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E. Nes and J. Washburn

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TRANSMISSION ELECTRON MICROSCOPE INVESTIGATION OF THE GROWTH OF COPPER PRECIPITATE COLONIES IN SILICON

E. Nes

University of Oslo, Institute of Physics, Blindern, Oslo 3, Norway,

and

J. Washburn

Inorganic Materials Research Division, Lawrence Radiation Laboratory, Department of Materials Science and Engineering, College of Engineering, University of California, Berkeley, U S A.

A B S T R A C T

The growth of copper precipitate colonies in high purity, dislocation free silicon single crystals has been examined by transmission electron microscopy. The colonies, being coplanar arrangements of copper-silicide particles on either {110} or {100} planes, nucleate and grow during rapid cooling from higher temperatures. The kinetics of the colony growth process has been analyzed in terms of a model based on repeated nucleation on a climbing dislocation. The possibility of having the growing copper-silicide particles dragged by the dislocations has been discussed, and a mechanism based on a particle dragging/dislocation climb effect has been suggested in order to explain the development of dendritic dislocation dipole branches.

1. INTRODUCTION

Rapid cooling of copper doped dislocation free silicon single crystals may cause the formation of star shaped agglomerats of precipitate particles. This precipitation effect has received considerable attention, especially by the application of infrared microscopy. Due to its limited resolution, this technique has primarily been applied to investigate the density and distribution of the agglomerates. On the morphology of the individual agglomerates, infrared microscopy has established that the precipitate configurations consist of planar "sword" like branches.[1-3] Transmission electron microscopy observations have demonstrated that the planar branches are agglomerates of tiny particles[4-6]. A detailed transmission electron microscope analysis of the internal structure and crystallographic nature of the copper-silicide precipitate configuration, was recently reported by the present authors[7-10]. Ref. 7 describes the agglomerates as dendritic shaped precipitate colonies, with the different colony arms being co-planar arrangements of precipitate particles enveloped by a dislocation loop. The crystallographic planes of the colony arms were either {110} or {100} . The enveloping dislocations were allways of a pure edge character, hence, the Burgers vectors involved were either $\frac{a}{2}$ < 110 > or a < 100 > . Throughout the rest of this paper the two different types of colony arms will be referred to as 110- or 100-colonies.

A simple colony growth model based on repeated nucleation on a climbing dislocation was proposed in Ref. 7. This model explained some of the colony characteristics, as the formation of planar precipitate arrangements and the presence of a surrounding edge dislocation loop. No attempts, however, were made to explain the growth phenomenon which caused the colonies to develop long dendritic dislocation dipole branches. This paper, is a continuation of the work published in Ref. 7. We report here on the results of a transmission electron microscope investigation of the colony growth process, and propose

a colony growth model capable of explaining the characteristic variations in colony morphology as described in Ref. 7 and below. Of importance for the discussion of the colony growth kinetics is the recent observation by Nes and Solberg[11,12] showing the dragging of copper precipitate particles by climbing edge dislocations in silicon. This observation suggests that precipitate migration is very likely to have occured during colony growth. It will be demonstrated that the high activation energy for dislocation pipediffusion in silicon may explain the tendency to dendritic growth.

2. EXPERIMENTAL

The silicon single crystals were obtained from Texas Instruments Co. The material was graded as Lopex (low oxygen dislocation-free silicon). The crystals were grown by a floating-zone technique in the form of cylindrical rods of 1 in diam. x 6 in. , with [111] as the growth axis. The resistance of the crystals was 50 Ω cm and the conductivity was n type.

The precipitate colonies nucleate and grow during rapid cooling from higher temperatures[7]. In order to study the growth process a series of specimens were given the following cooling treatment: From the isothermal annealing temperature, T_h , the specimens were cooled at a rate which was known to give large precipitate colonies, and by interrupting this cooling by a rapid quench at the temperature T_q , the colonies were frozen in at the stage of development reached at this quenching temperature. By choosing an appropriate series of temperatures, T_q , the growth of the colonies was followed.

Two series of experiments have been performed. One starting with a holding temperature, T_h , at about 925 °C and the other with T_h about 850 °C. In both cases the subsequent cooling rate was about 8°C/sec. For the different

specimens this cooling rate was interrupted at different temperatures, T_q , selected at 25 °C intervals from the holding temperatures down to about 600 °C .

Wafers, about 1 mm thick and with [111] , [110] and [112] surface orientation were cut from the sylindrical rods. Following the heat treatments. Foils for electron microscope investigation were prepared by chemical polishing in a standard way. The colonies were examined both in a Siemens Elmiscope electron microscope operating at 100 kV, and a high voltage Hitachi electron microscope operating at 650 kV.

3. EXPERIMENTAL RESULTS

The 110- and 100-colonies exhibit characteristic differences which may be summarized as follows: The enveloping dislocation in the 100-colonies forms long narrow branches in the orthogonal < 110 > directions of the {100} plane and thus giving these colonies a dendritic shape (see Fig. 7 a in Ref. 7). A typical feature of the dendritic branches is that a precipitate particle is located at the tip of each branch. The structure of the 110-colonies were described as a nearly even distribution of particles on {110} planes, enveloped by a roughly circular dislocation loop[7]. Continued investigation, however, has demonstrated that also 110-colonies have a tendency to grow by forming narrow dendritic branches. Figure 1 shows a star-shaped colony consisting of 110 type colony arms only. As can be seen from Fig. 1 the dislocations form long narrow dipole branches in the <112> directions of the {110} colony plane. Note that also these dipole branches have a particle attached to each tip.

During the cooling the colonies nucleate at about 800 °C whether the holding temperature was 925°C or 850°C. This is consistent with the results given in Ref. 7; that varying the holding temperatures in the range 820 °C to 974 °C caused no change in precipitate colony size. Thus copper appears to have been present in a concentration corresponding to the solid solubility at about 800°C.

3.1. Growth of 110- colonies.

A 110-colony at an early stage of development is presented in Fig. 2. This precipitate-dislocation loop configuration was frozen in at 773 °C. The elongated half-loop is oriented in the $[01\bar{1}]$ direction, and as can be seen from Fig. 2 b the precipitates are aligned as a bead string along the dislocation. The dislocation is out of contrast in the $[1\bar{1}\bar{1}]$ reflection, Fig. 2 b, while in strong contrast in the $[2\bar{2}0]$ reflection; this is consistent with a a/2 [101] Burgers vector.

The transition from this elongated loop configuration into the familiar {110} planar precipitate arrangements is demonstrated in Figs. 3 and 4. The growth in these two cases was stopped at 725 °C and 701 °C respectively. In Fig. 3 the elongated loop configuration is partially preserved. The geometry of the particle-dislocation configuration is outlined in Fig. 3 b. As can be seen from this sketch the initial half-loop configuration (broken line) is located in the (100) plane. A series of observations confirms that in the first growth stage the 110-colonies appear as elongated loops on {100} planes. Consequently at this stage the dislocations are not in a pure edge orientation. The left part of the initial elongated loop in Fig. 3 a has started to climb on the (101) planes into a helical configuration, leaving precipitates behind.

Figure 4 shows a 110-colony interrupted in its development at a temperature 24 °C below that of the one in Fig. 3. Thus a more developed (101) arrangement is obtained. The contours, however, of the initial elongated loop configuration, oriented in the $[01\bar{1}]$ direction and located in the (100) plane, is still clearly visible. The rows of precipitates marked A, B and C in Fig. 4

are interpreted as representing successive positions of the climbing dislocation. Note that the large precipitate marked D in Fig. 4 is followed by a depleted zone in the $[\bar{1}01]$ direction. Such depleted zones are frequently observed within 110-colonies, Figs. 5 and 6. These zones are elongated in the <110> direction and an oversized precipitate particle is always located at the zone-end pointing in the climb direction. The zone in Fig. 6 contains two large particles from which two new dislocation loops have been nucleated. Figure 6 also clearly demonstrates that the particles within the 110- colonies are distributed in rows due to the repeated nucleation process on the climbing dislocation. Another interesting detail revealed by the micrograph in Fig. 6 is that the dislocations rather than being smooth lines as in Fig. 5 may consist of pieces of straight segments oriented in either <110> or <112> directions.

3.2. Growth of 100-colonies

Figs. 7[13,14] and 8 represent early stages in the development of two 100-colonies. Both are oriented in the [101] direction and both have a a[010] Burgers vector. The growth of these colonies was interrupted at 762°C and 707 °C respectively. The precipitate-dislocation dipole configuration in Fig. 7 ends (or begins) in a large precipitate inside the foil, while the configuration in Fig. 8 runs through the entire thickness of the foil. Figure 7 also illustrates the beginning of the dendritic character of the 100-colony, as a freshly formed branch appears in the $[\bar{1}01]$ direction.

The micrograph in Fig. 9 represents a part of a 100-colony in a (110) surface foil. This precipitate colony was stopped in its growth at 629 °C. As the size of the colonies observed in this foil were about equal to those found in specimens cooled at a rate of 8°C/sec down to room temperature, it is concluded that when reaching the temperature of about 650 °C the 100-colonies are fully developed.

4. DISCUSSION

The precipitate colonies are nucleated heterogeneously, and it was suggested in Ref. 7 that the nucleation centers were minute silica particles. Although no such particles were detected in the as-grown silicon crystals, their presence was postulated based on the observed bulk distribution of colonies in a growth ring pattern[7]. Due to the lattice mismatch between the copper-silicide particles and the silicon matrix, the growth of the copper-silicide nuclei will cause a severe lattice strain unless vacancies are being absorbed to accomodate the particle-matrix mismatch. The transition from a nucleus copper-silicide precipitate to a particle associated with a dislocation loop (or loops) has not been observed experimentally. The results, however, show that loops of different Burgers vectors are formed, i.e. $\frac{a}{2}$<110> and a<100>. Following the formation of dislocation loops, repeated nucleation, as described in Ref. 7, results in the generation of planar branches in a star configuration.

The a<100> Burgers vector dislocations may be nucleated directly or be a result of a reaction between $\frac{a}{2}$ <110> dislocations. This latter mechanism has been suggested by Baker et al.[15]. Since a reduction in core energy is expected, this reaction may be energetically favorable. Why the $\frac{a}{2}$ <110> dislocation loops of the 110-colonies in the initial stage also prefer to grow on {100} planes cannot be considered established. This growth mode, however, lasts for a short time only, after which the habit plane of the 110-colonies is also given by pure climb.

In order to explain the appearance of precipitate colonies on stacking faults in steels, Silcock and Tunstall[16] proposed a mechanism based on repeated nucleation on a climbing Frank partial dislocation. The sketches in Fig. 10 a-d outline the principle of this repeated nucleation model. A similar mechanism for the repeated nucleation on an unfaulted edge dislocation loop was proposed by the present authors in Ref. 7. Although this simple mechanism explains the planar colony arrangement of particles and the presence of a surrounding edge dislocation loop, other characteristic aspects of the colony structure are not accounted for. For instance, the above model predicts the distance, d, between rows of precipitates, Fig. 10d, to be equal to about half the distance, l, between particles within a row. The present results show that within 110-colonies d frequently is much larger than l, Fig. 6. Another effect, not explained by Silcock-Tunstall model, is the startling colony growth phenomenon causing long narrow dislocation dipole branches with a precipitate attached to the tip of each branch. Both of these effects, however, may be accounted for in terms of a repeated nucleation mechanism if it is assumed that the particles, while growing, are also being dragged by the climbing dislocations. This assumption can be considered justified based on the recent work by Nes and Solberg[11,12]. By performing an in situ hotstage transmission electron microscope investigation, Nes and Solberg were able to follow the dragging of copper-silicide particles by climbing dislocations. If the particles in Fig. 10 also were being dragged along while they were growing, this explains why d may be much larger than l.

Climb of the dislocation is caused by the chemical climb force due to the local vacancy subsaturation near a growing precipitate. Except for this dragging effect, the sequence between consecutive nucleations

may still follow the pattern schematically illustrated in Fig. 10. The experimental results also show that this growth mode is most typical for 110-colonies. However, deviations from this regular growth mode are observed, as the colonies sometimes form long dendritic dipole branches. It is suggested that this dendritic growth effect can be the result of a low core diffusivity along the dislocation line. A low core diffusivity will cause the exchange of vacancies between some of the more widely spaced growing precipitates and the dislocation to be localized. This should occur when l, in Fig. 10, exceeds a certain critical value l^*, where $l^* = \sqrt{D_c \tau}$ · D_c is the core diffusivity of silicon atoms and τ is the time between consecutive nucleations. Having $l \gg l^*$ a situation arises where the climb rate of the dislocation near a precipitate and the migration rate of the precipitate may both exceed that of the connecting dislocation segments, resulting in the formation of a long dendritic dipole branch. The growth rate of the colonies at about 700°C is about 10^{-4} cm/sec, and the rows of particles within a colony are spaced about 2000Å apart (Fig. 6); this gives $\tau = 0.2$ sec. By taking the activation energy for core diffusion equal to about half that of self diffusion in bulk[17], this gives $l^* \simeq 1000$Å. From the micrograph in Fig. 6, l can be seen to vary from 3 - 500Å, thus for 110-colonies, l is usually less than l^* and consequently the typical growth mode for these colonies can be schematically described by the model in Fig. 10. When the 110-colonies occasionally develop dipole branches, these grow in the <112> directions of the colony plane, Fig. 1. These represent low energy orientations for the straight dipoles as in these directions the dislocations are expected to dissociate[18,19].

For the growth of 100-colonies, it appears that l almost always is larger than l^*, see Fig. 7a in Ref. 7. Therefore, 100 type colonies always grow by the dendritic precipitate dragging mechanism. The dendrites in the 100-colonies grow in the <110> directions. It is suggested that this represents a low core energy orientation for the a<100> Burgers vector dislocation.

ACKNOWLEDGMENTS

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FIGURE CAPTIONS

Fig. 1. Star-shaped colony with the different arms occupying {110} type planes. Surface orientation (111). Note the tendency to grow by forming dendritic dipole branches in the <112> directions.

Fig. 2. A 110-colony stopped in its growth at 773°C. (a) Strong dislocation contrast. (b) The dislocation is nearly out of contrast.

Fig. 3. A 110-type colony in a (110) surface foil. This colony was frozen in at 725°C. The sketch illustrates the transition from growth on the (100) plane into a helical expansion on (101) planes.

Fig. 4. A 110-colony in a (101) surface foil. This colony was stopped in its growth at 701°C. The contours of the initial (100), $[01\bar{1}]$ configuration is still visible.

Fig. 5. Depleted zones in the $[\bar{1}10]$ direction within a 110-colony.

Fig. 6. Part of a 110-colony showing a depleted zone in the $[\bar{1}01]$ direction, note the distribution of particles into rows due to the repeated nucleation process.

Fig. 7. A 100-colony stopped in its growth at 762°C. Surface orientation (110). A freshly nucleated branch is growing in the $[\bar{1}01]$ direction.

Fig. 8. Part of a 100-colony frozen in at 707°C. The two micrographs (a) and (b) show the dislocation in and out of contrast respectively. This is consistent with an a[010] Burgers vector.

Fig. 9. A small part of a 100-colony in a (110) surface foil. This colony was interrupted in its growth at 629°C.

Fig. 10. Stages in the repeated nucleation process on a climbing edge dislocation. (After Silcock and Tunstall, Ref. 16.)

0 0 0 0 3 9 0 2 1 7 7

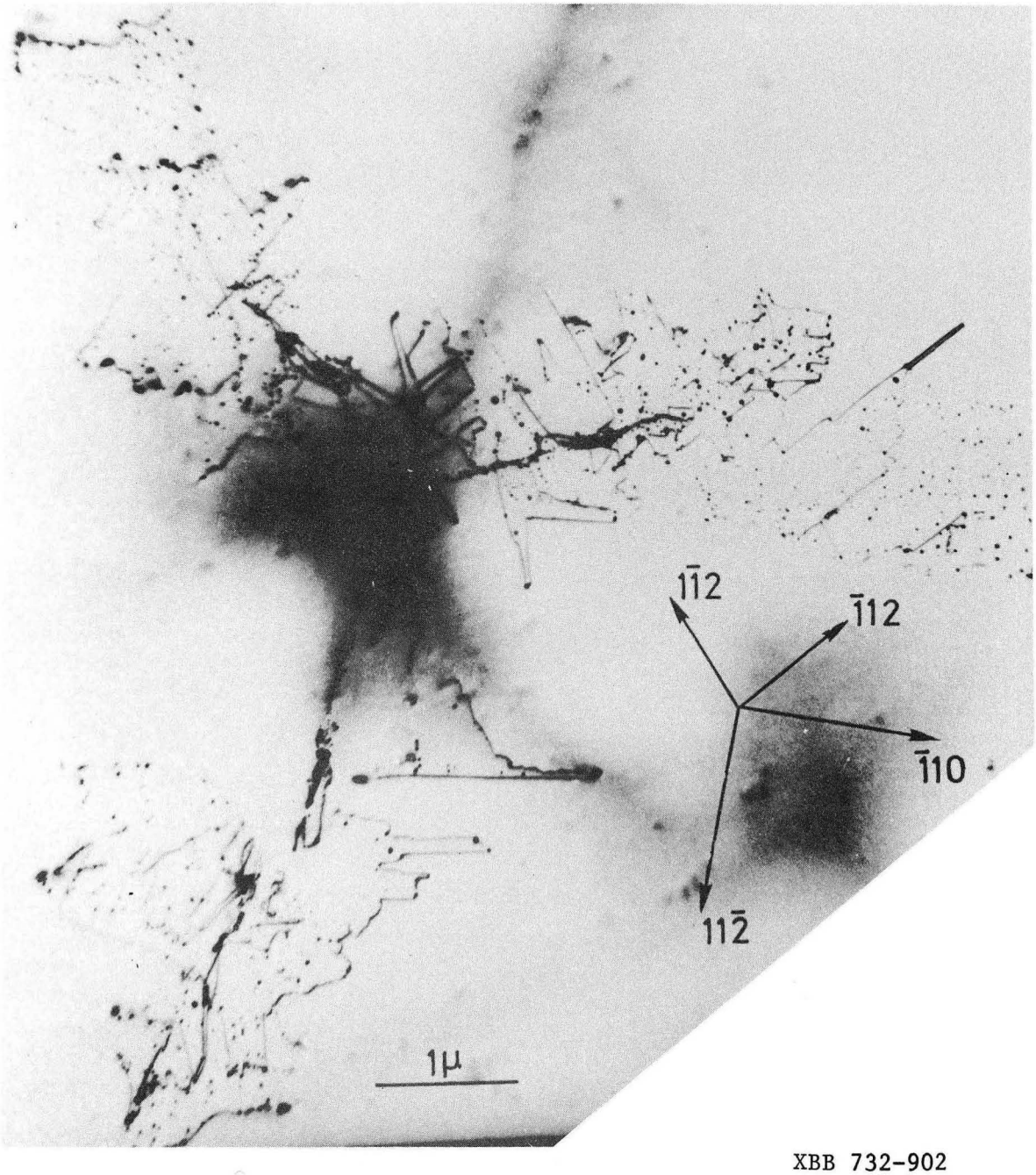

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Fig. 1

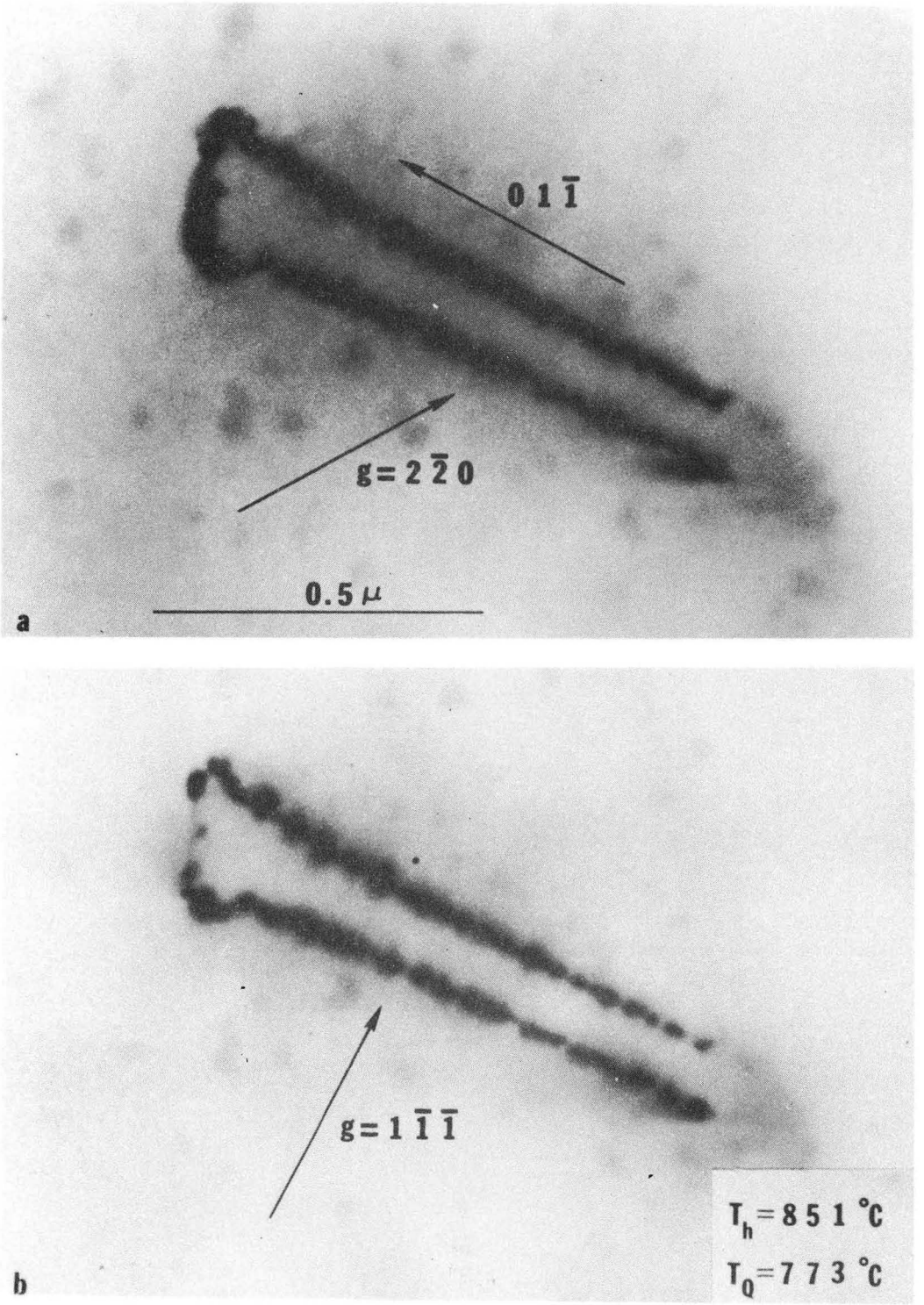

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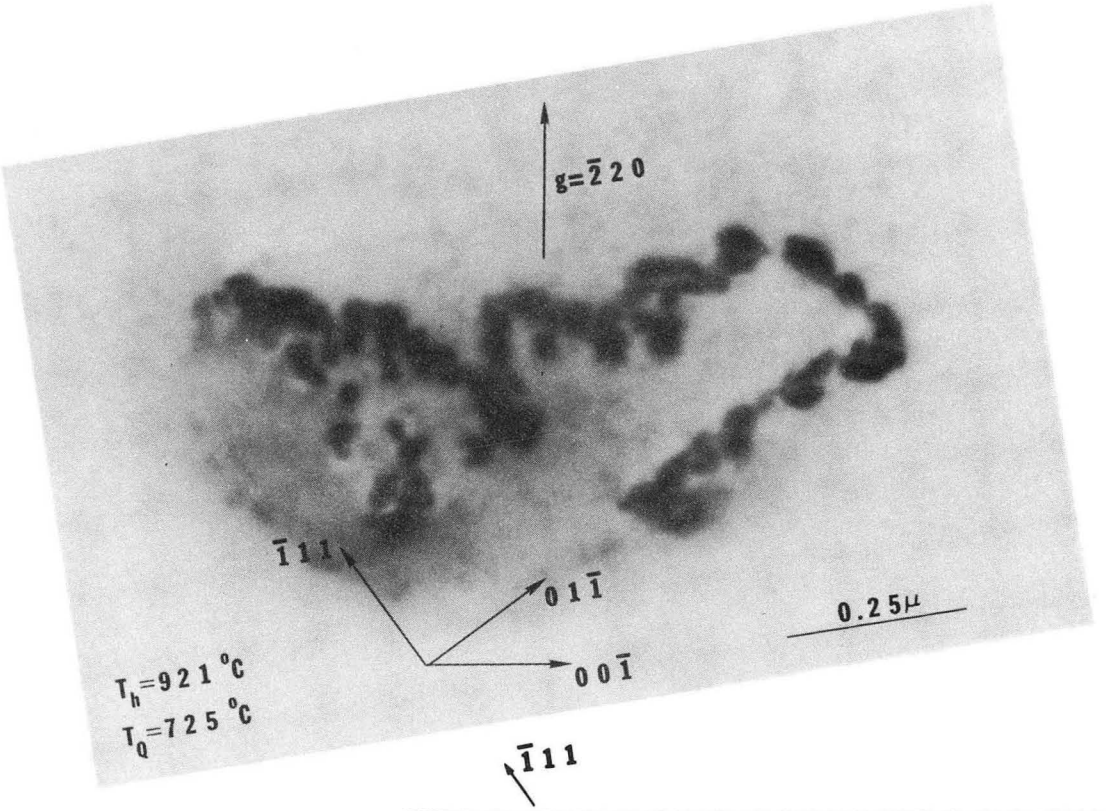
Fig. 2

0 0 0 0 3 9 0 2 1 7 8



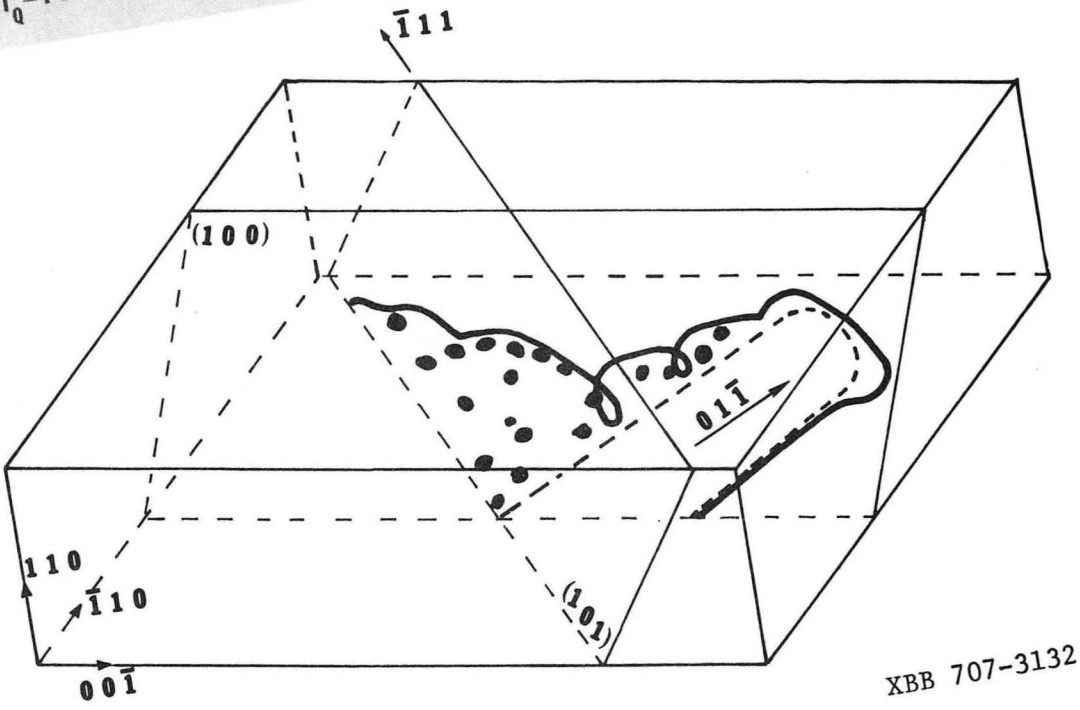


Fig. 3

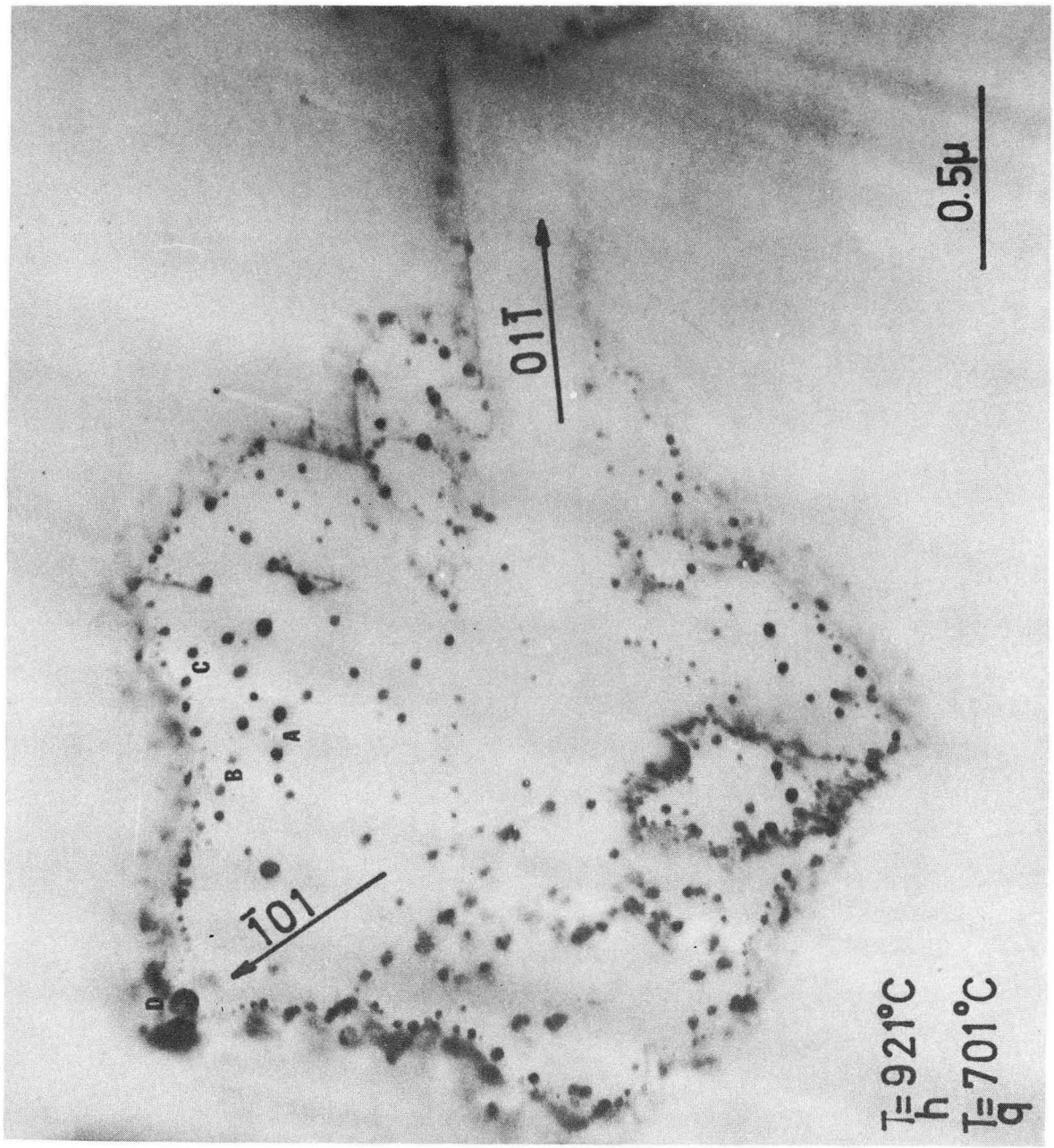


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Fig. 4

0 0 0 0 3 9 0 2 1 7 9

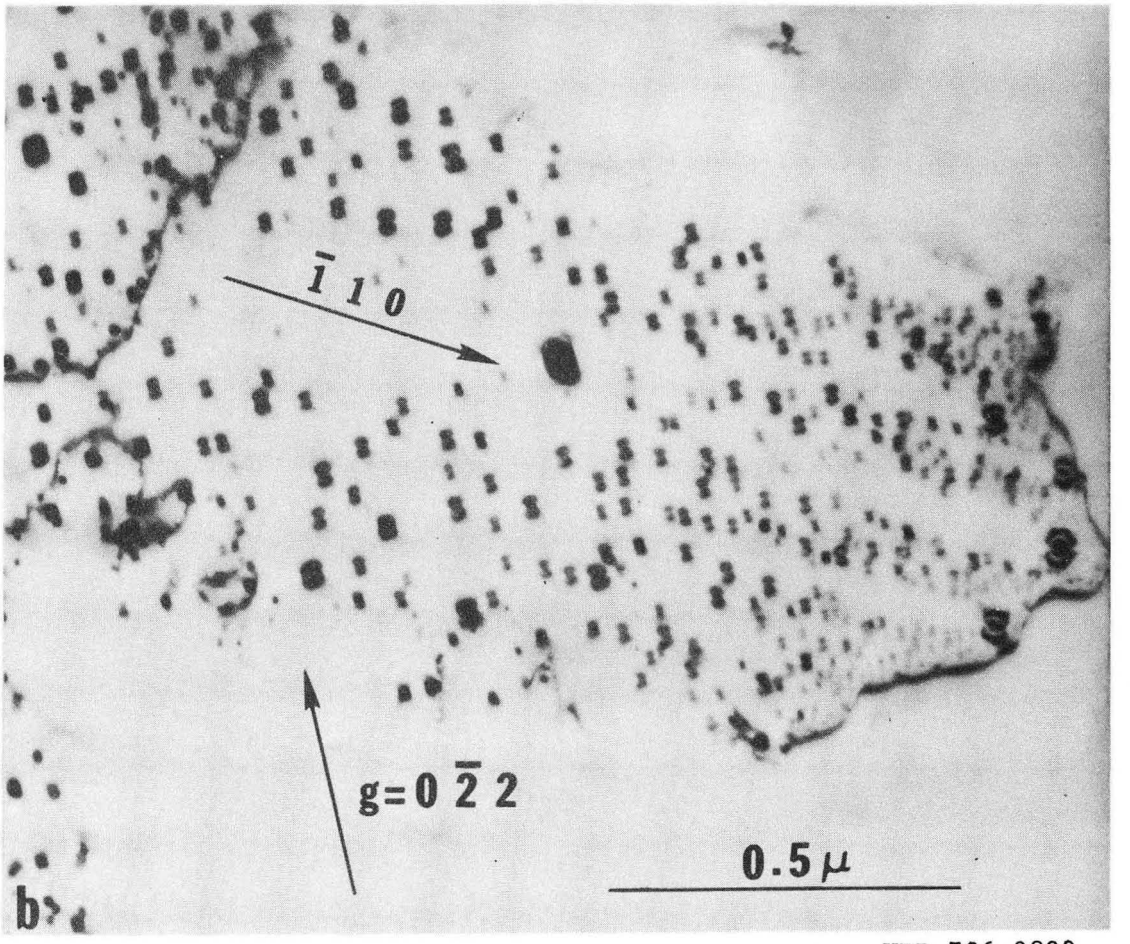

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Fig. 5

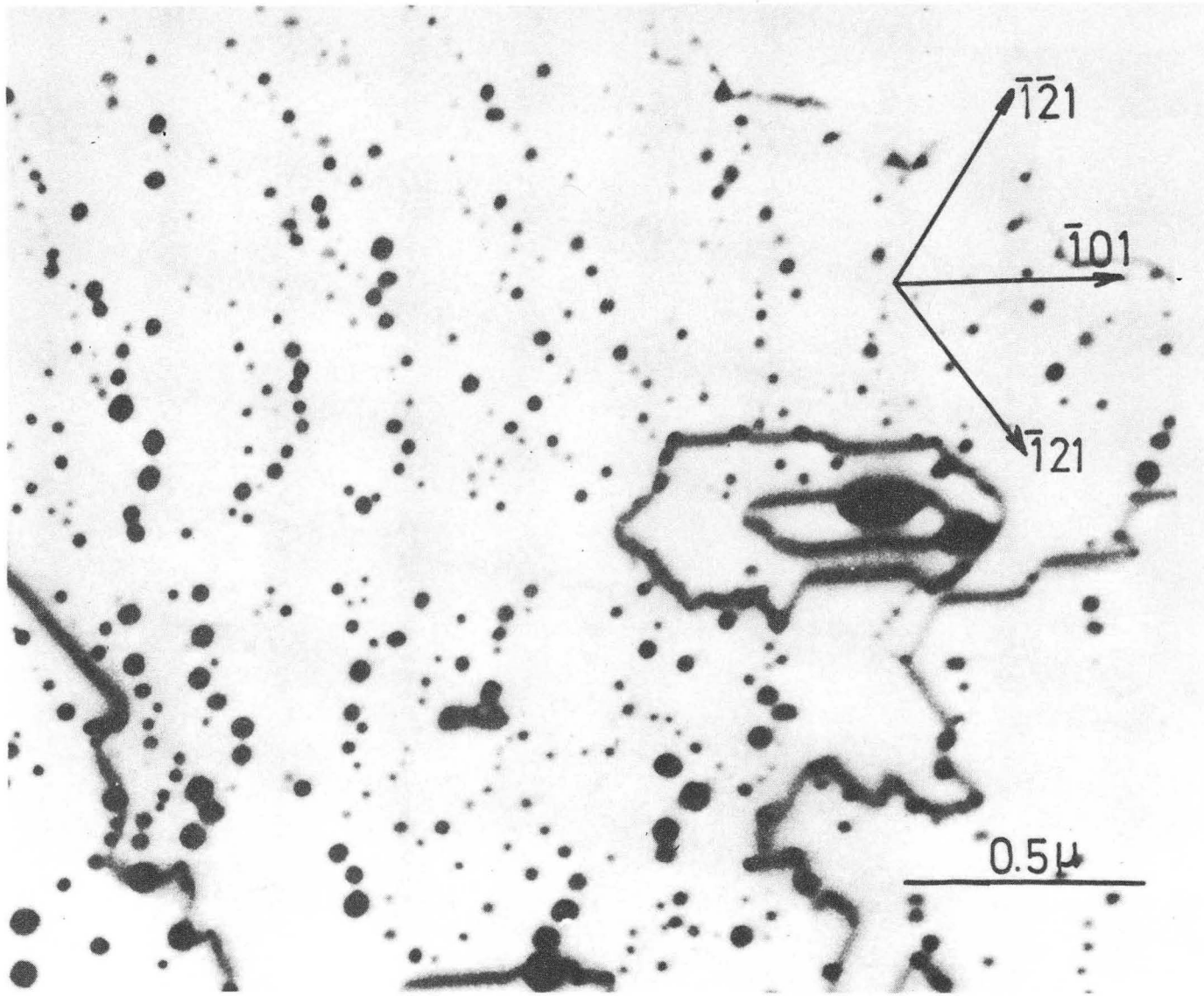

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Fig. 6

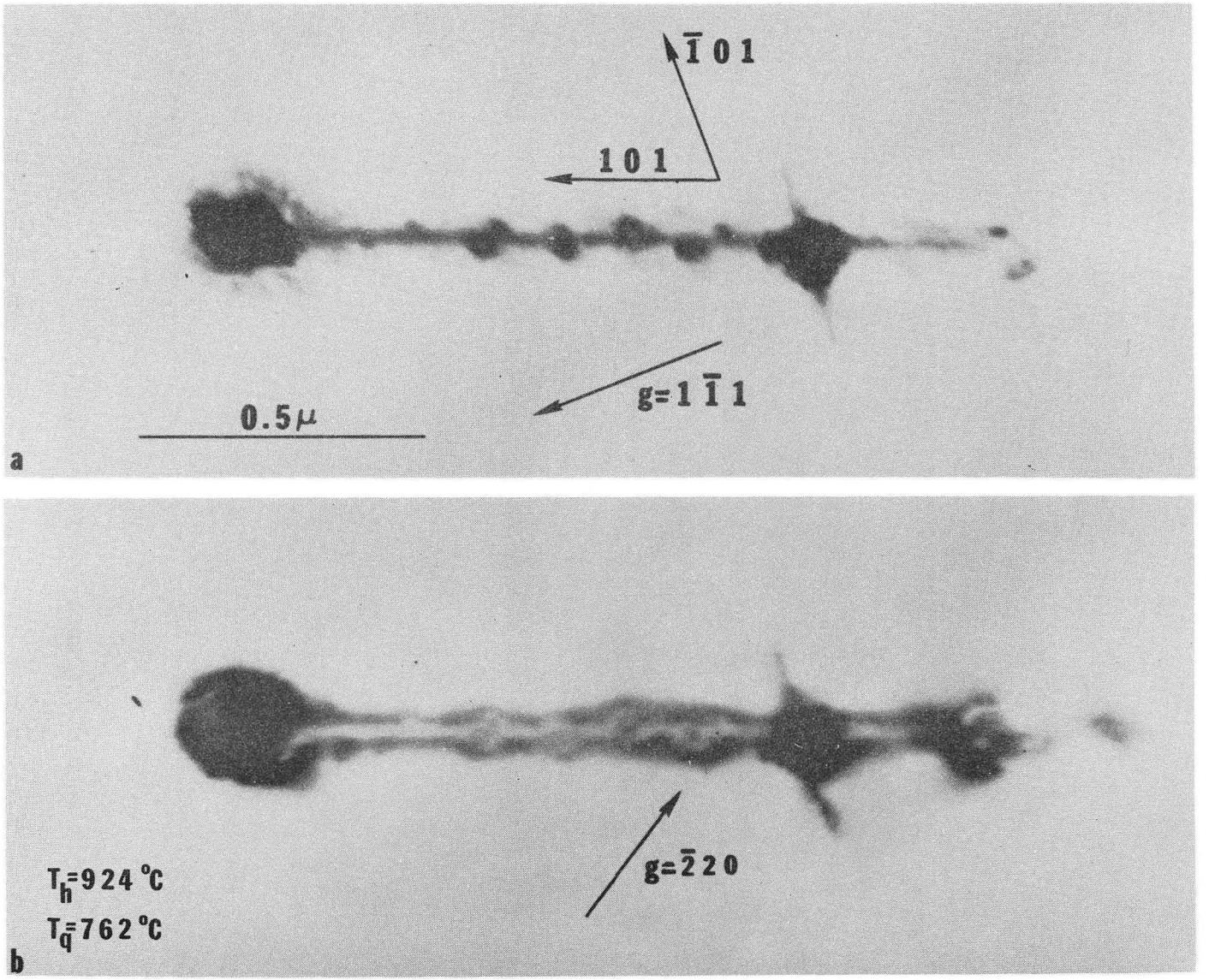

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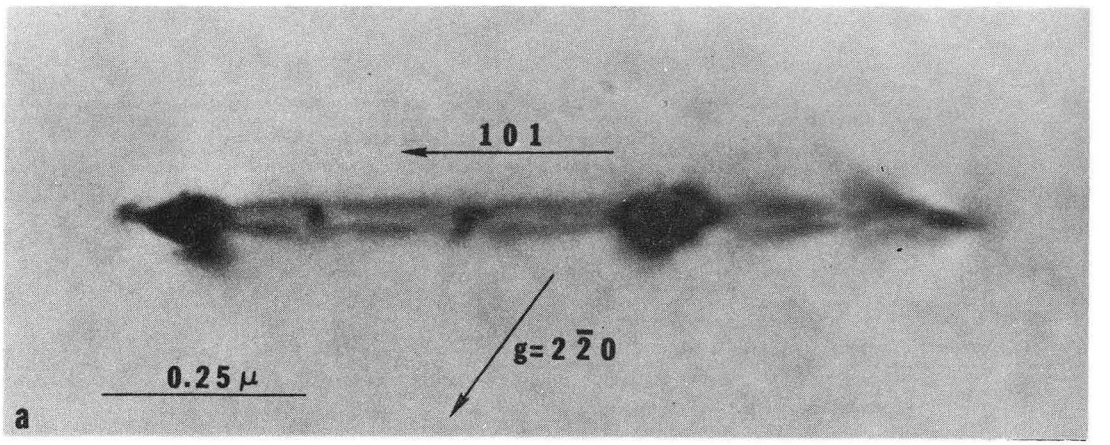
Fig. 7



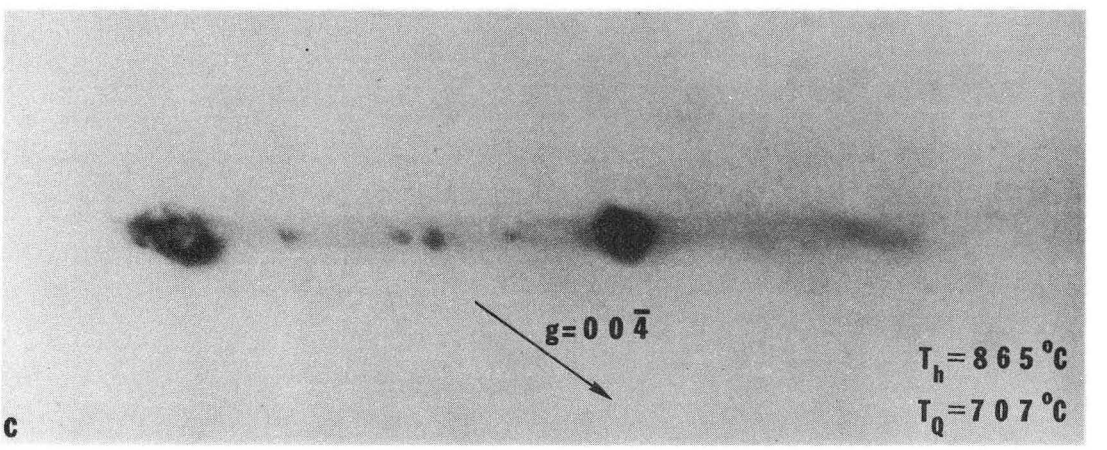


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Fig. 8

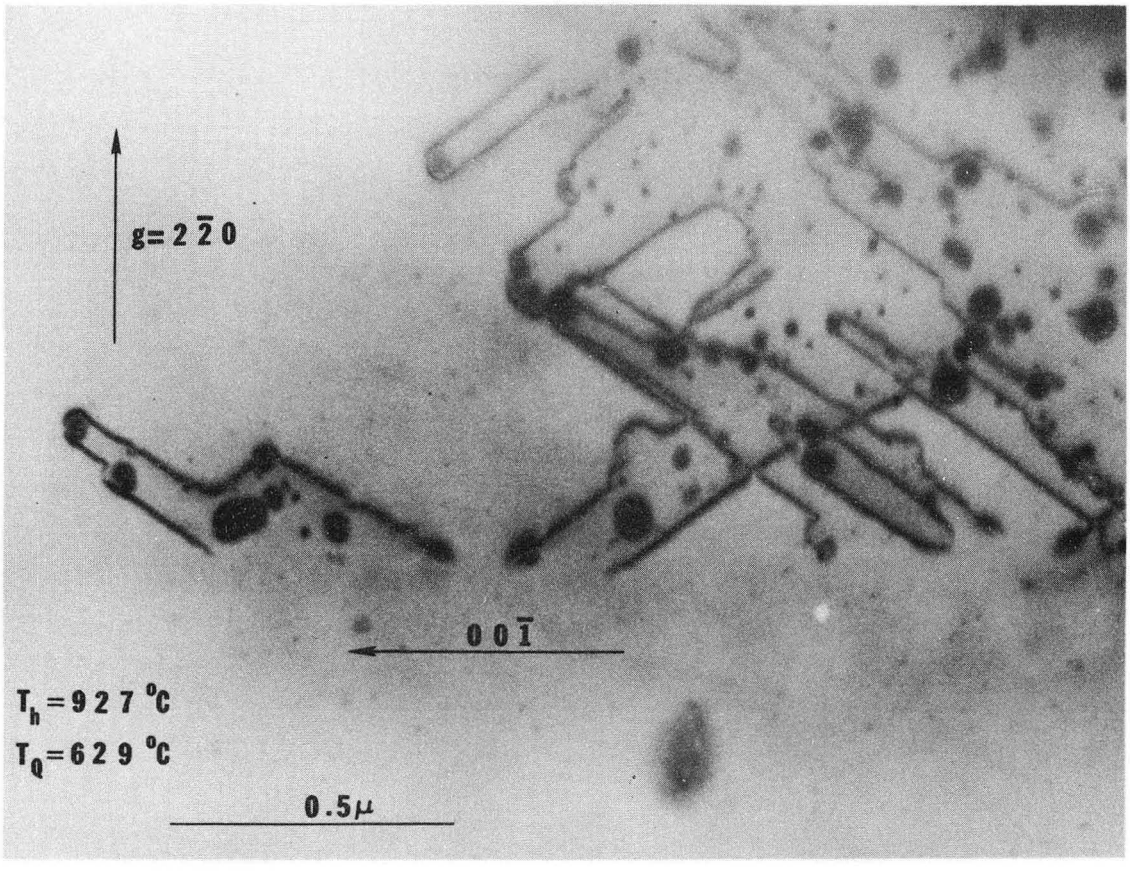

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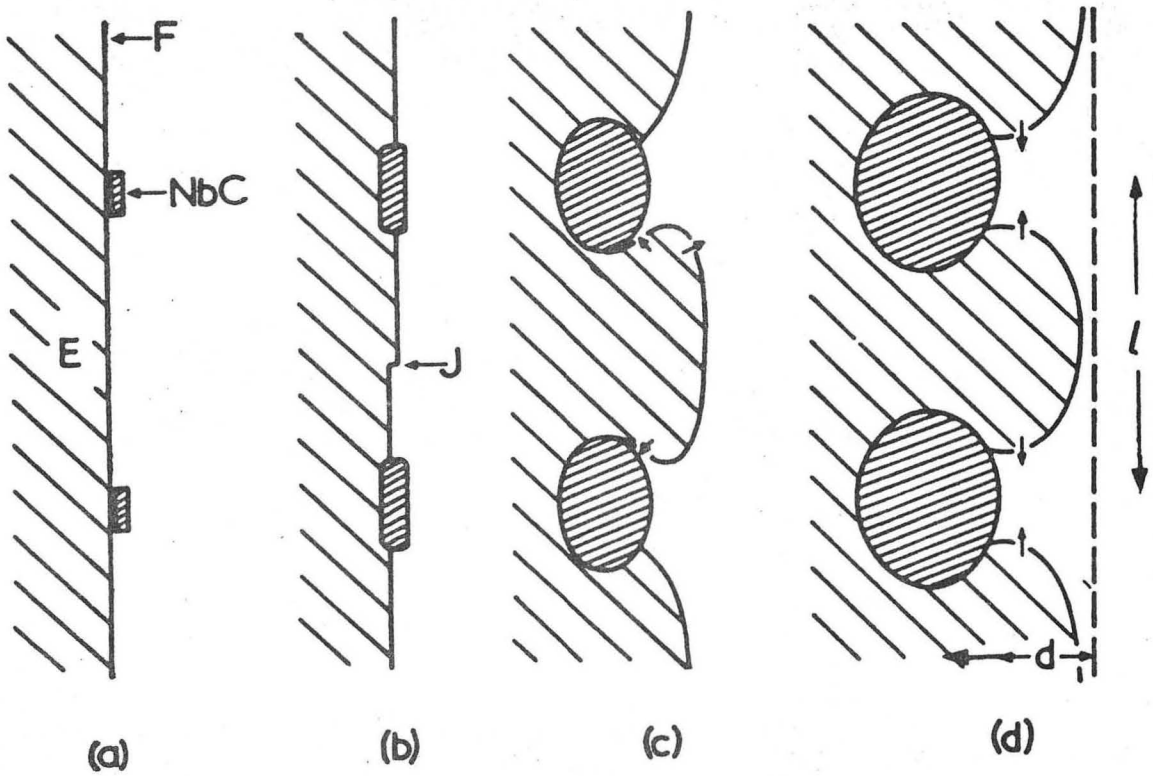
Fig. 9



XBL 732-5774

Fig. 10

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