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1 MeV ELECTRON IRRADIATION OF SOLID Xe NANOCLUSTERS IN Al: AN IN-SITU HRTEM STUDY*

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Abstract

Thin film samples of a simple embedded nanocluster system consisting of solid Xe precipitates in Al have been subjected to 1 MeV electron irradiation in a high-voltage electron microscope. High-resolution images have been recorded on videotape in order to monitor the changes to the system resulting from the passage of electrons through the film. Inspection of the video recordings (in some cases frame-by-frame) reveals that complex, rapid processes occur under the electron beam. These include, movement of small clusters, coalescence of neighbouring clusters, shape changes, the apparent melting and resolidification of the Xe, and the creation and annealing of extended defects within the Xe lattice. A tentative interpretation of some of the observations is presented in terms of the electron-induced displacement processes at the surface of the clusters.

Introduction

Although inert gas bubbles in a variety of materials have been under study since the 1950s and evidence of high gas pressures in nanometre-sized bubbles was obtained in the 1970s it was only in 1984 that solid room temperature precipitates of the heavier inert gases were discovered using electron diffraction.[1,2] For argon, krypton and xenon in a variety of fcc metals, the precipitates were determined to be epitaxial (but non-commensurate) with the substrate. In hcp metals the precipitates were observed themselves to have an hcp structure,[3] again epitaxial with the substrate, and in bcc metals they were observed to have an fcc structure with the densely packed (111) planes in the inert gas in contact with the densely-packed (110) planes in the metal.[4]

A system consisting of nanometre-sized solid inert gas precipitates in a solid matrix arguably constitutes the simplest example of embedded nanoclusters that it is possible to fabricate and thus serves as a useful model for more complex systems. Recent research in our laboratories has been aimed at using displacing (ion) irradiation to nucleate and grow metallic nanoclusters in an insulating substrate; in such experiments the irradiation is observed both to disperse the metal from large clusters and nucleate small clusters from the dispersed metal. In such a system it is difficult to distinguish between the effects of defect creation within the substrate, ion beam mixing at interfaces, ballistic displacement of metal atoms out of the nanoclusters and effects of charge build-up and ionisation within the substrate.

The experiments reported in the present paper were designed to simplify the above considerations and, in particular, to examine the effects of defect generation in the matrix on embedded nanoclusters: essentially, charge and ionisation effects are expected to be largely eliminated by the use of a conducting substrate, and the use of high-energy electrons rather than ions should minimise displacements of the (heavy) precipitate atoms rendering the creation of vacancies and self-interstitial atoms (SIAs) in the matrix the major effect of the irradiation.

Experimental

Thin Al discs, 3mm in diameter were mechanically cut from 99.999%-pure starting material and annealed at 400 °C. TEM specimens were made by electropolishing using an electrolyte of $HNO_3:CH_3OH$ at −20 °C. Ion implantations were carried out at room temperature with 30 keV Xe ions to a dose of 3 x 10^{16} ions cm^{-2}. Some specimens were then vacuum-annealed at 300 °C for 30 minutes to reduce radiation damage within the substrate and to consolidate the Xe within the precipitates. Templier *et al.* have reported that such annealing results in sharper bright-field precipitate images and more intense diffraction from the solid Xe.[6]

HRTEM was performed using a JEM ARM-1000 high-voltage TEM operated at a voltage of 1 MV. Most of the HRTEM images were recorded with incident electron beam tilted approximately 3° from an Al <110> direction, as reported by Furaya et al. elsewhere in these proceedings,[7] in order to provide clear Xe images. A (non-Scherzer) defocus of approximately −76 nm was used essentially to filter out information from the aluminium substrate and provide clear Xe images.[7] Using a video camera and an on-line image processing system (giving a 5-frame average) images were obtained with sufficient contrast and intensity to be recorded directly onto standard S-VHS videotape at a frame rate of 25 s^{-1}. With the frame averaging, the temporal resolution of the system was thus approximately 0.2 seconds.

A 1 MeV electron may transfer a maximum of 161 eV to an aluminium atom and only 33 eV to a Xe atom. The 161 eV Al recoil can transfer a maximum of 91 eV to a Xe atom. Under the viewing conditions used for these experiments a displacement rate of approximately 1 dpa per minute for the aluminium has been estimated.

Results and Discussion

Despite the simplicity of a system consisting of inert gas precipitates in an elemental metal substrate and the fact that the electron energy was almost certainly insufficient to displace Xe atoms out of precipitates into the Al, the behaviour of the Xe precipitates under irradiation was complex. In particular, we observed: (i) continual changing of the (faceted) shapes of the precipitates, (ii) the propagation of extended defects through the precipitates, (iii) the migration of small Xe clusters, (iv) the coalescence of precipitates in close proximity and (v) changes in contrast which we believe indicate melting of individual precipitates. Note that HRTEM at lower electron energies has given no indication of any of these phenomena occurring at room temperature.[8] We therefore conclude that all observed changes result from the high-energy electron irradiation and would not otherwise occur at room temperature.

Clearly, in a short paper it is not possible to discuss all of the above phenomena. We will therefore discuss (i) and (ii) above in some detail.

(i) *Precipitate Shape Change*

Figure 1 shows four images, digitised from the video-recording of the experiment, of a single Xe precipitate taken at different times (indicated in seconds in each image) from an arbitrary starting time. The images have been recorded with the electron beam incident close to a <110> zone axis, under conditions such that contrast from the Al is faint but the Xe atom columns are clearly visible as black spots.[7] The precipitate at t=0 is clearly faceted and the image is consistent with a {111} octahedron with 6 {100} truncations. For comparison, a schematic illustration of the [111] and [110] projections of such a precipitate is shown in figure 2. With the exception of the image taken at 94 seconds, the images in figure 1 all appear to correspond to this structure although the number of Xe atoms in each of the planes that bound the structure varies from image to image. At 94 seconds, the precipitate departs somewhat from the truncated octahedron shape as a consequence of having "missing" atoms at one vertex of the structure.

In many images (e.g. t=0 image in figure 1), {111} Al fringes are visible enabling a comparison to be made between the Xe and Al interplanar spacings. The ratio of the lattice constants of the two materials exhibits values ranging from 1.39 – 1.44 yielding a lattice constant for the Xe in the range 0.56 – 0.58 nm. Assuming that a macroscopic equation of state (EOS) is valid for such small particles and using an EOS due to Ronchi,[9] the atomic density that this range of lattice spacing represents, corresponds to pressures between 25 and 50 kbar. A spherical cavity in a metal whose collapse due to surface tension forces is balanced by an internal pressure would be expected to have an equilibrium pressure P_{eq} given by:

$$P = 2\gamma/R \quad \text{.................................}(1)$$

where R is the radius of the cavity and γ is the surface tension (surface free energy) of the cavity/gas interface, which in the case of a cavity containing inert gas is approximately equal to the surface free energy of the metal surface.[10] The projected "radius" of the precipitate in figure 1 is in the range 1.2 to 1.5 nm for which equation (1) yields values in the range 15 – 18 kbar. implying that the precipitate is probably close to equilibrium pressure.

The impact of 1 MeV electrons with aluminium atoms in an Al plane immediately in front of the Xe precipitate (w.r.t. the electron beam) will tend to inject Al atoms into the Xe. Such atoms may be expected to diffuse through the Xe to one of the 14 planes making up the Al cavity. This clearly will have a randomising effect on the cavity shape; however the Al adatoms arriving on the cavity facets might be expected to surface diffuse until becoming trapped at a ledge or vertex. In time, this process may result in the growth of an extra plane of atoms on a facet. Essentially, this is a process whereby Al atoms are transferred from one facet to another. In addition, electron impacts with the Al atoms in the rear facets of the cavity (w.r.t. electron beam) will leave additional Al vacancies at the surface of the cavity thus randomising the atomic arrangement on the facet and augmenting the cavity volume. However, the precipitate may be able to interact, via strain fields, with the large numbers of mobile vacancies and self-interstitial atoms (SIAs) caused by displacement events in the aluminium as has been seen for ion irradiation of He bubbles in Al.[11] In this way, the system may act to keep the precipitate at equilibrium pressure (thus preventing any net growth) with a shape tending towards the minimum energy form defined by the Wulff construction.[12, 13]

(ii) *Extended defects in the Xe precipitates*

The above interpretation of the changing shape of the precipitate has been largely in terms of the changing shape of the aluminium cavity bounding the Xe, but changes in the shape of the cavity have inevitable consequences for the atomic arrangement of the Xe within. In the section of videotape from which figure 1 has been taken, the Xe atom columns appear to be continuously rearranging themselves with extended defects appearing and sweeping through the precipitate. An example of such a process can be seen in figure 3 which shows six images digitised from a section of the video-recording of the experiment in which a stacking fault appears in a Xe precipitate and subsequently moves through the precipitate over a period of 20 seconds. The numbers in each image again correspond to the time in seconds. Note that the time period that these images span is significantly shorter than that in figure 1.

At t=1.4 seconds the arrangement of the Xe atom columns changes with an apparent stacking fault appearing along the line indicated by the arrow. The image is consistent with relative shear of the part of the precipitate to the left of the arrow with respect to that to the right such that the stacking sequence at this line is hcp rather than fcc (stacking sequence ...ABCABABC...). It is unlikely that a defect appearing as suddenly as this could result from the accumulation of individual Al atoms as described in section 1. However, an inert gas precipitate whose pressure rises significantly above equilibrium pressure may be able to punch out a dislocation loop. The energetics of such a process lead to the conclusion that a loop may be punched when a precipitate attains a pressure greater than or equal to a critical value, P_{lp}, given by:

$$P_{lp} = P_{eq} + \mu b/R \quad \text{.................................(2)}$$

where μ is the shear modulus of the material, b is the burgers vector of the loop whose radius R is generally assumed to be equal to that of the precipitate.[10,14,15] For a precipitate such as that shown in figure 2 with a "radius" in the range 1.5 – 2 nm, equation 2 yields a value of 40 – 53 kbar. The range of pressures, 25 – 50 kbar, that correspond to the observed range of Xe lattice spacings indicates that the conditions necessary for loop-punching may be met in some precipitates at some times and indeed some precipitates have been observed to discretely increase their volume by one plane of Al atoms.

The augmentation of the cavity volume by one Al plane on a facet, as a result of loop-punching, would necessitate a "repacking" of Xe into this space that could give rise to the observed shear. Over some period of time following this event, the accumulation of Al atoms, replacing the missing plane row-by-row as described in section (i), would then result in the movement of the defect across the precipitate as observed.

It should be emphasised that the above interpretation is speculative and further measurements are underway in our laboratories in an attempt to determine with greater certainly the nature of the defects and processes observed.

Conclusions

1 MeV electrons have been used both to provide high resolution images and to produce displacement damage in thin Al foils containing solid room temperature Xe precipitates. Despite the relatively small amount of energy that each electron can transfer to Al and Xe atoms, numerous processes are observed to occur as a result of the irradiation. These include continual changing of precipitate shape, formation and movement of extended defects in the precipitates, the migration of small Xe clusters, coalescence and melting of precipitates.

Shape changes are believed to be due to randomisation and reconstruction of facets as a result of sputter-induced transfer of Al atoms between facets, and surface diffusion of Al adatoms on the facets. In addition, loop-punching may occur. "Repacking" of the solid Xe in the aluminium cavity following shape changes gives rise to the formation and motion of extended defects within the Xe precipitates.

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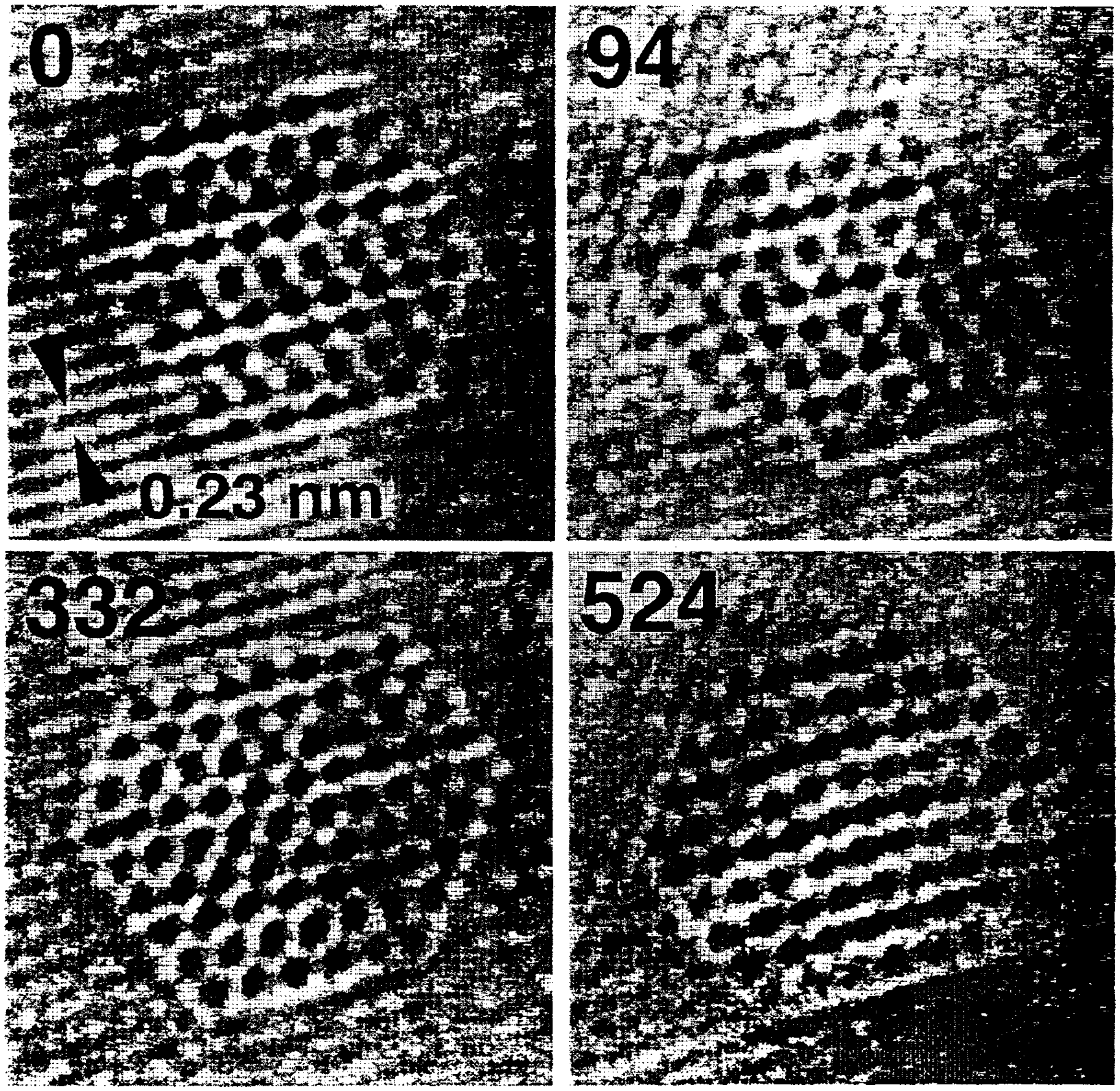
Figure Captions

Figure 1. HRTEM images digitised from videotape of a xenon precipitate in aluminium undergoing shape changes induced by 1 MeV electron irradiation. Each image is an average of 5 frames. Numbers indicate time in seconds.

Figure 2. Schematic diagram of a {111} octahedron truncated by 6 {100} planes in [111] and [100] projection.

Figure 3. HRTEM images digitised from videotape illustrating the electron-induced formation and movement of an extended defect in a xenon precipitate in aluminium.


0
0.23 nm
94
332
524

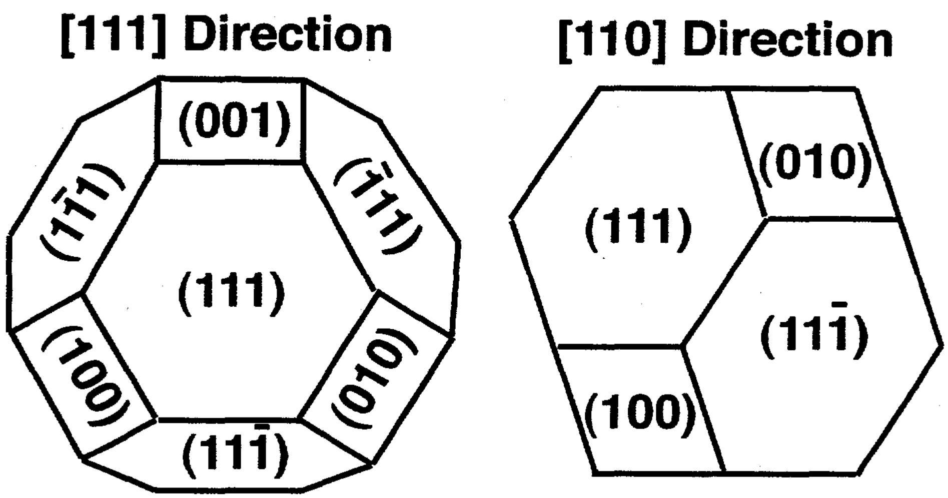
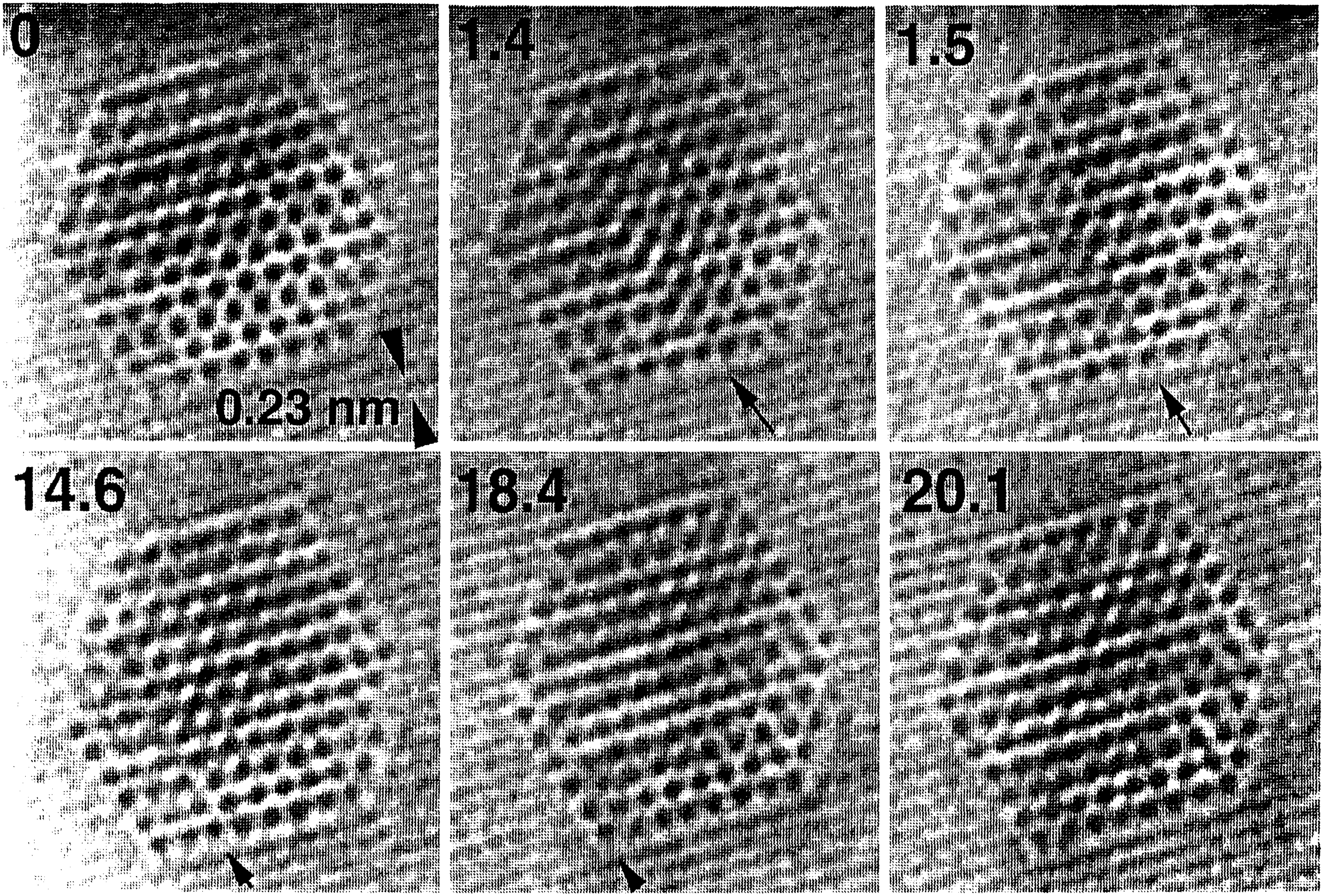


Fig. 2. S.E. Donnelly et al.: 1 MeV Electron Irradiation of Solid Xe Nanoclusters in Al — an in-situ Study


0
1.4
1.5
0.23 nm
14.6
18.4
20.1