{01}$ ), which is maximum for  $n_1 = n_2 = n_3 = \dots = n_N$ . A similar argument holds for the empty sites. Thus, the most likely distribution has islands of equal thickness and equal spacing.

Fig. 1 shows the most probable island spacing as a function of temperature and coverage for the micro-canonical one-dimensional Ising model. The functional forms of these curves are in good agreement with the experimental observations for annealed O/Cu(110). However, the expected fluctuations, even for the micro-canonical ensemble, are large. Below it is demonstrated that asymmetric short range interactions on a two-dimensional lattice can give evenly spaced stripes with high probability.

### III. Two-Dimensional Monte Carlo Simulations

The Monte Carlo simulations performed here, [16], use similar interaction energies to those reported earlier [6] with the important addition of a next-nearest neighbor attraction in the  $\langle 1\bar{1}0 \rangle$  direction as suggested by Witterlin *et al.* [7]. Additional interactions include stability for strings of at least four adatoms. This is consistent with the STM data in which strings of several adatoms were

observed to move as units across the surface [4–6]. The interaction energies that we use are shown in Fig. 2 and are described below.

Although O and Cu are both mobile, it is sufficient to consider one mobile species in the Monte Carlo simulations. These are referred to below as nuclei, and they consist of an oxygen adatom bonded to a single Cu adatom with the bond between the two unbreakable. The nuclei are adsorbed on a fcc[110] lattice. The number of nuclei used was determined by the experimental coverage of oxygen ( $\Theta$ ) and was conserved for the duration of the simulation (canonical ensemble). The diffusion of the nuclei was modeled as isotropic. The short range interactions used in this model were initially approximated by the behavior of this system as observed by STM [4–6], and were originally used to describe the structure of the unannealed surface [6]. First, the  $\langle 001 \rangle$  nearest-neighbor interaction, Fig. 2a, was chosen to be attractive as is implied by the formation of strings. Next, the  $\langle 001 \rangle$  diagonal next-nearest neighbor interaction, Fig. 2b, is included to account for the experimental observation that kinked strings are also commonly observed [6]. The attractive interaction between strings along the  $\langle 1\bar{1}0 \rangle$  direction, Fig. 2c, is included to reproduce the observation of coalescence of strings into stripes and its magnitude is on the order of the interaction energy measured by Besenbacher *et al.* [17]. The only repulsive interaction is the  $\langle 1\bar{1}0 \rangle$  nearest-neighbor, Fig. 2d. This interaction is invoked to give the void or missing row observed experimentally, and the preferential growth of islands/stripes in the  $\langle 001 \rangle$  direction. The additional four nuclei chain interaction, Figs. 2e and 2f, accounts for the observation that chains of four or more nuclei are more stable than chains of fewer nuclei and move across the surface as a linked unit [5].

Starting with randomly distributed nuclei at 640K, we find that strings of nuclei rapidly form. Upon cooling from 640K to 293K fairly evenly spaced stripes of nuclei form. Typical Monte Carlo simulation results are shown in Fig. 3. The numbers and spacings of these stripes depend upon the coverage, but are the same for multiple runs at a given coverage. We find that from *ca.*  $8 \times 10^4$  up to *ca.*  $10^7$  moves per nucleus, we obtain identical results for lattices of  $30 \times 30$  Cu atoms. We find similar results for lattices of  $30 \times 30$ ,  $60 \times 60$ , and  $128 \times 128$  Cu atoms, as well as for asymmetric lattices, all

with periodic boundary conditions. The structures formed were also independent of the initial configuration. The same striped phases resulted either from nuclei initially distributed randomly or when one large complete island (stripe) initially contained all nuclei.

Fig. 4 shows the simulated stripe spacing ( $D$ ) vs. coverage using only the short-range interactions given above. This result is in qualitative agreement with the experimental O/Cu(110) data — Fig. 2a of Ref. [2]. The small fluctuations in our data, obtained by several repeated simulations at the same coverage, are approximately the size of the points in the Fig. 4. Note that the vertical scale of the data in Fig. 4 varies dramatically with the interaction energies chosen.

In our simulations, by randomly adsorbing Cu–O nuclei at 294K followed by the same number of steps as for high temperature/annealed adsorption, we reproduce the previous STM data [4–6] and simulations [6] which resulted in disordered strings. These starting conditions resulted in some clustering of strings as seen by STM in Ref. [7]. However, starting with one perfect stripe several nuclei wide, we find that at 294K in  $10^7$  attempted moves per nuclei that this island broke up into the same number of stripes found for the annealed surface at this coverage. We take this as evidence pointing toward the striped phases being equilibrium structures in our simulations.

#### IV. Conclusions

By considering the strong adatom attraction in the  $\langle 100 \rangle$  direction as the determining interaction in string formation, and the weaker adatom attraction in the  $\langle 1\bar{1}0 \rangle$  direction as determining the string-string interactions, we modeled the O/Cu(110) system using a one-dimensional Ising model. Even in this simple equilibrium model equally spaced bands were obtained with spacings and widths vs. coverage and temperature, in qualitative agreement with Fig. 2 of Ref. [2].

The essential qualitative features observed in the STM measurements of [2–6] on the O/Cu(110) surface at room temperature and upon annealing have been reproduced using simulations which consider only short range interactions including a weak adatom attraction in the  $\langle 1\bar{1}0 \rangle$  direction.

This is in contrast to the suggestion that long range forces need be invoked in order to explain the annealed data [2,18]. It has been demonstrated that long range ordering can be obtained with short range interactions. This behavior is evident in the one-dimensional Ising model, albeit with large fluctuations. In two-dimensional Monte Carlo simulations the behavior exists with much smaller fluctuations.

The formation of the equally spaced stripes on the O/Cu(110) surface is at least partially due to that particular configuration simply having the highest degeneracy (from the Ising model). The interface entropy leads to distributions of stripes with approximately equal widths and approximately equal spacings. We believe that the interface entropy and short range forces play an important role in the formation of the experimentally observed striped supergrating phases for O/Cu(110). As with stress, short range forces and entropy alone might be insufficient to describe the narrow experimental distributions of stripe widths and spacings. This would be analogous to step-step interactions in which Bartelt *et al.* have shown that the narrow distribution of terrace widths on surfaces are due to both entropy and stress terms [13,14]. We conclude that a combination of entropy and stress should lead to the observed *narrow* stripe distributions for O/Cu(110). Future directions include modeling the temperature dependence and the kinetics of the formation of this system as well as other possible causes of long range ordering [19].

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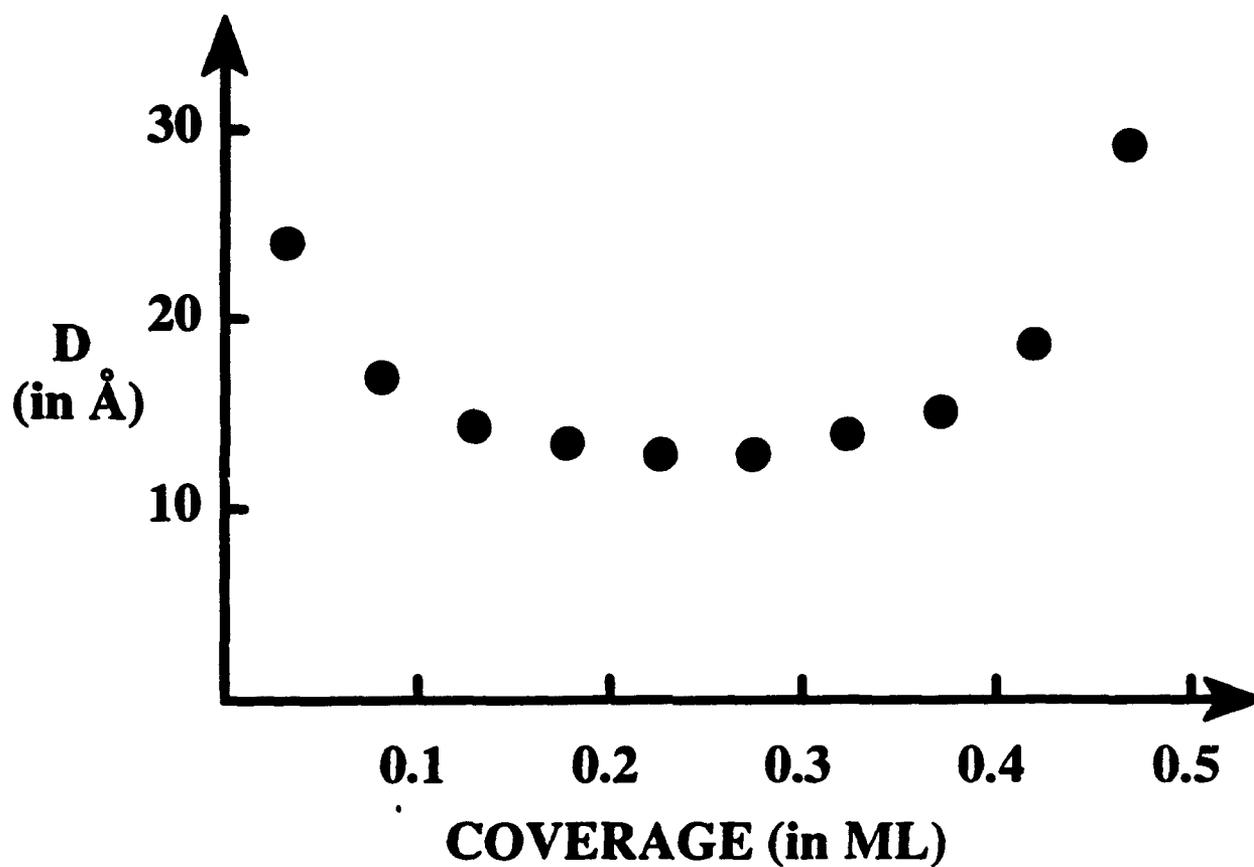
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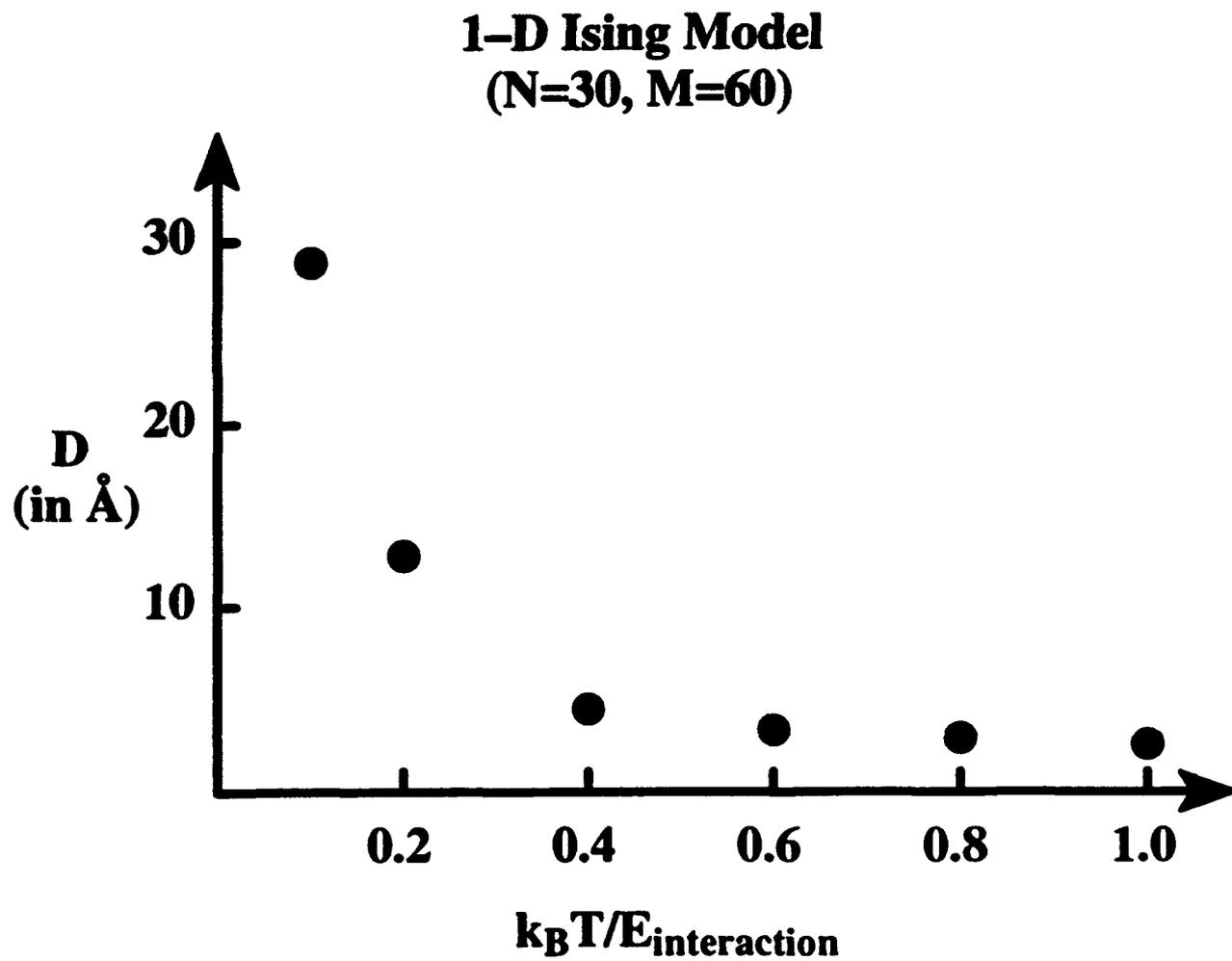
**FIGURE CAPTIONS**

1. Stripe spacing ( $D$ ) as a function of a) coverage (at  $J/T = -5$ ) and b) temperature at half monolayer coverage for the 1-D Ising model with  $M=60$  sites.
2. Interactions used in the Monte Carlo simulations. The second layer Cu atoms of the Cu(110) surface appear as the large white circles, the top layer Cu atoms appear as dark gray circles, the O atoms appear as small white circles, and the reference CuO nuclei appear in solid black. The black heavy ringed top layer Cu atoms highlight the CuO nuclei interacting with the reference nuclei: a solid white with black ring denotes one possibility, while gray with black ring denotes all equivalent possibilities. The stability gained by the reference nuclei is in each case: a)  $-109$  meV, b)  $-109$  meV, c)  $-26$  meV, and d)  $+1690$  meV. In addition, the stability gained if there are four nuclei in a string is: e)  $-77$  meV and f)  $-154$  meV.
3. Typical examples of simulation results for coverages: a) 0.16 ML, b) 0.22 ML, c) 0.26 ML and d) 0.37 ML. Periodic boundary conditions are used.
4. Stripe spacing ( $D$ ) vs. O atom coverage on the Cu(110) surface after cooling from 640K to 294K deduced from Monte Carlo simulations allowing *ca.*  $10^6$  moves per adatom. The displayed data point size approximately represents the error.

**1-D Ising Model**

( $M=60$ ,  $k_B T/E_{\text{interaction}}=0.2$ )

**Fig. 1a**

**Fig. 1b**

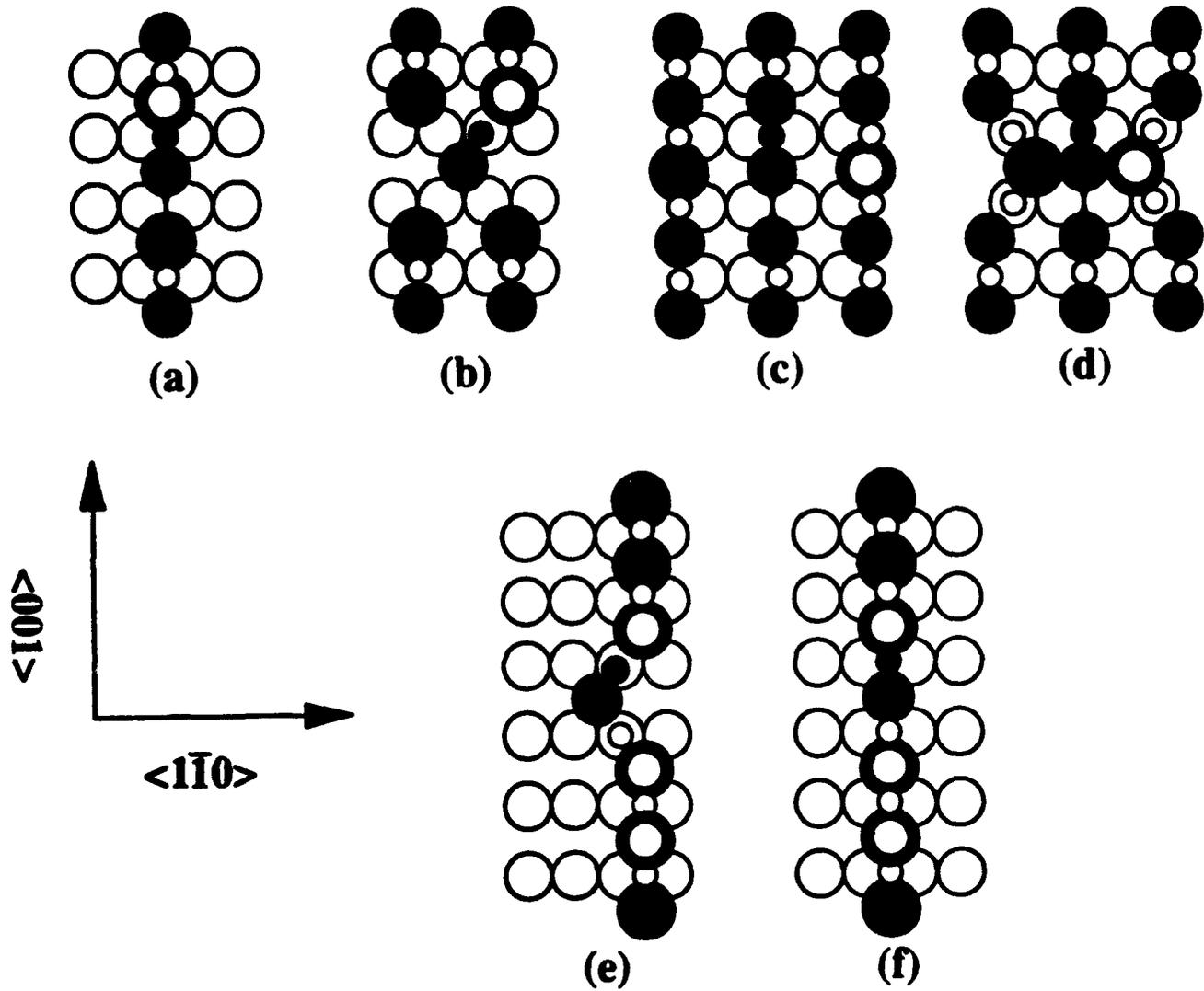


Fig. 2a-f

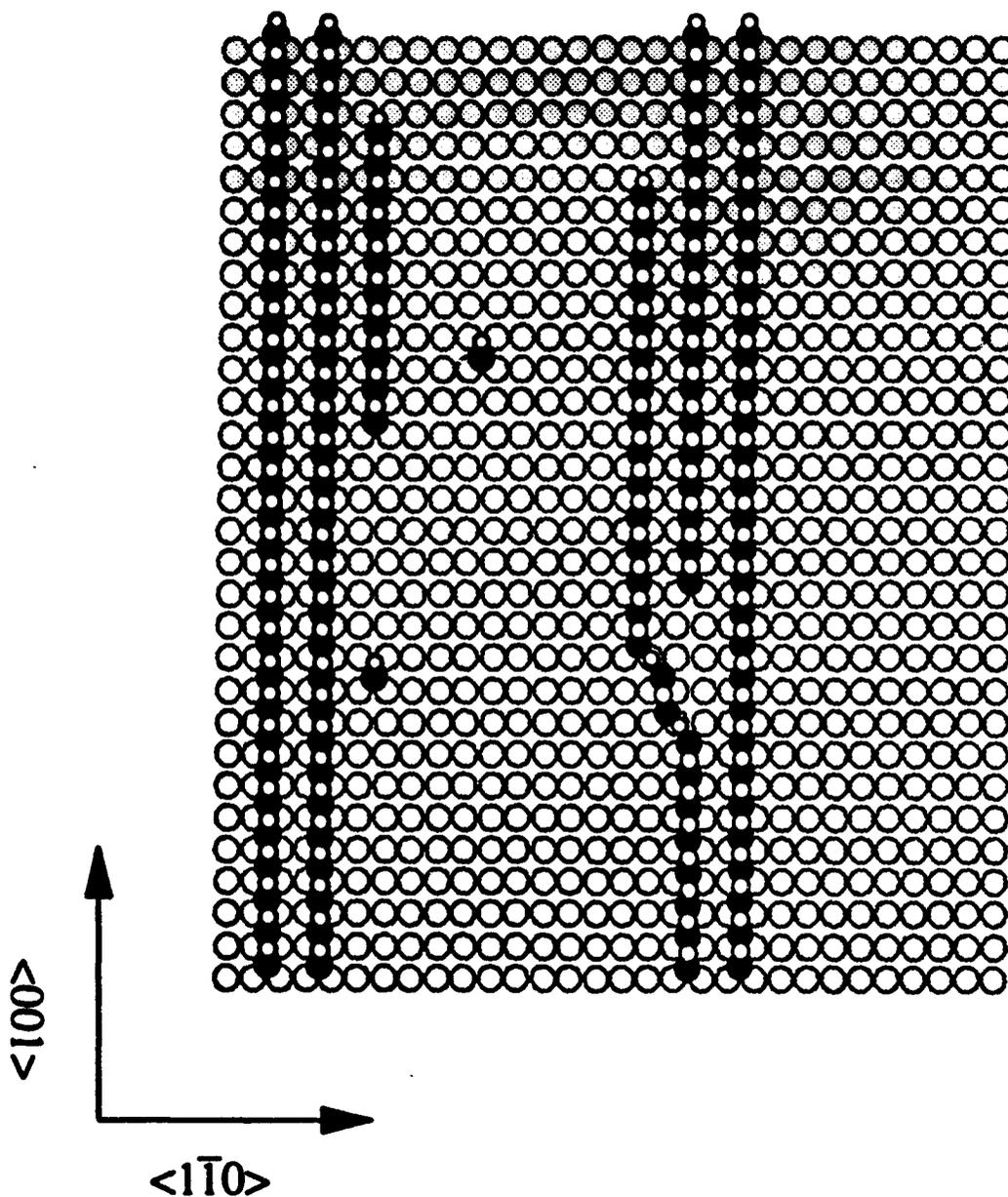


Fig. 3a

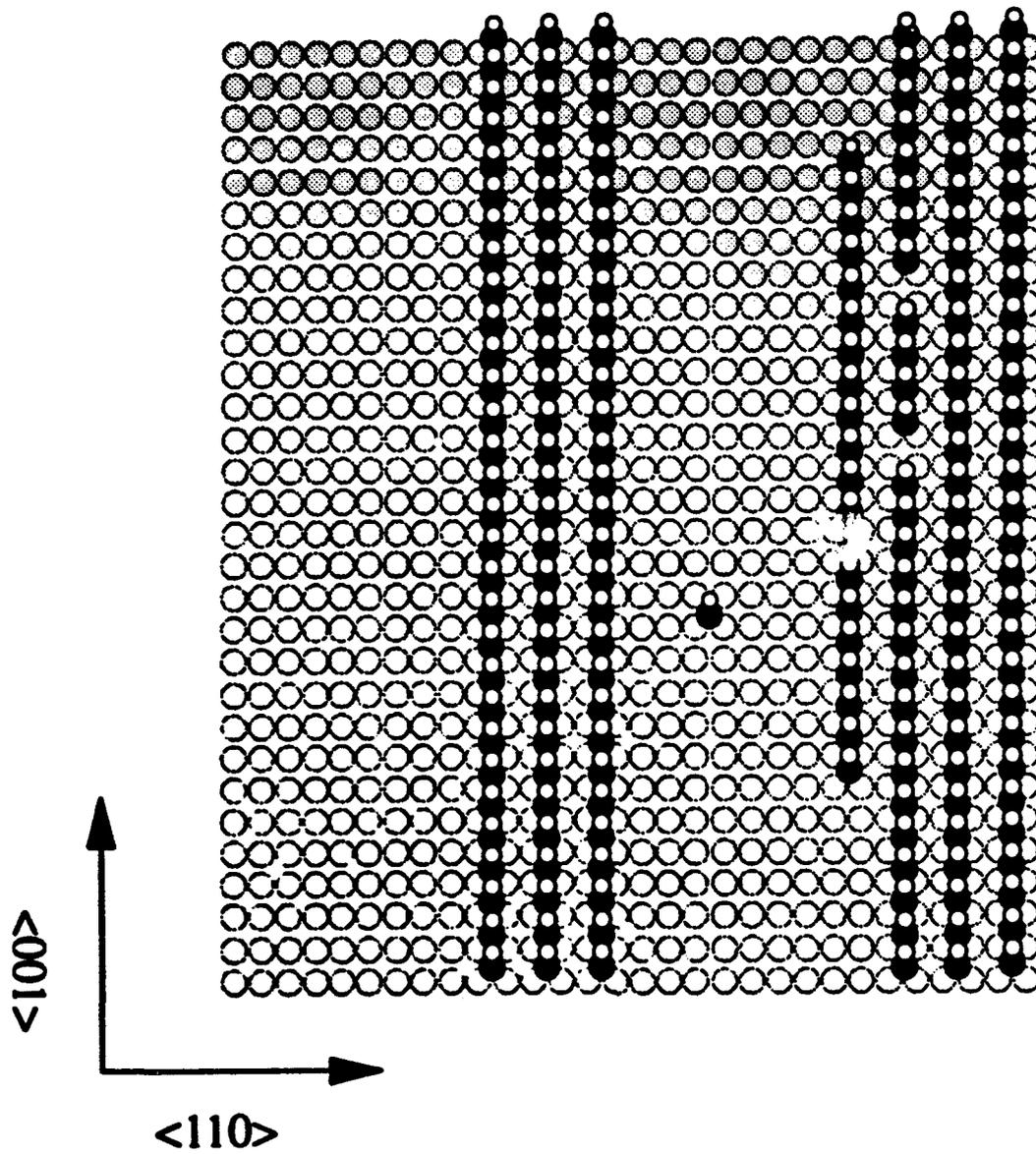


Fig. 3b

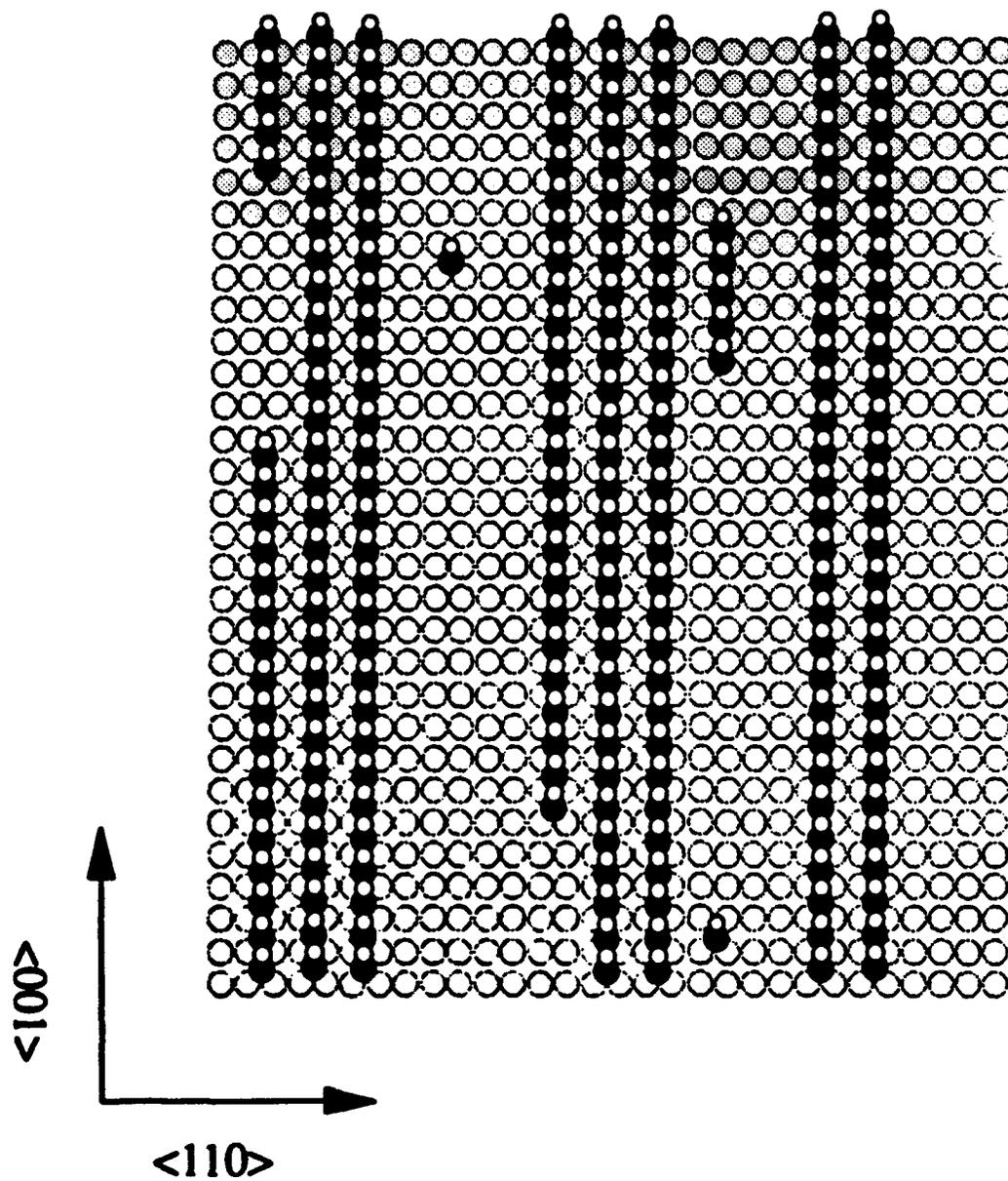
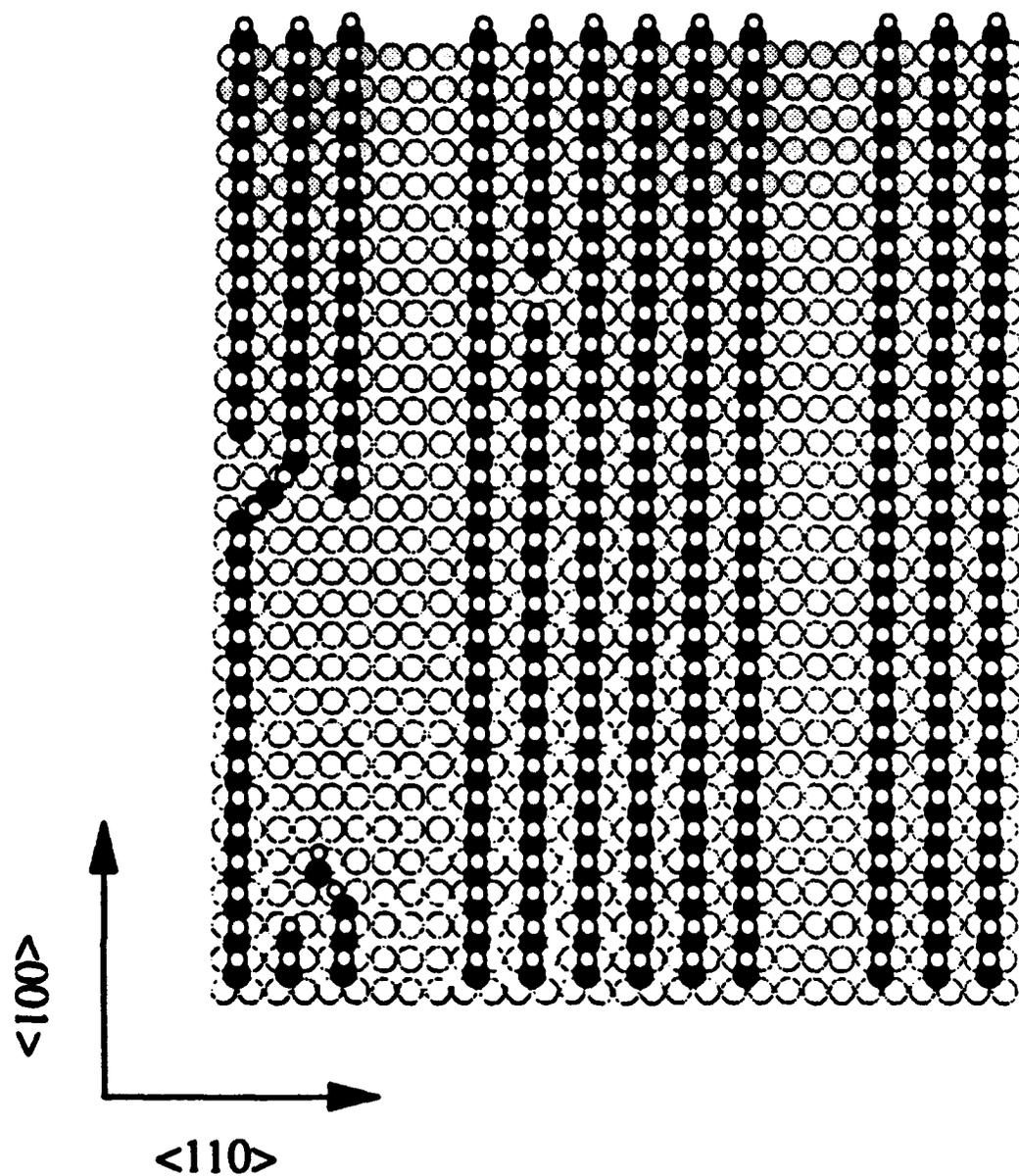


Fig. 3c



**Fig. 3d**

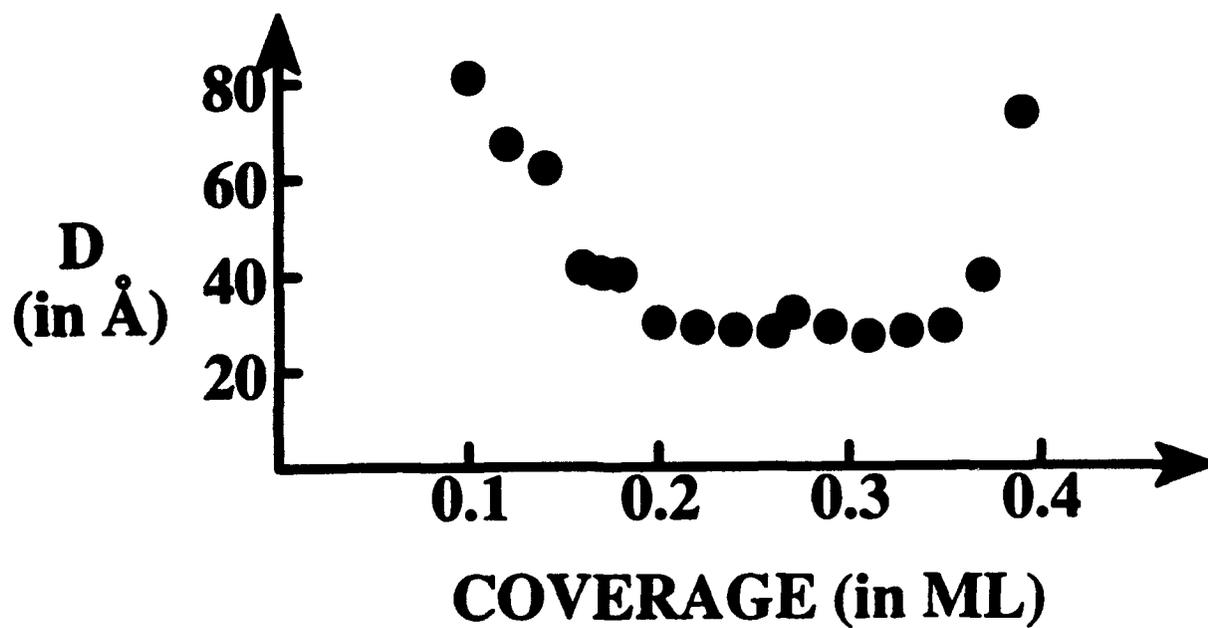


Fig. 4