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Kinetic Pathway in Stranski-Krastanov Growth of Ge on Si(001)

by

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ABSTRACT

The transition from 2D to 3D growth of Ge on Si(001) has been investigated with scanning tunneling microscopy. A metastable 3D cluster phase with well-defined structure and shape is found. The clusters have Ge lattice constants and a {105} facet structure. Results suggest that these clusters provide an easy kinetic path for formation of "macroscopic" Ge islands.

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The growth of Ge on Si has been a subject of intense study for several years, driven by the desire to create Si-Ge heterojunction superlattices, which would form the basis of optoelectronic devices.[1-4] Because of the ∿4% lattice mismatch between Ge and Si, Ge grown on Si(001) grows in a layer-by-layer mode for only several layers, after which 3D islands form.[5-9] In order to improve the likelihood of 2D layer formation, the use of surfactants has been suggested and some success achieved.[10] This system is an example of Stranski-Krastanov growth, one of three basic growth modes postulated on the basis of interface thermodynamics. If the lattice constants are not too different and the surface energy of material "A" is larger than that of "B", "B" will wet "A", forming a layer that is strained, until the effects of the "A" interface are no longer felt (typically 1-3 layers). After these several layers, the free energy of the new "B" surface is sufficiently lower so that there no longer is an energy benefit in further wetting of strained "B" by new "B", compared to the formation of "B" clusters. These then form from newly arriving flux.

This simple picture of growth rests on the assumption of thermodynamic equilibrium: the free energy of a "macroscopic" 3D cluster competing with that of an epitaxial film. Details of the kinetics of S-K growth, including diffusional processes, the transition from 2D to 3D, and the existence of possible intermediate phases, are in general not known. In this Letter, we report a scanning tunneling microscopy (STM) study of the transition from 2D growth to 3D growth for Ge on Si(001). We

establish the existence of an intermediate phase between 2D layers and "macroscopic" 3D clusters. This intermediate phase consists of small clusters with a precise facet crystallography and a specific alignment with respect to the substrate. We demonstrate that these clusters must be part of the kinetic pathway between the 2D layers and the final 3D clusters. Understanding their crystallography may allow a determination of the atomic forces that play a role in Ge-on-Si growth.

The experiments are carried out in a UHV chamber operating in the 10^{-11} Torr range with a STM, a LEED system, and deposition sources. Substrates are nominally flat Si(001) wafers, with an actual vicinal angle, determined by STM, of $\sim$0.04°. The substrates are cleaned by heating briefly to $\sim$1525K, which leaves them with a very low defect density and regularly spaced steps. Ge is evaporated from a wafer at a system pressure of $<3\times10^{-10}$ Torr, for several substrate temperatures. The substrate is quenched to room temperature immediately after deposition or annealing and transferred to the STM. The deposition rate is determined by counting atoms on STM images of the surface after a submonolayer of Ge is deposited at $\sim$475K, a temperature at which diffusion is sufficiently slow so that only a negligible amount of Ge is lost to substrate steps.[11] There is no evidence, using STM, of contamination more than 12 hours after initial substrate cleaning.

To investigate 2D growth we deposited Ge from 0.1 to 3 ML's at a variety of temperatures. Submonolayer doses of Ge form 2D islands either at steps or freely on Si terraces, similar to homoepitaxy of Si.[11,12] Multiple layers, grown at typical temperatures (e.g., 3 ML's at 775 K), have a rough growth front often involving 2 to 3 layers in a 200Å x 200Å area. This roughness is reduced after annealing at higher temperatures (e.g., 875 K) for a few minutes. The layers maintain their 2D nature, confirming that 2D growth is not a result of kinetic limitations but actually corresponds to the equilibrium structure.

Deposition beyond 3ML leads to Ge cluster formation. However, in addition to the large, widely separated clusters that have been observed[5-9] we find a large concentration of small clusters with well-defined properties. Figure 1 shows two STM images of these small clusters as well as a large one. A scanning electron micrograph (SEM) over a much larger area is also shown in Fig. 1. Only the large clusters are visible in SEM. The SEM image shows that the bases of the large clusters are all square with sides parallel to <110> directions. STM scans on these large clusters indicate that they have very complicated facet structures, with mostly {113} planes, confirming earlier work.[8] They are terminated on top with perfect Ge(001) surface.

The major new feature of our observations is the small clusters. In both these and the large clusters, the crystal structure is a "continuation" of that of the Si substrate, (i.e., bond orientations are the same) but the shapes of the clusters

are quite different. The small clusters have predominantly a prism shape (with canted ends), in some cases a four-sided pyramid, with the same atomic structure on all four facets as shown in Fig. 2. They grow on the strained 2D Ge layers, which appear not to be modified. Their principal axes are strictly along two orthogonal <100> directions. By carefully measuring the relevant length and angle parameters, the facets are determined to be {105} planes. We propose the following model for the structure, as shown in Fig. 3. The {105} plane is simply a vicinal (001) surface tilted up 11.3° (the angle measured by STM is 11±1°) with the projection of the surface normal lying along <100>, i.e., at 45° to either of the substrate dimer row directions. The facet plane thus consists of {001} terraces separated by single-atomic-height steps along <010>. Each terrace is one face-centered-square unit mesh wide. To reduce dangling bonds, surface atoms desire to dimerize. However, every other atom at upper edges does not have another atom with which to pair. These atoms are absent, making the periodicity parallel to the substrate 2a, where a is the side length of a face-centered square, 5.66Å for bulk Ge. The periodicity up the face of a facet is 2.5a, because it takes two steps for the dimer orientation to rotate back and at each step there is an additional 1/4a shift. The unit mesh is therefore rectangular, 2a x 2.5a. With 1.5% uncertainty in our x- and y-gain calibration, we determine that these clusters have bulk Ge lattice parameters. Between these small clusters, the 2D Ge layers still have the Si lattice parameter, again with 1.5%

uncertainty.

An interesting aspect of these clusters is their generally elongated base shape and base orientation and the perfection of the facet planes. The facets are always perfectly formed; i.e., we never observe a partly completed layer on a facet. This observation is in accord with well-known concepts about the stability of low-free-energy surfaces. In such situations it is difficult to nucleate a new layer, but once it does it completes very rapidly. As the surface area grows, it becomes increasingly difficult to nucleate a new layer and the clusters slow in their growth. Because all four facets are the same, they must have the same surface free energy and sticking coefficient for arriving atoms. The prism axes are at 45° to the dimer row directions, and therefore the substrate does not provide any preference in terms of surface stress[14] or anisotropic diffusion.[15] We suggest here that their elongated shape is caused by portions of <100> steps (running at 45° to the dimer row directions) that are formed in the Ge layers during growth. There are two orthogonal sets of these steps on surfaces that are miscut in the manner of Fig. 1, corresponding to the principal axes of the clusters we observe. The steps are equivalent, unlike <110> steps. They appear to act as cluster nucleation sites. This conclusion is supported by STM measurements on samples miscut toward <100>. On such surfaces, all steps are equivalent and oriented in one way. Small clusters now predominantly form with ridges aligned along these steps. Because the density of the appropriate orientation of steps is now also greater, the number density of small

clusters is much larger and their size is reduced. Recent work[16] claims that a partial relaxation without dislocations exists between Ge clusters and the Si substrate. We can not unequivocally determine whether a discrepancy exists between this work and our results. The clusters in Ref. 16 appear to be early stages of the large clusters. Results on our small clusters, which are not shown in Ref. 16, show at least a partial relaxation, uniformly over the cluster height. We speculate that the influence of steps can produce the lattice relaxed structures we observed.

What is the role of these clusters in the transition from 2D to 3D structure? We believe that they are an intermediate step in the formation of the large clusters, a metastable phase that provides, at lower temperatures, an easier kinetic pathway for the accommodation of arriving atoms than nucleation of a large cluster. Several observations support this. First the concentrations of the small and large clusters are drastically different, being, for example, $\sim 7 \times 10^{10}$ cm^{-2} and $\sim 4 \times 10^{7}$ cm^{-2}, respectively for the conditions shown in Fig. 1. The corresponding volume of the large clusters is $\sim 10^{3}$ that of the small ones. Hence, it appears that the small clusters are much easier to nucleate on the 2D layers than the large ones. Second, as the dose is increased at constant temperature, the ratio of small to large clusters increases. Third, small clusters form preferentially at lower growth temperatures, T < 800 K; growing at 850K results in only large clusters. Fourth, upon annealing at 850K for 10 minutes, almost all small clusters vanish and more

large clusters form. These observations indicate that the small clusters are a metastable phase.

In summary, we have used STM to study the S-K growth of Ge on Si(001). We have discovered a metastable 3D phase consisting of small clusters that have a specific facet crystallography and alignment of their principal axes with respect to the substrate. The clusters consist of prisms or four-sided pyramids with four equivalent {105} facets. We believe that they are heterogeneously nucleated at <100> steps and that this provides an easy way for the initial formation of clusters. Large clusters are also observed; they are widely separated, with no apparent preferential nucleation site. We suggest that they may nucleate homogeneously when the concentration of small oriented, heterogeneously nucleated clusters gets high enough, possibly through the preferential growth of one small cluster at the expense of others. There is no evidence of a denuded zone around large clusters, indicating that the large clusters do not "capture" all the small clusters within an area, as has been observed in other systems.[17] This leads us to the following picture. Small clusters form more easily and hence preferentially form first and at higher concentration. They are metastable and, if either the flux is shut off or the temperature raised sufficiently, will laterally evaporate to provide atoms for large clusters. In the intermediate range (typical growth temperatures and deposition rates) they may act to trap arriving atoms temporarily. As their growth slows (because of the desire, mentioned earlier, to form perfect facets) a larger proportion of

the incoming flux finds its way by diffusion to the large islands. Hence the small clusters act to mediate the growth of the large ones, affecting the kinetic path to the equilibrium cluster formation. A theoretical study of formation and structure of these intermediate phases may shed light both on the energetics of the 2D Ge surface and on the kinetics of the S-K transformation.

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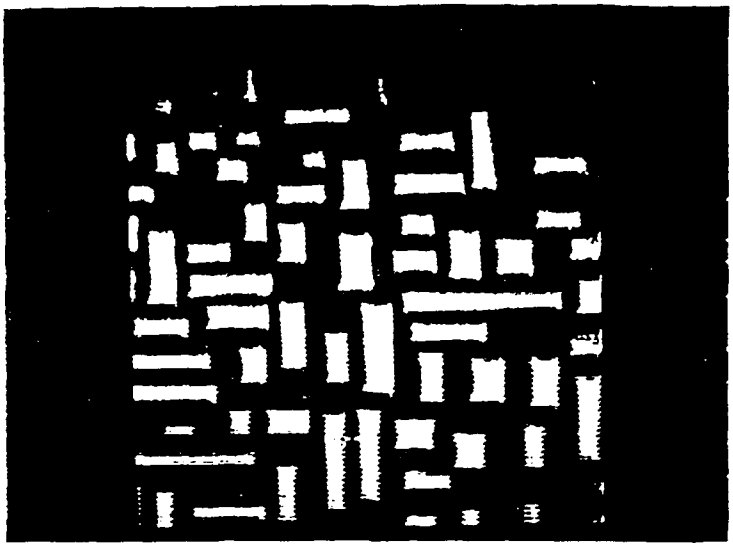
Figure Captions

Fig. 1 STM and SEM images of Ge clusters on Si(001). a) STM image, 2500 x 2500 Å. Clusters have rectangular or square bases, in two orthogonal orientations, corresponding to <100> directions in the substrate. Clusters are ≲1000Å long and 20-40Å high. b) STM image 8000x8000Å, showing a large cluster surrounded by many of the small clusters shown in a). The large cluster is ∿250Å high. Because of this height and an STM tip effect, the large island appears irregular in shape. The image is shown in a curvature mode, to remove the large height difference. c) SEM image showing large clusters. The square sides are parallel to <110> directions. The small clusters are not visible in SEM.

Fig. 2 STM images of single small cluster. a) Normal height grey scale plot 400x400Å; the height difference is 28Å. b) curvature-mode grey scale plot. The crystal structure on all four facets as well as the dimer rows in the 2D Ge layer around the cluster are visible. The 2D layer dimer rows are 45° to the axis of the cluster. c) a perspective plot of the cluster.

Fig. 3 Model of cluster facets. a) unreconstructed (105) plane projected onto (100) plane; b) reconstructed (105) plane projected onto (001) plane. In both only top-layer atoms are shown to avoid confusion. Side views of the associated (001) terraces and steps are shown at the left. c) An STM scan on one of the facets, 100x100Å.

Each bright spot in the image corresponds to a pair of dimers. The unit mesh with the displaced center can easily be observed. The top of the cluster corresponds to the top of all three panels.



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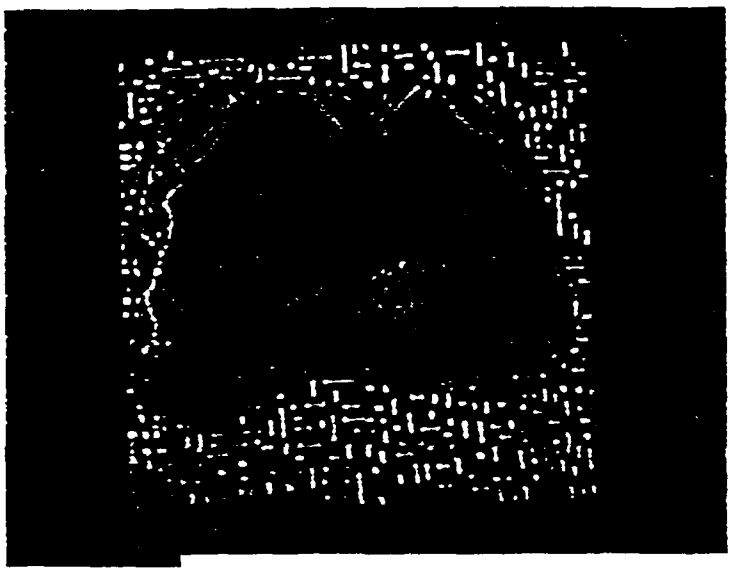

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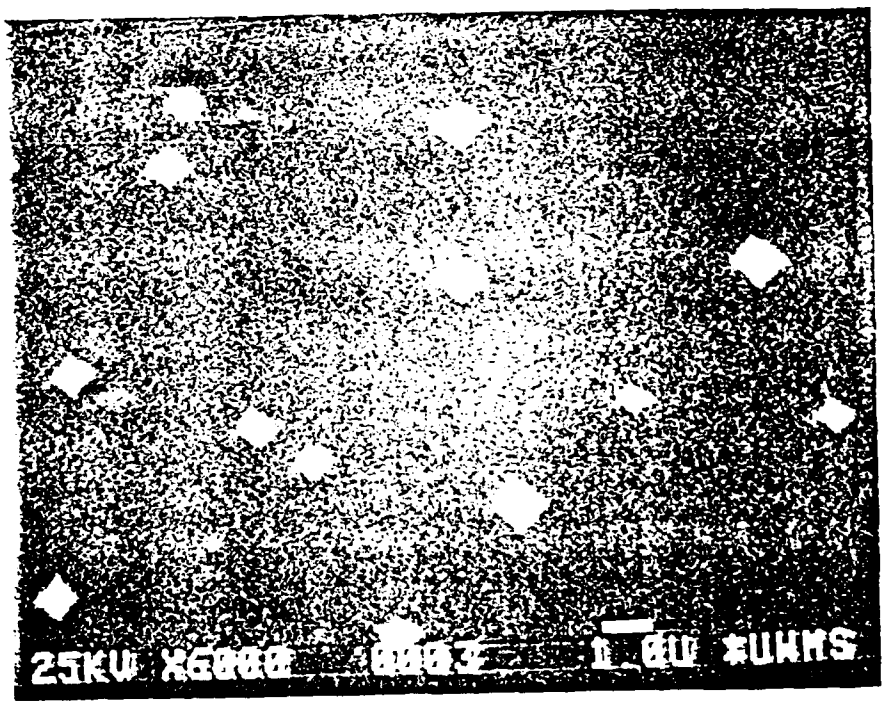

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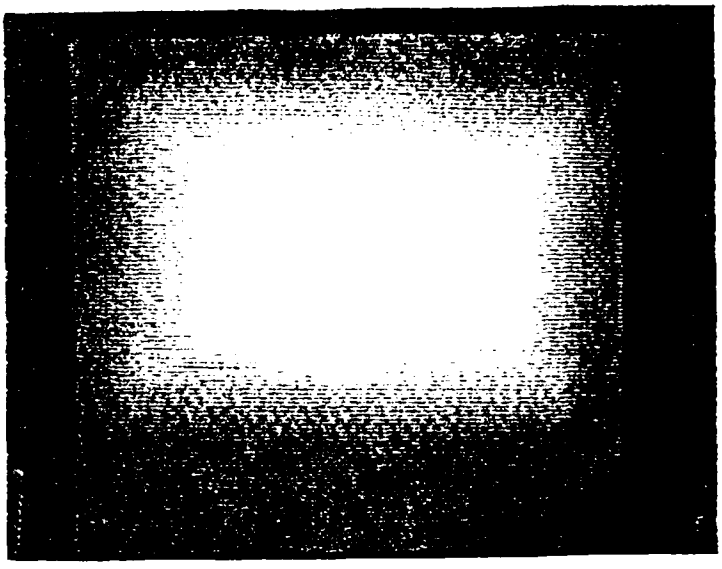
Fig. 1



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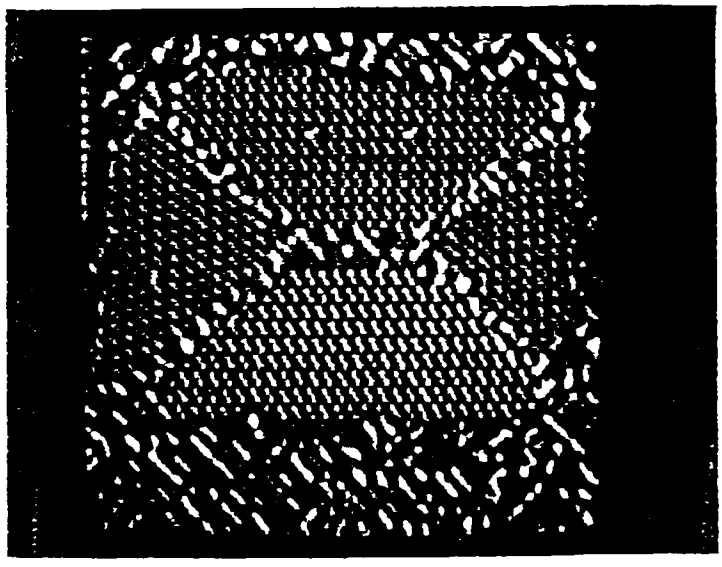

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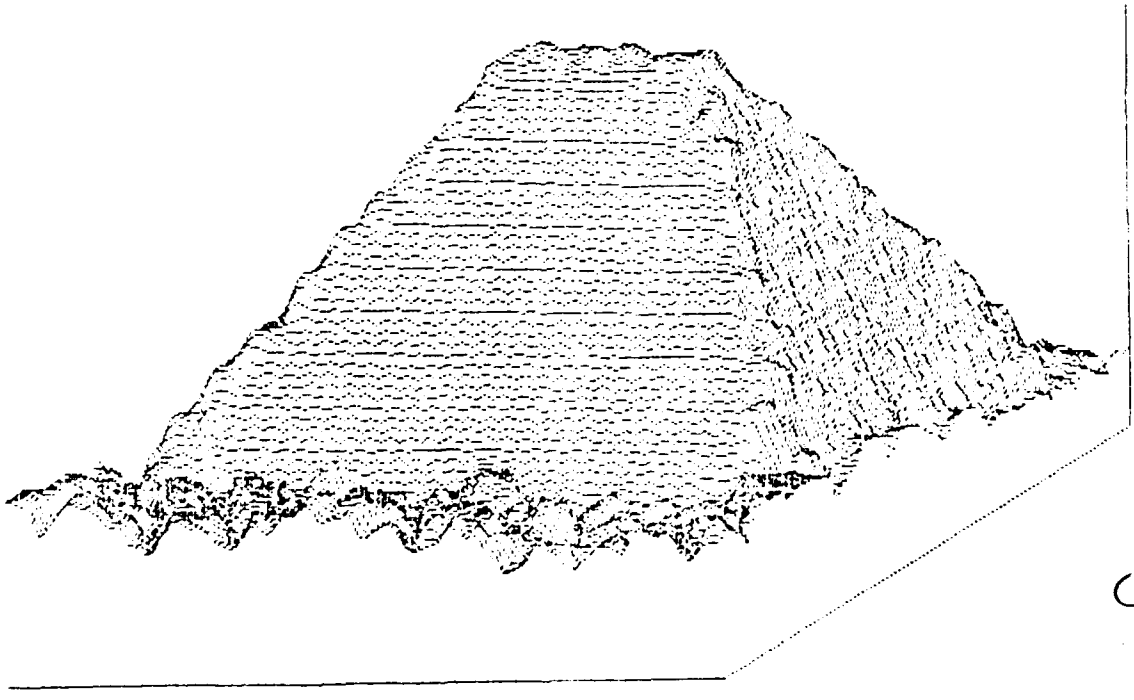

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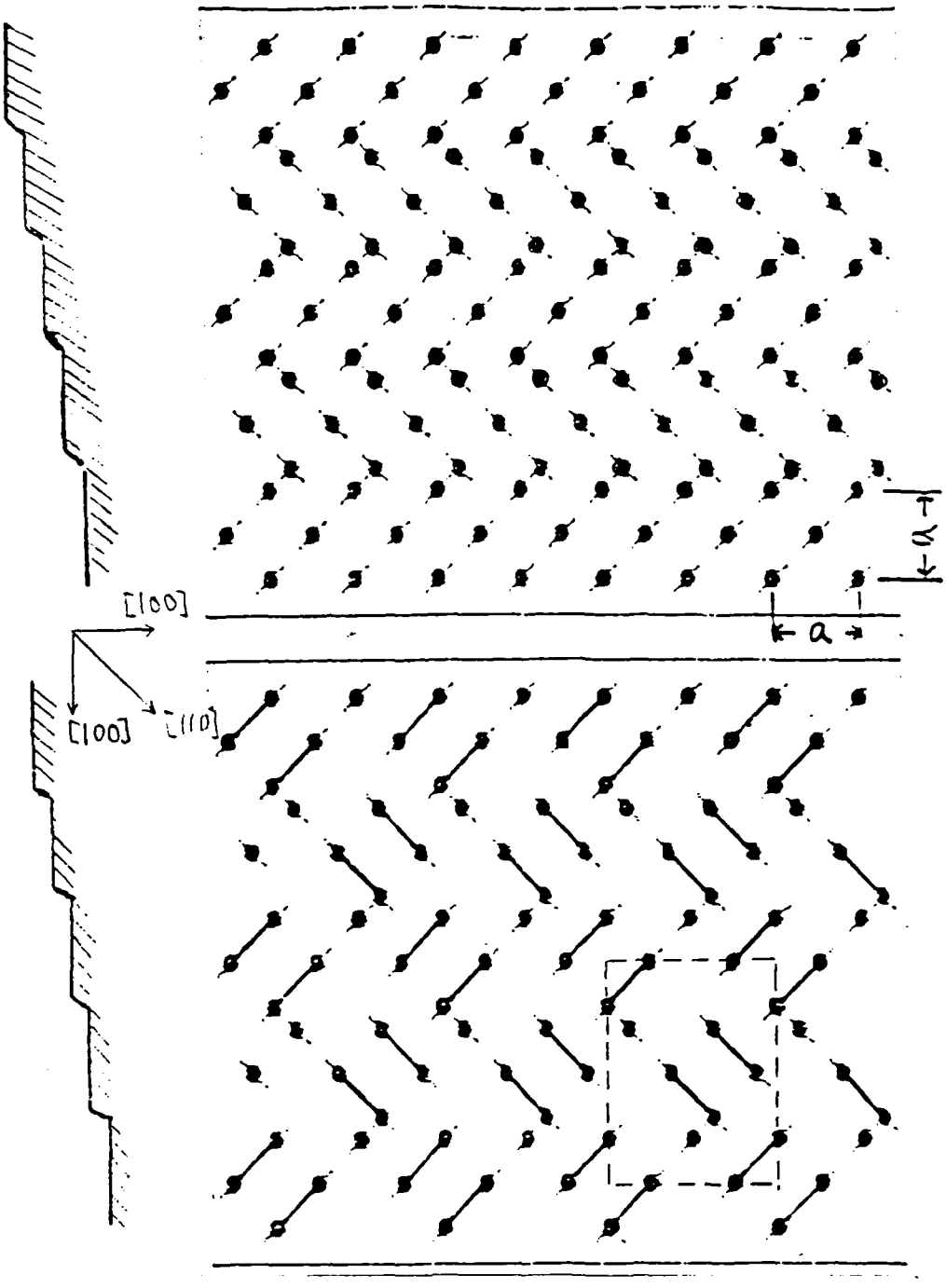
Fig 2



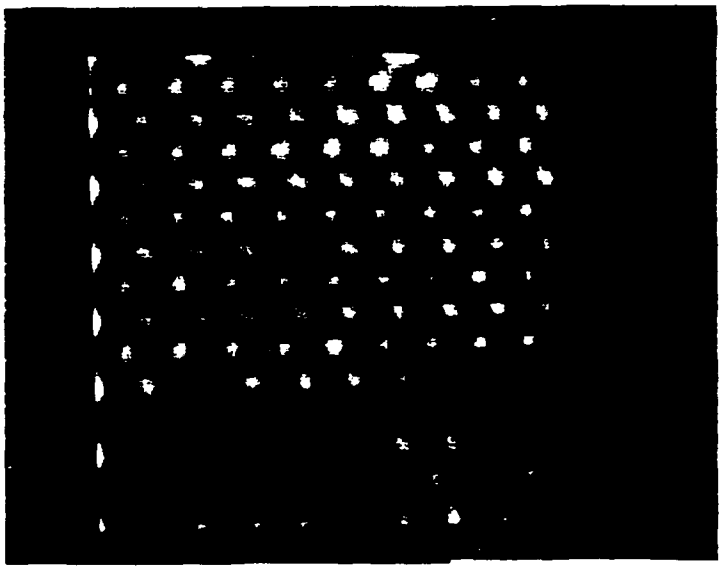


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Fig. 3