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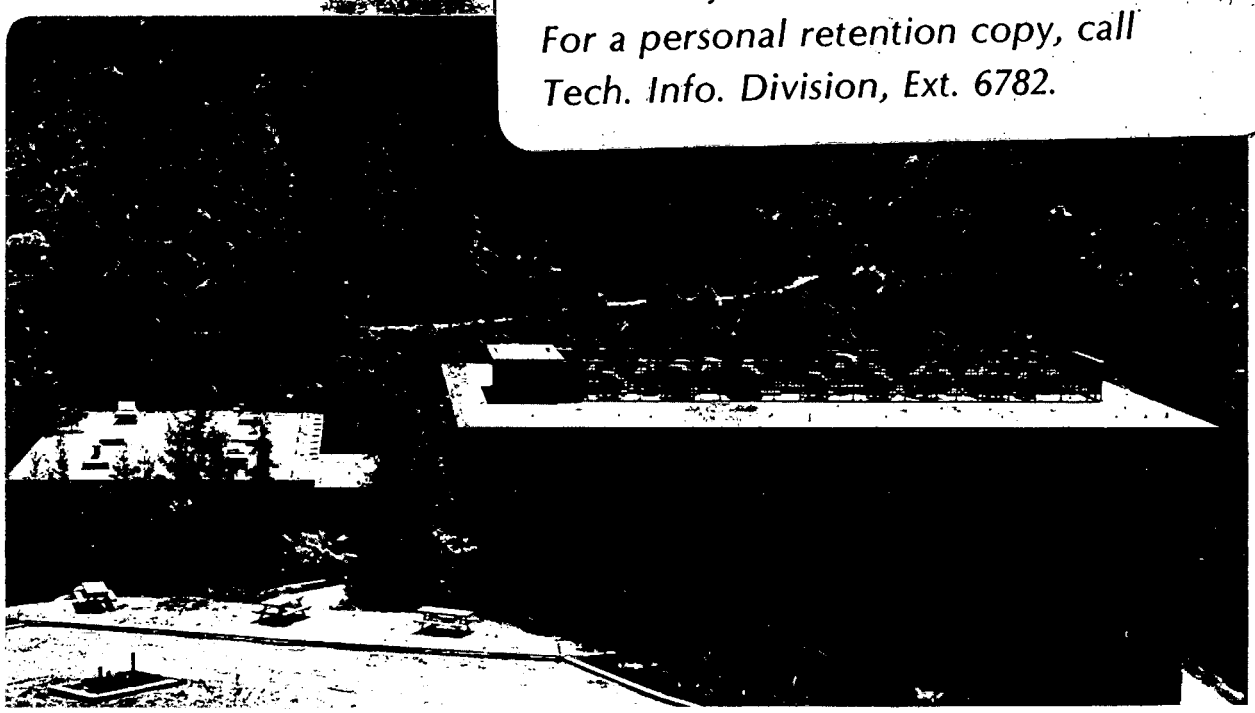

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THE CRYSTALLINE TO AMORPHOUS TRANSFORMATION IN SILICON

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ABSTRACT

The mechanism of the crystal to amorphous transformation during ion damage in silicon has been investigated using high resolution lattice imaging electron microscopy. Sharp interfaces were observed between amorphous and crystalline regions in partially amorphous silicon. Simulated lattice fringe images for increasing Frankel pair concentrations were generated which suggest that a sharp change in lattice fringe visibility implies a sharp change in structure.

The critical displacement damage necessary to produce an amorphous layer for 11 MeV As implants was shown to increase with temperature and to agree well with the calculated displacement energy absorption vs depth. Amorphous regions were observed to shrink during room temperature 1.5 MeV electron irradiation which suggests that radiation induced shrinkage can contribute to the temperature dependence of the critical dose for amorphization.

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INTRODUCTION

The range of structures possible within the various materials usually classified as amorphous silicon is still not clearly defined. In addition the mechanism by which crystalline material is converted to an amorphous structure by radiation damage has not been well understood. From the technological point of view the characterization of primary and secondary defects produced in silicon by ion implantation and subsequent annealing has recently assumed greater importance. As solid state devices shrink in size the need to better understand the radiation damage that accompanies implantation of a dopant and the annealing of the radiation-induced defects becomes critical in the choice of processing steps. For most ion implants the dose is sufficient to form an amorphous layer in silicon if the implant temperature is at room temperature or below. It is the purpose of this paper to further consider the mechanism of formation of amorphous layers in silicon. For a review see Gibbons.(1)

RESULTS AND DISCUSSION

Recently it has been estimated(2) that heavily damaged crystalline silicon "relaxes" to an amorphous state when about 10 percent of the atoms have been displaced from their lattice sites at a temperature low enough to prevent long range migration of the elementary point defects. As the implantation temperature rises the critical fraction of displaced atoms increases rapidly. 11 MeV implantation of As into Si clearly illustrates this temperature dependence. In Fig. 1 the crosssection transmission electron microscope pictures of the buried

amorphous layers for 10^{15} As/cm^2 into (100) silicon at 300°K and at 77°K are compared to the calculated displacement energy absorption vs depth. Within the uncertainties of the calculation the front and back boundaries of the amorphous zones occur at the same total displacement energy absorbed and in agreement with the model of Morehead and Crowder[3] the 300°K implant requires considerably more displacement damage to produce amorphous material. The energy per unit distance (ev/A) deposited into nuclear stopping, which is closely related to the total number of displaced atoms, has been generated from the tables of Brice.[4] The critical absorbed energy densities at 77°K and 300°K were 2.1 x 10^{21} KeV/cm^3 and 4.56 x 10^{21} KeV/cm^3 respectively. In these high energy implants the amorphous crystal boundary nearest the surface occurs at a depth where the energy absorption vs depth is increasing only slowly over a wide depth range. This provides significant volumes of material for study that are damaged nearly to the point of becoming amorphous and also material that is almost but not quite 100 percent amorphous.

A point that has never been entirely clear is whether or not damaged crystal zones that contain more than some critical concentration of point defects undergo a relaxation to a lower energy amorphous structure which is in some way distinctly different from a crystal containing a high density of vacancies, divacancies, interstitials, diinterstitials, etc. If such a relaxation does occur there should be sharp interfaces in partially amorphous material separating region that have relaxed from those that have not. In this paper some recent

observations using high resolution lattice imaging electron microscopy are presented that are consistent with the hypothesis that a sufficiently damaged crystal does relax to the amorphous state at some critical point defect concentration. Figure 2 shows (a) a small amorphous zone surrounded by crystalline material and (b) a crystalline island surrounded by amorphous material (b). At the places where the interface is seen edge-on the lattice fringes characteristic of crystalline material end abruptly; in a distance of the order of an atomic dimension the image changes from distinct fringes to the mottled image characteristic of an amorphous material. The simulated images in Fig. 3 show that such a sudden disappearance of lattice fringes would not be expected unless there is an abrupt change in structure. Using a fully dynamical multi-slice computation scheme[5] the lattice fringe images of {111} planes in <110> oriented silicon under tilted illumination conditions are compared for increasing Frenkel pair defect concentrations: (a) no defects, (b) 5 percent, (c) 10 percent and (d) 15 percent. The unit cell included 890 atoms with a crystal thickness of 40Å. The simulation incroporates all the microscope parameters characteristic of the instrument used for the images in Fig. 2: electron acceleration voltage, E_0 = 100 kV, spherical aberation coefficient, C_s = 1.2 mm, defocus, ΔZ = -880Å. The defects were introduced by removing silicon atoms at random with their random replacement in the lattice at <110> split interstitial configurations. It is clear from these results that for a gradual increase in point defect concentration there is a corresponding gradual change

in the image from perfect fringes to less and less distinct fringes. At 15 percent Frenkel pair concentration the image is close to that characteristic of an amorphous material. In partially amorphous silicon two phases were observed to coexist; the amorphous state does not appear to be reached simply by increasing the point defect and defect cluster concentrations until lattice order gradually disappears.

The formation of 100 percent amorphous silicon during ion damage apparently does involve the formation of increasing numbers of small amorphous zones and possibly the growth of these amorphous zones if the point defect concentration in the surrounding damaged crystal rises above a critical concentration. The small amorphous zones formed near the end of the range of an implanted heavy ion appear to have sharply defined boundaries. The position of the boundary of the zone presumably corresponds to the surface inside of which the critical concentration of point defects necessary for the damaged crystal to amorphous transformation has been exceeded. In a crystalline matrix these small zones should be only metastable so long as the point defect concentration in the surrounding crystal stays below the critical level. They should shrink by a net transfer of atoms across the interface from the amorphous side to the crystalline side. Migration of an amorphous-crystalline interface requires an activation energy above 2.4 eV.[6,7] At room temperature the thermally activated rate of migration would be negligible. Simultaneously to the formation of amorphous zones, however, interstitials and vacancies,

which are mobile at room temperature, will be created in the crystalline material. All the previously formed amorphous-crystalline interfaces should act as sinks for these defects. Their recombination at the interface and other radiation induced transfers of energy to atoms at the interface should provide the necessary activation energy for continuous athermal shrinkage of all existing amorphous zones. According to this model a 100 percent amorphous layer would be formed or not formed depending on the relative rates of formation of new amorphous zones and shrinkage of existing ones.

At liquid nitrogen temperature where self interstitials and vacancies are immobile in silicon the shrinkage rate will be negligible and the point defect concentration in the crystalline regions should also increase to the critical concentration at which amorphous zones might expand.

At the other extreme at high temperature the point defect concentration except near the ends of ion tracks will never exceed the critical and amorphous zones will shrink faster than new zones are created. A continuous amorphous layer is therefore never formed.

Radiation induced shrinkage of amorphous zones is potentially an attractive alternative explanation for the temperature dependence of the critical dose for amorphous layer formation to that proposed by Morehead and Crowder[3] and as modified by Gibbons[1] The result of an experiment to test the concept of radiation induced shrinkage of amorphous zones is shown in Fig. 4. Here a deep buried amorphous layer was produced by As implantation in Si at 11 MeV. A cross-section

transmission electron microscopy specimen taken from this wafer was then irradiated in the beam of a 1.5 MeV electron microscope at room temperature while under observation. The electron beam was located for increasing times near each of the amorphous-crystal boundaries. In every case the crystalline material grew at the expense of amorphous material. In the partially amorphous region small amorphous zones surrounded by crystal shrank and small crystal regions surrounded by amorphous material grew. Some apparently new crystalline zones appeared in what, with the resolution available, looked like 100 percent amorphous material, indicating that minute crystalline islands had been present.

For 1.5 MeV electron irradiation at room temperature no new amorphous zones are expected to form, the primary damage should consist entirely of isolated interstitial silicon and silicon vacancies. These mobile point defects apparently caused the amorphous-crystalline interfaces to move so as to increase the volume of crystalline material. Thermal migration of an amorphous-crystalline interface requires a temperature of about 400°C.[7] In this case it was estimated that the electron beam heating of the specimen could not have been more than 100°C. The experiment was also repeated with low and high beam currents to produce different amounts of specimen heating. The effect was found to be insensitive to beam current. Therefore it was concluded that the observed migration of the amorphous-crystalline interfaces was radiation induced.

Electron damage or light ion damage can not produce amorphous zones directly. However, at low enough temperature statistical fluctuations of point defect concentration or in the case of tight ion bombardment, overlap of heavily damaged volumes[1] is assumed to nucleate amorphous zones. High resolution electron microscopy suggests that in these cases amorphous zones may also be nucleated heterogeneously. If dislocation lines are present or are formed by precipitation of vacancies or interstitials to form a small dislocation loop then the "bad material" at the core of a dislocation might act as a nucleus for growth of an amorphous zone. The amorphous zone seen in Fig. 1b is located at an edge dislocation as can be seen by counting the lattice fringes to the left and to the right.

Definite proof that a sufficiently damaged crystal relaxes to a distinctly different amorphous structure is still lacking. A direct observation of growth of a small amorphous zone during electron irradiation at low temperature would be required. This observation may be possible by combining high resolution lattice imaging of a small amorphous zone with electron irradiation of the same area in the 1.5 MeV electron microscope at 77°K.

Relaxation of a crystal region with a high enough point defect concentration to an amorphous structure like that described by random network models[8,9] is most easily imagined at low temperature where the damage in the crystal is rather homogeneous, consisting largely of individual vacancies and interstitials. At room temperature for silicon the damage would be much more complex. The smallest defects with

appreciable life times are the divacancies and probably clusters of two or more interstitials. There would also be a continuous spectrum of larger complexes. As the temperature is further increased the smallest defects will increase in size until finally small interstitial type dislocation loops predominate. It is not clear at what stage in this progression to larger and larger defects it would still be possible for a transformation or relaxation to an amorphous structure to occur. Studies of the secondary defects that result from regrowth of amorphous layers suggest that the structure of amorphous silicon formed at low and high temperature by ion implantation is not the same.[10] Amorphous layers formed in (111) Si by ion damage at 77°K or room temperature regrow to crystalline material that contains numerous microtwins. This is not the case for regrowth of amorphous layers in (111) Si formed above room temperature. In this case only dislocation lines are formed. One possible explanation for these effects is that amorphous material formed at higher temperature is less homogeneous. It may also contain minute crystalline islands. At high temperatures (> 200°C) where vacancies and interstitials are highly mobile it may also be difficult to eliminate the last small crystalline regions because any vacancy or interstitial formed within it has a near-by sink, the amorphous/crystal interface. For an inhomogeneous amorphous layer the regrowth front as it crystallizes epitaxially on the underlying crystal may always remain very rough on a microscopic scale so that no {111} facets on which microtwins might nucleate ever have a chance to develop during migration of the front.

CONCLUSIONS

1) The simulated high resolution lattice fringe image of {110} silicon becomes gradually less and less regular with increasing Frenkel pair concentration. For a Frenkel pair concentration of 15 percent, the image closely resembles that characteristic of an amorphous material.

2) The amorphous zones formed near the ends of heavy ion tracks in silicon have sharp interfaces separating the amorphous zone from the surrounding crystal. This is consistent with the hypothesis that a crystal containing a high enough point defect concentration can relax to a distinctly different amorphous structure at least at low enough temperature. Final proof, however, awaits an observation that amorphous zones can grow during electron irradiation at low temperature.

3) Amorphous zones surrounded by crystalline material do undergo radiation induced shrinkage at room temperature where elementary point defects are mobile. This provides an attractive explanation for the temperature dependence of the critical energy absorbed in nuclear stopping that is required to form amorphous material.

4) Amorphous silicon even restricting consideration to those structures produced by radiation damage is without much doubt a class of materials with structures ranging from something like the idealized random network models to structures that are considerably less homogeneous.

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FIGURES

Figure 1. Comparison of XTEM measured α-C interface depths with calculated displacement energy absorption vs depth at LN_2 and room temperature.

Figure 2. Lattice fringe pictures of (a) a small amorphous region at a dislocation core and (b) a small crystalline island in an amorphous matrix.

Figure 3. Computer simulated lattice fringe images of {111} planes in <110> Si with increasing Frenkel pair defect concentrations (a) no defects, (b) 5 percent, (c) 10 percent, and (d) 15 percent.

Figure 4. Effect of electron irradiation on partially amorphous region produced by an 11 MeV As implant.

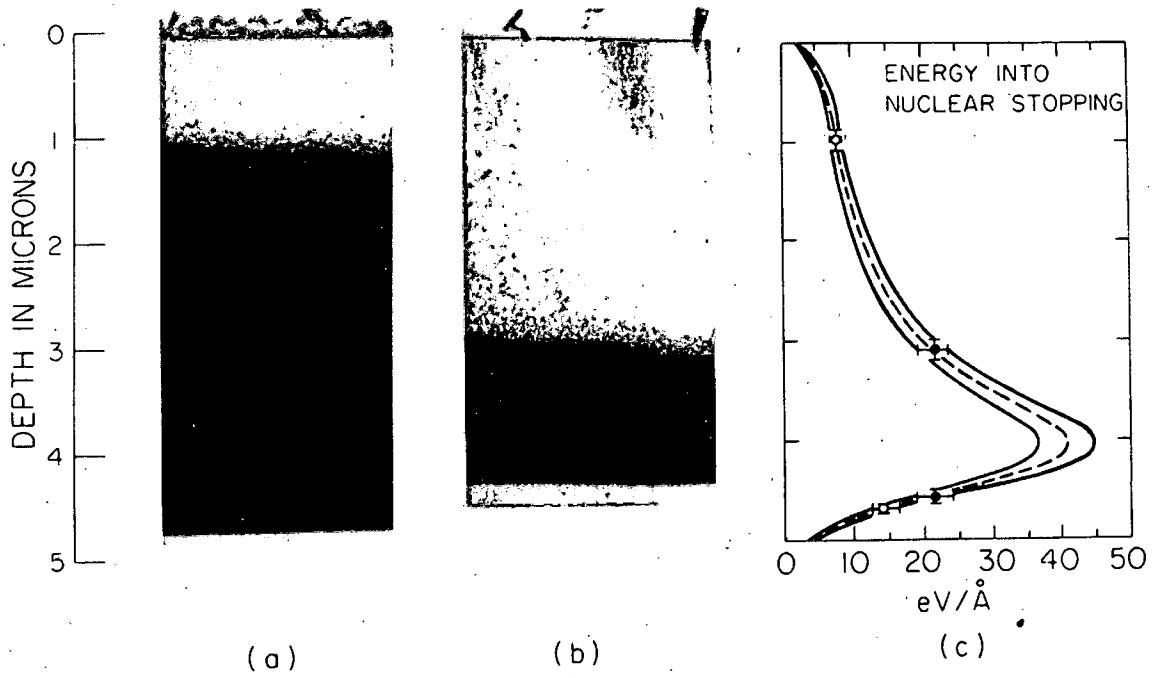

Fig. 1

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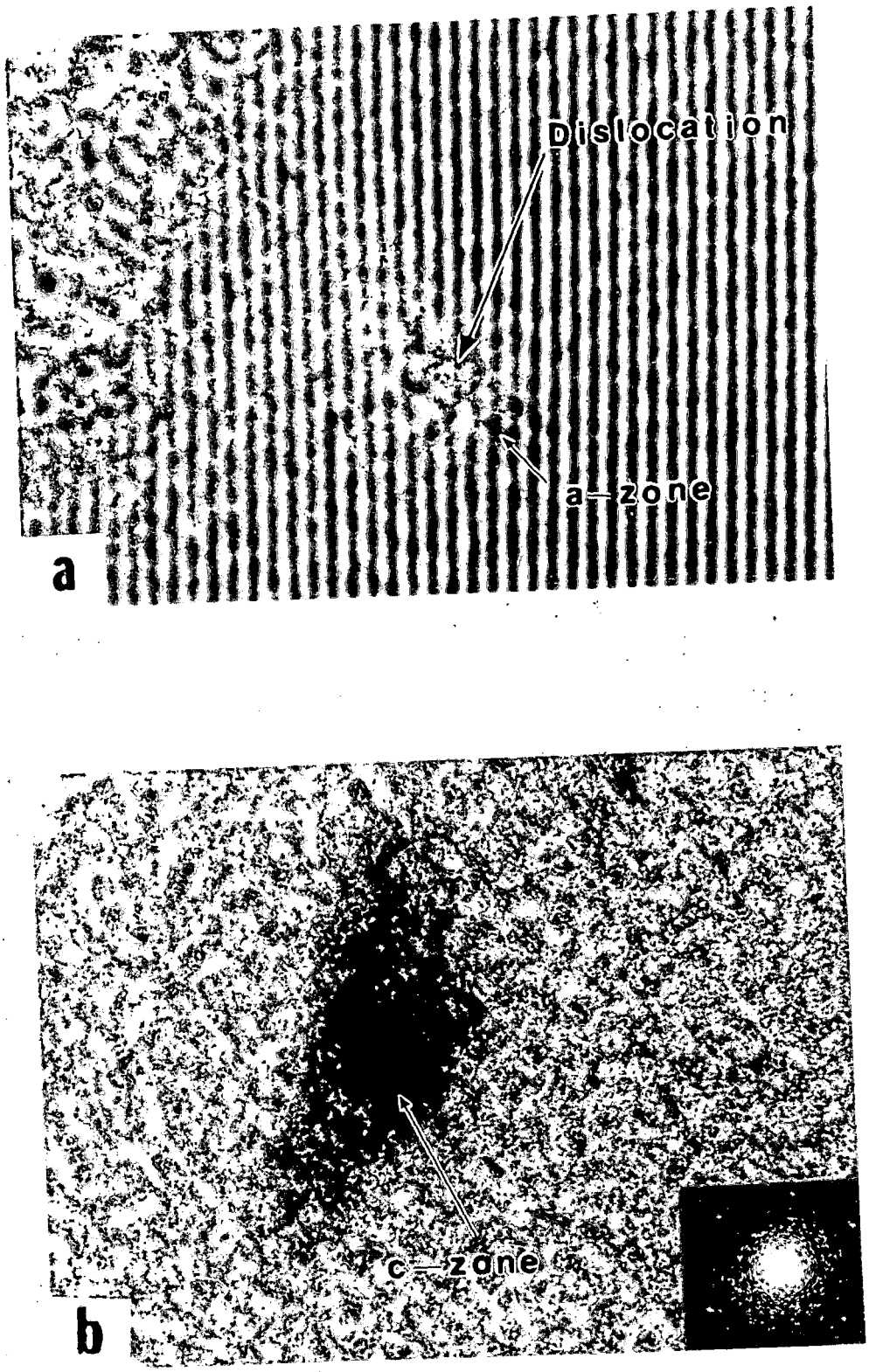

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Fig. 2

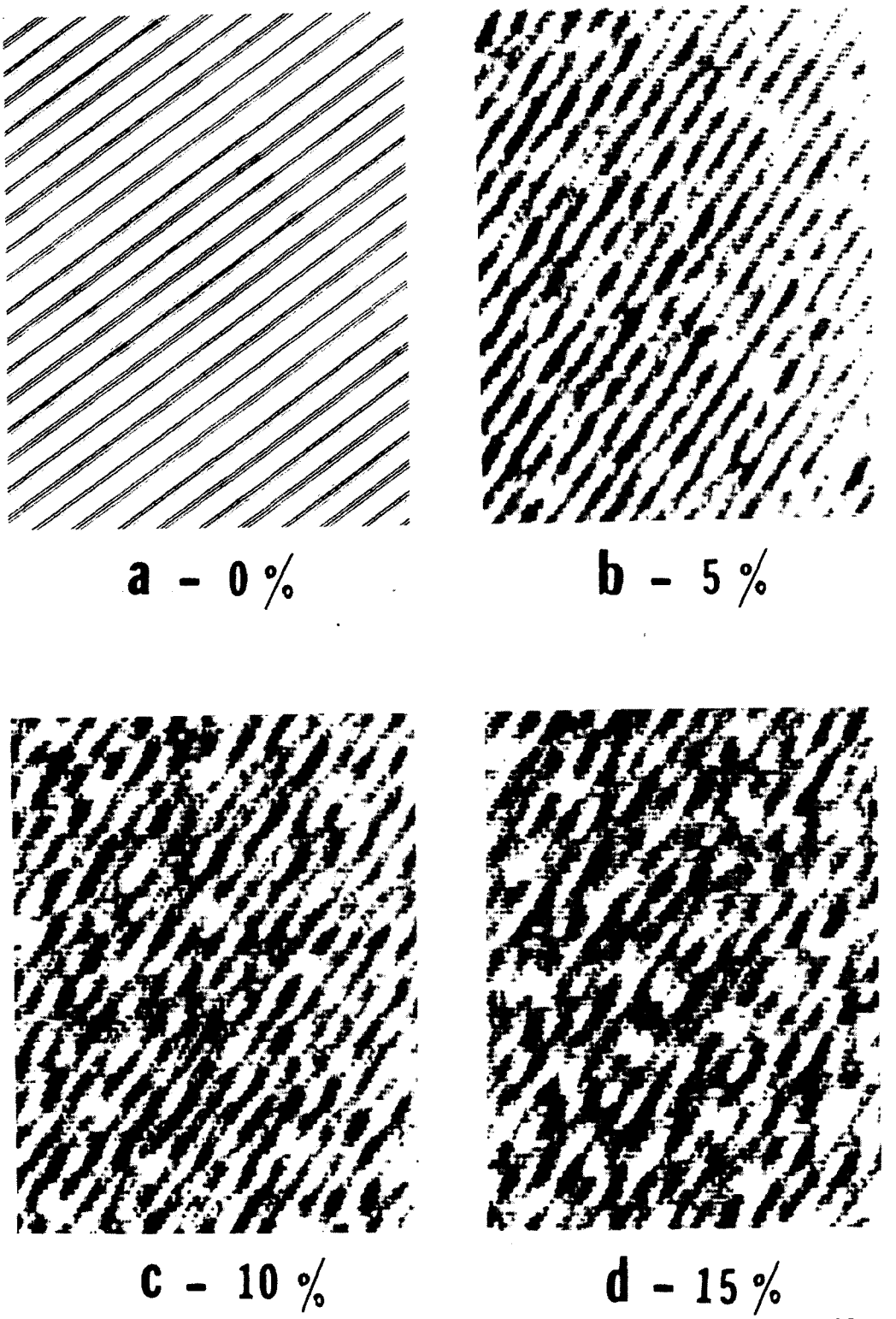

Fig. 3

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ELECTRON IRRADIATION INDUCED MIGRATION OF AN AMORPHOUS/CRYSTALLINE INTERFACE

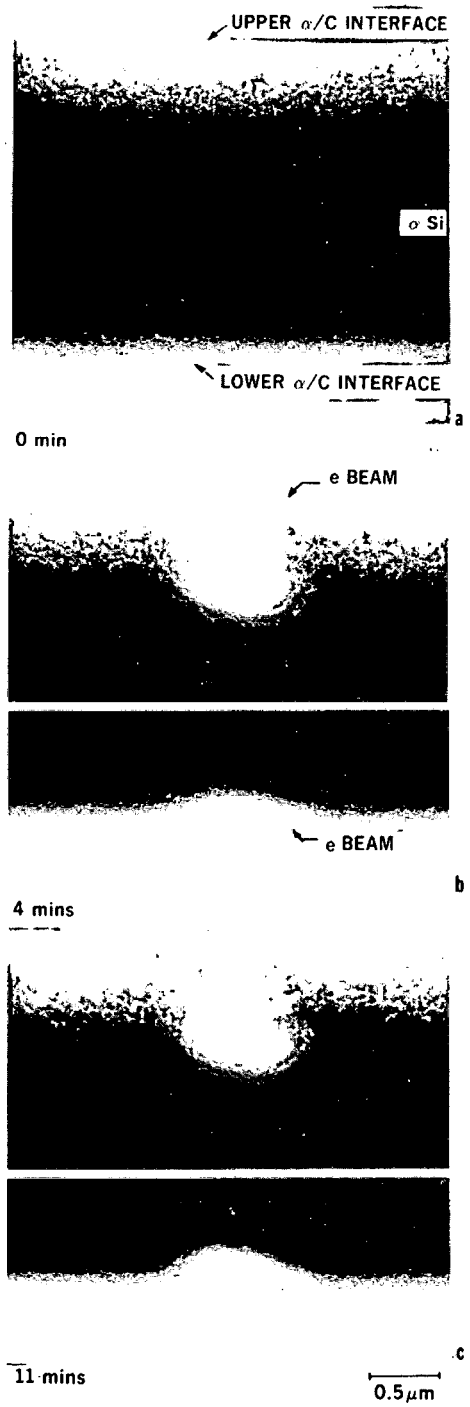

Fig. 4 XBB 828-7366

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