Title
Some Roles for TEM in the Development of New Materials

Author
Westmacott, K.H.

Publication Date
1990-04-01

LBL-29589

Lawrence Berkeley Laboratory
UNIVERSITY OF CALIFORNIA

Materials & Chemical Sciences Division

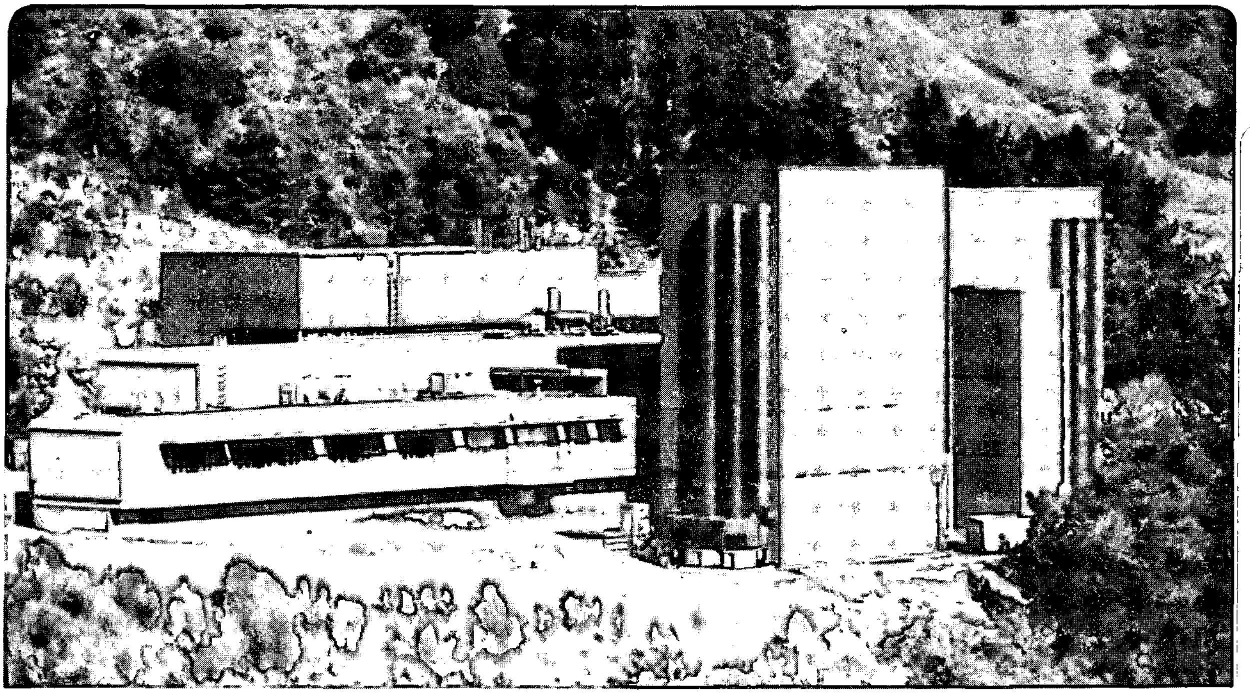
National Center for Electron Microscopy

To be presented at the New Materials '90 Conference,
Osaka, Japan, October 1–5, 1990, and to be
published in the Proceedings

Some Roles for TEM in the Development of New Materials

K.H. Westmacott

April 1990



Prepared for the U.S. Department of Energy under Contract Number DE-AC03-76SF00098.

DISCLAIMER

LBL-29589

SOME ROLES FOR TEM
IN THE DEVELOPMENT OF NEW MATERIALS

K.H. Westmacott

National Center for Electron Microscopy
Lawrence Berkeley Laboratory
University of California, Berkeley, CA. 94720

Presented at New Materials '90 Conference,
Osaka, Japan
October 1-5, 1990

This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Materials Sciences Division of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.

SOME ROLES FOR TEM IN THE DEVELOPMENT OF NEW MATERIALS

K. H. Westmacott
Managing Director
National Center for Electron Microscopy, U. S. A.

A fundamental understanding of the growth mechanism of expitaxial metal films on semiconductor substrates has important implications in a number of key technological areas. Of equal importance is a thorough knowledge and understanding of the interface structure and its relationship to properties. High voltage transmission electron microscopy using both conventional and high resolution imaging and diffraction provides a powerful tool for addressing important questions relating to thin film growth and interface structure. In the present contribution some recent applications of advanced TEM techniques to fundamental issues will be discussed. In each case studies of interface structures have revealed interesting effects of relevance to a broad range of problems.

1. Ionized Cluster Beam Deposited Films

The ionized cluster beam technique for depositing thin films was invented by Takagi and colleagues at Kyoto University in the early 1970s [1]. Since then it has undergone numerous improvements to reach its present highly sophisticated form. Extensively instrumented deposition chambers for laboratory scale work and commercial application have been built.

The main merit of the ICB method is its proven ability to promote the growth of high quality heteroepitaxial films in a large variety of substrate/overlayer combinations using cold substrates and pressures in the 10^{-9} torr range. These films have great potential for exploitation in both basic research to resolve fundamental issues, and in technologically important electronic, optical and electron-optic applications.

Yamada and co-workers have performed extensive pioneering experiments to grow a broad variety of metal, semiconductor, optical and insulating epitaxial films and demonstrate the applicability of the technique to crucial micro-electronic processes [2,3]. Important advantages of ICB films over films prepared by other deposition techniques include better thermal stability, improved resistance to electromigration failure, and uniform film deposition on the stepped or grooved surfaces used in VLSI applications. The goal of electron microscopy studies is to characterize and model film microstructures of as-deposited films and during subsequent in-situ annealing treatments using conventional techniques. High (atomic) resolution techniques are applied to determine the atomic structure and properties of both the film homophase interfaces (grain boundaries) and the heterophase film/substrate interface.

Conventional TEM micrographs and diffraction patterns of ICB Al grown on {100}Si and on {100}Ge single crystal substrates are shown in fig. 1(a) and (b) respectively.

It is important to note that matching is obtained by considering 4 Al{110} planes and 3 Si{110} planes. Apparently it is only necessary for atom layers in the two structures to match periodically at short intervals rather than have each and every layer matching. (The validity of this procedure has been established by studying the orientation relationships found for a large number of disparate systems [5].) For the Al on Ge the corresponding conditions are (001)Al || (001)Ge; [100]Al || [110]Ge, i.e. the Al is rotated 45° from the cube-cube orientation. The lattice mismatch with this orientation relationship is ~1%.

This simple model provides a basis for predicting systems likely to exhibit epitaxy and the structure and orientation relationship of the resulting films.

The new generation of high resolution microscopes capable of resolving structure at the sub-2Å level may be employed to determine atomic positions in grain boundaries, even in close-packed metals such as Al, and heterophase semiconductor/metal interfaces.

Fig. 2 shows two such micrographs taken on NCEM's Atomic Resolution Microscope; an asymmetric boundary in a <110>ICB Al bicrystal (a); and a (110)Al/(001)Si overlayer/substrate interface (b), taken from a cross-section of an ICB bicrystal. Detailed information on atomic arrangements at interfaces may be derived from such pictures. A comparison of experimental images and the structures predicted from first principle calculations has recently been successfully conducted for a symmetrical $\Sigma 99$ grain boundary in ICB Al [6]. Work in progress is designed to examine the effects of introducing controlled amounts of selected impurities into the boundary. Fundamental research of this kind can form the basis for designing materials with controlled microstructures and improved properties.

Direct information on the nature of the heterophase interface produced during ICB deposition can be obtained from Fig. 2b.

2. Hexagonal Silicon

An unusual, hexagonal, form of silicon is found when single crystals are indented in the temperature range 400-650°C. First reported by Soviet workers [7] and subsequently studied in detail by Pirouz et al. [8], this material offers interesting possibilities for perhaps developing new devices. The hexagonal silicon forms by a mechanism associated with mechanical twinning. It is present only in small amounts as ribbons emanating from the highly stressed region under the indent. A direct image of a diamond-hexagonal lath of silicon in the diamond-cubic matrix is shown in fig. 3a.

3. Controlled Precipitate Morphologies

In advanced materials applications it is becoming increasingly apparent that microstructural fine-tuning is required to optimize properties. Experiments are being conducted on a model Al-Ge alloy system to explore to what extent precipitate structures can be tailored. Because of the importance of interface structure on material properties, it is interesting to vary this parameter.

In Al-Ge alloys given appropriate quench-age treatments, pure germanium precipitates from solution with many different morphologies and orientation relationships. Plate precipitates with different crystallographic shapes grow with low index habit planes, lath and rod precipitates along low index directions, and tetrahedral and octahedral precipitates with cube-cube orientation relationships.

Changes in precipitate form can be studied in-situ in a high voltage microscope equipped with a heating stage. Fig. 4 shows a sequence of micrographs of a Ge precipitate lath in Al recorded at different temperatures. Several features are of interest. It is seen that the end of the lath which lies along <110>Al || <110>Ge undergoes a faceting to roughening transition as the temperature is cycled between a higher and lower limit. Depending on the particular temperature, different facets develop. At the lowest temperature the plate is exactly rectangular in shape. Another interesting observation is that dissolution of the precipitate occurs only from the {110} ends of the lath. This is related to the fact that the other faces of the lath are bounded by {111} planes in the precipitate.

4. Phase-Change Optical Data Storage Films (M. R. Libera et al. [11])

In a recent application of the HVEM, the microstructures of multilayer thin films used for phase-change optical data storage were studied. The increased electron penetration at high accelerating voltages was necessary to observe the $Al/SiO_x/TeGeSn/SiO_x/Al$ multilayer structures. Films with and without the Al overlayer were compared. The increased cooling rates attained with the metal overlayer had a significant effect on the microstructure as may be seen in fig. 5 (courtesy of M. Libera).

I hope that in this brief description of recent applications of electron microscopy to materials research, the utility of the techniques has been conveyed

Acknowledgements

I am grateful to numerous colleagues, particularly Dr. U. Dahmen, for their contributions to this work. This work is supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Materials Sciences Division of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.

References

1. I. Yamada, H. Inokawa and T. Takagi, J. Appl. Phys. **56**, 2746 (1984).
2. ISIAT Symposia 1-14, Kyoto Univ., ed. T. Takagi (1977-1990).
3. I Yamada, Mat. Res. Soc. Symp. Proc. **128**, 113, **152**, 183 (1989)
4. U. Dahmen and K. H. Westmacott, Scripta Metall. **22**, 1673 (1988).
5. W. Lojkowski et al., Acta Metall. **36**, 69 (1988).
6. U.Dahmen et al., Phil. Mag. Letters (1990) in press; Ultramicroscopy (1990)
7. V. G. Eremenko and V. I. Nikitenko, Phys. Stat. Sol. (a) **14**, 317 (1972).
8. P. Pirouz et al., Acta Metall. Mater., **38**, 313, 323, 329 (1990).
9. T. Y. Tan et al., Phil. Mag. **A44**, 127 (1981).
10. K. H. Westmacott and U. Dahmen, Ultramicroscopy (1990) submitted.
11. M. R. Libera et al., Mat. Res. Soc. Proc. San Diego, CA (1989).

Figure 1: On Si the Al is deposited in two different {110} orientations to form a continuous bicrystal structure [4]. On Ge the Al deposits as a {100} single crystal. It has been customary in the literature to regard as extraordinary epitaxial growth of materials with such disparate lattice parameters ratios (1.34 for Si/Al and 1.40 for Ge/Al). However, this view takes no account of the orientation relationship in which the overlayer is deposited on the substrate. In fact this is the key to understanding the observed epitaxy. Epitaxial growth occurs in an orientation such that lattice match is optimized in the plane of contract between substrate and overlayer. For Al on Si the matching planes and vectors are $(110)_{Al} \parallel (001)_{Si}$; $[001]_{Al} \parallel [110]_{Si}$ and $2[110]_{Al} \parallel {}^{3}/_{2}[110]_{Si}$ with lattice mismatches of 5.5% and 0.5% respectively.

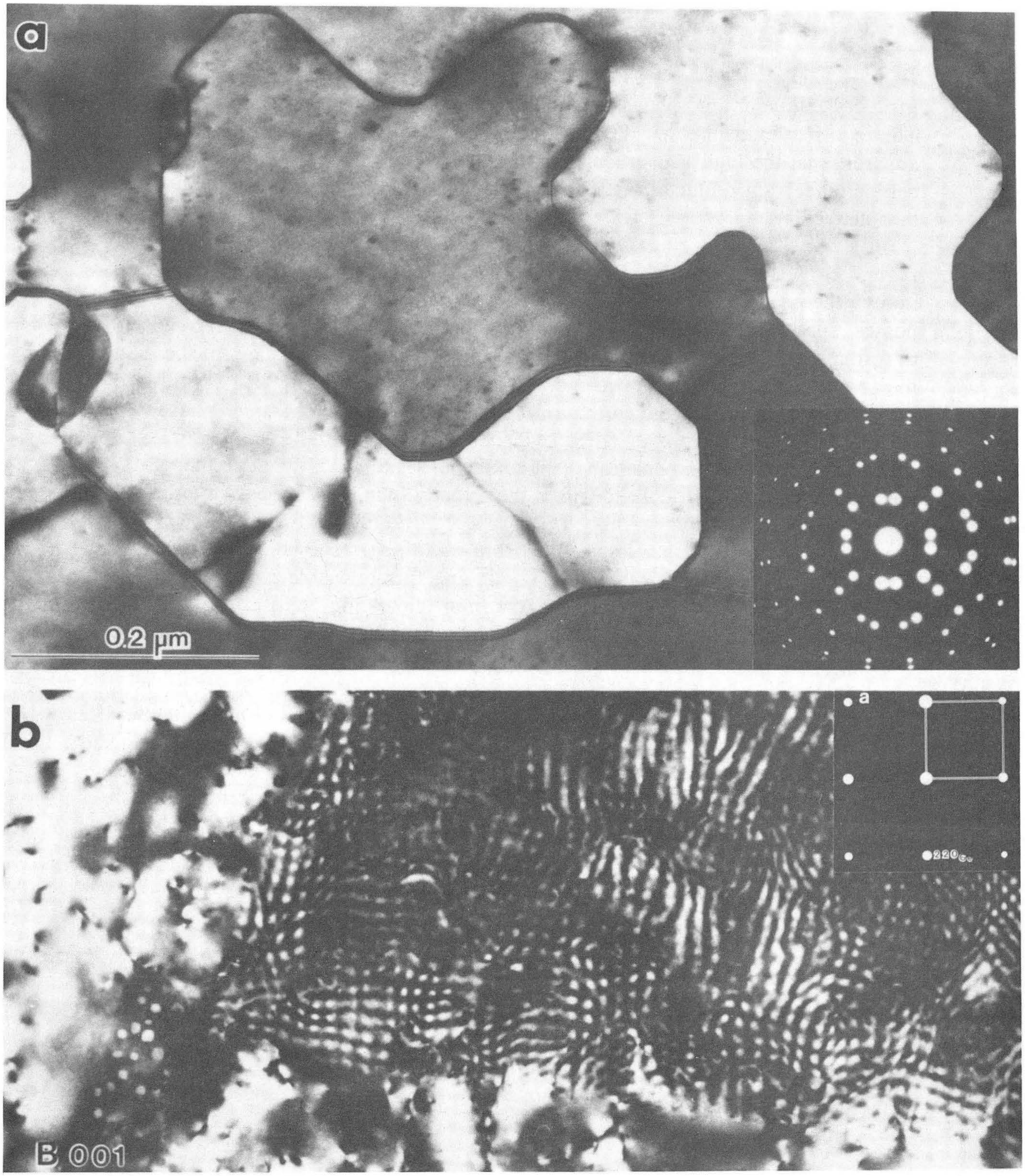
Figure 2: The Al/Si interface is clearly seen to be flat to the atomic level; the crystalline Al and Si is continuous and defect-free right up to the interface and there

is no crystalline or amorphous transition layer such as an oxide or impurity layer. This is direct evidence that the substrate is atomically clean at the outset. It is apparent that the interface structure is relaxed as indicated by the arrows, unlike certain other semiconductor/metal interfaces where the crystals remain rigid across the interface

Figure 3: The change in crystal structure across the interface is clearly evident even though the ribbon is heavily faulted. The {511} habit plane has been shown to possess special properties [9] in that the interface is completely coherent by virtue of formation of alternate 5- and 7-membered rings. A schematic diagram showing the geometric relationship between the two phases is given in fig. 3b. It will also serve to explain briefly the formation mechanism for the hexagonal phase. In heavily deformed regions of silicon where extensive twinning has occurred, a secondary twin, with composition plane on the alternate {111} plane in the <110> zone, will occasionally nucleate within the primary twin, T_1. On passing into the matrix, for reasons of compatibility T_2 is produced by a reverse twinning shear with a resulting change in crystal structure from dc to dh as shown. Efforts are in progress to produce the dh silicon as a continuous film to enable further studies of structure and properties to be made. A further interesting possibility is that by applying the principles to compound semiconductors, new materials with the wurtzite phase might be synthesized from a sphalerite substrate.

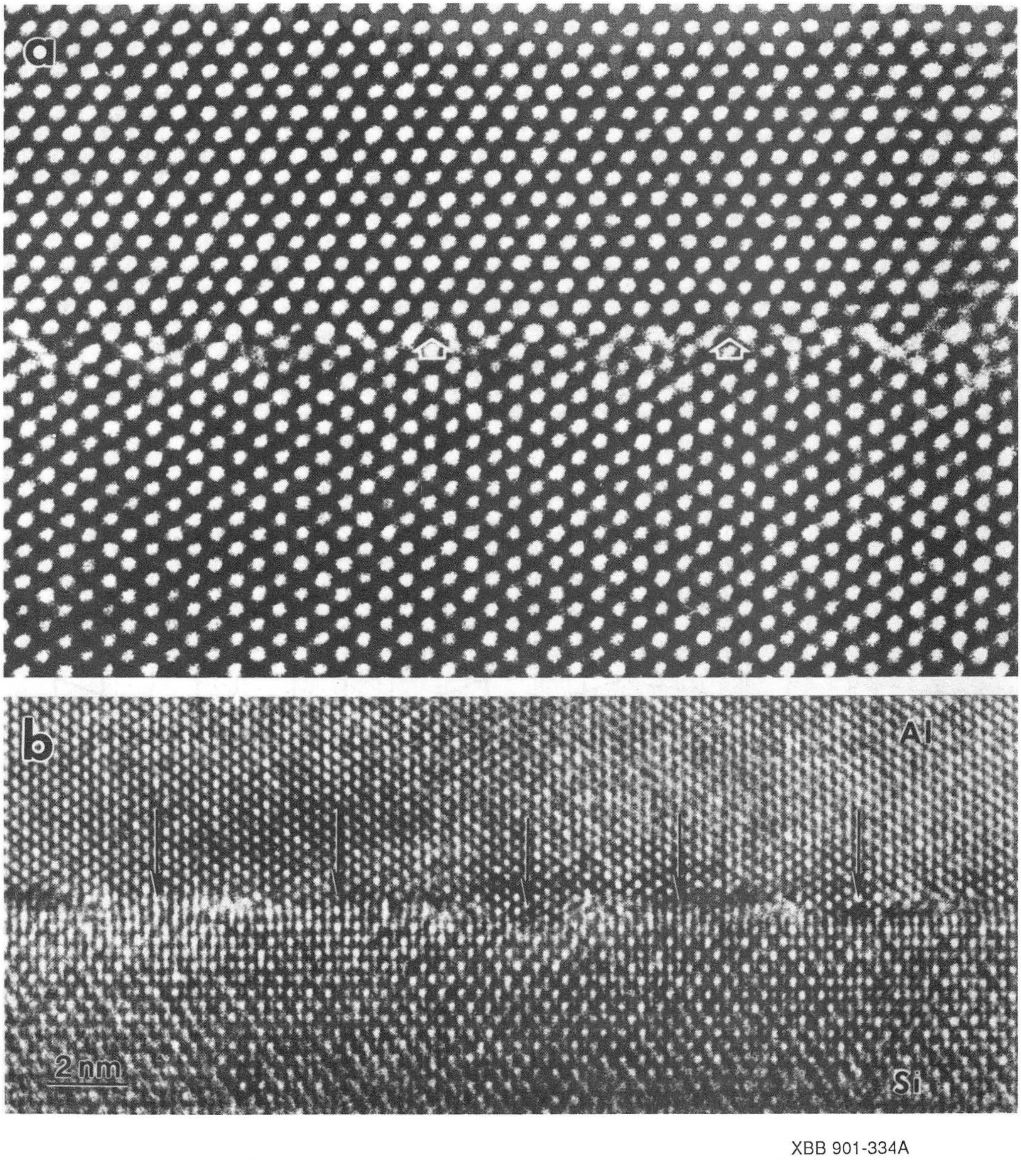
Figure 4: In other heating experiments on tetrahedral and octahedral precipitates, it is found that a transformation to a spherical shape occurs at temperatures near the phase boundary. On cooling back down from this temperature, all the precipitates refacet and acquire an octahedral form [10]. The results of this brief research summary indicate that the potential exists for modifying precipitate morphologies and hence interface structure by judicious heat treatments thus influencing properties.

Figure 5: These micrographs and diffraction patterns show the effect of pulsed-laser irradiation of 50 mW incident power on the structure of films containing a crystallized band. In the non-aluminized films (A and B) the pulsed region remains crystalline whereas an amorphous phase has formed in the coated films (C and D). Subsequent laser annealing causes crystallization of the amorphous spots. These studies are invaluable in optimizing the film properties and structure to achieve high density information storage.



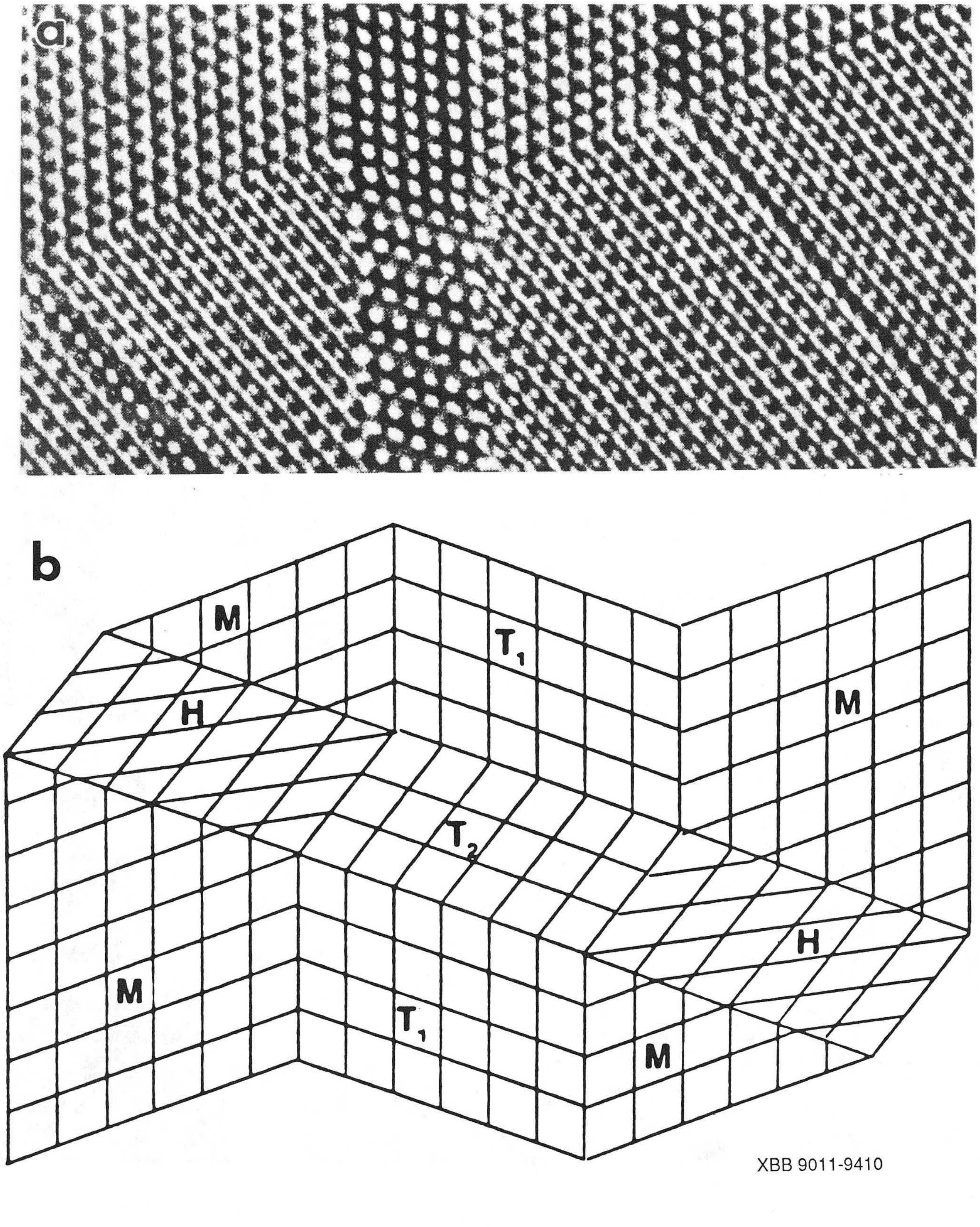
XBB 886-6529A

Figure 1



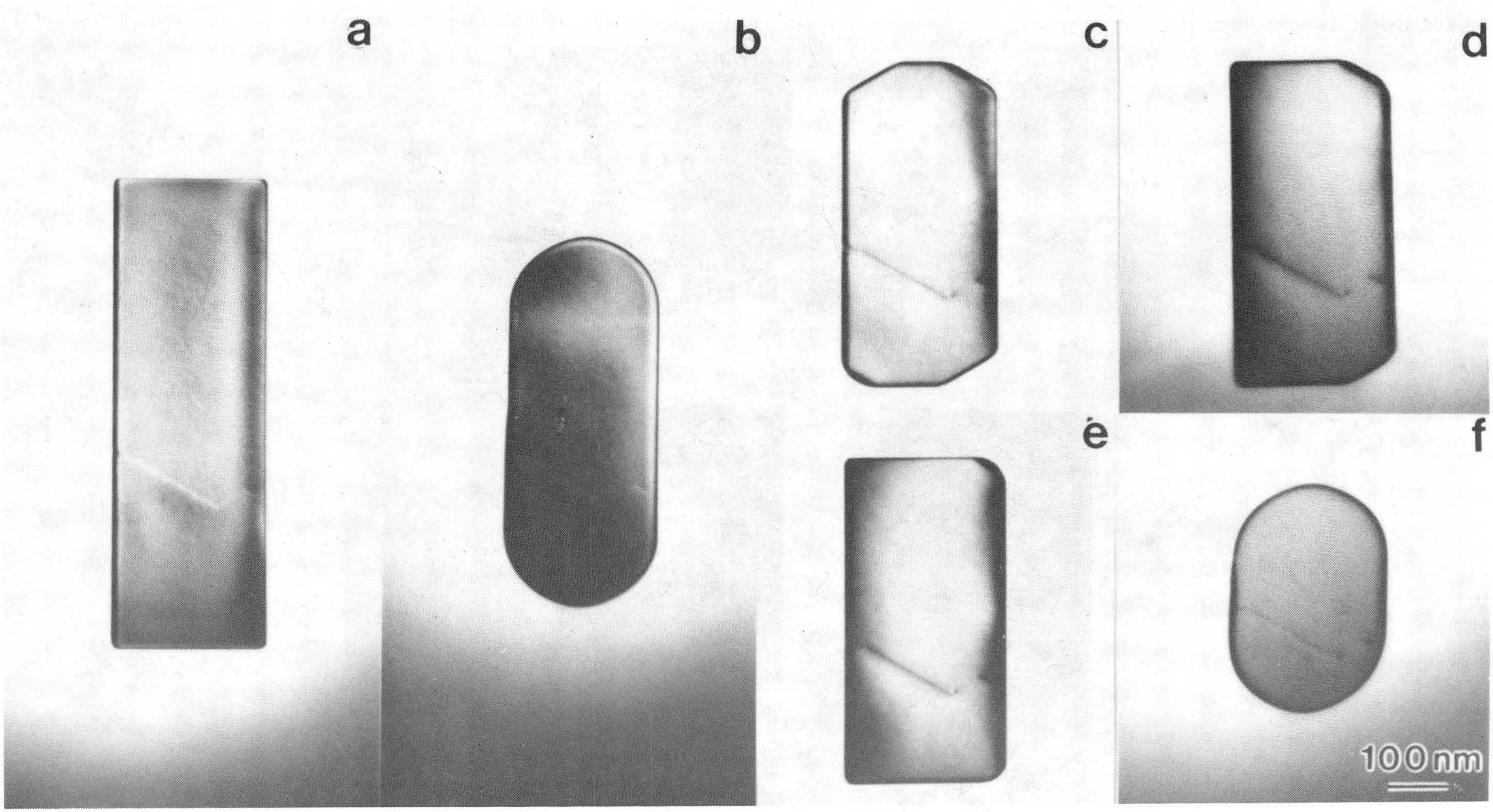
XBB 901-334A

Figure 2



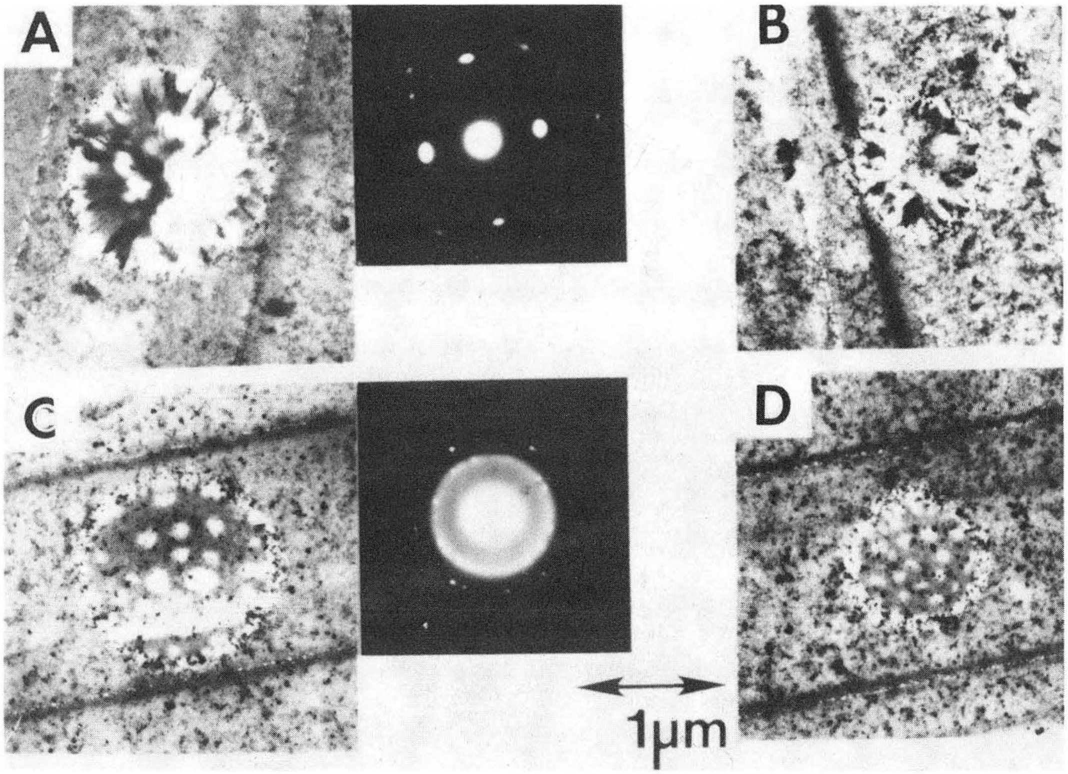
XBB 9011-9410

Figure 3



XBB 906-4599A

Figure 4



XBB 9011-9411

Figure 5