References

FUJIMOTO, F. (1959). *J. Phys. Soc. Jpn*, **14**, 1558-1563.
FUJIMOTO, F. (1960). *J. Phys. Soc. Jpn*, **15**, 859-867.
FUJIMOTO, F. (1965). *Z. Naturforsch. Teil A*, **20**, 367-379.
GOODMAN, P. & MCLEAN, J. D. (1976). *Philos. Mag.* **34**, 861-876.
GOODMAN, P. & WARBLE, C. E. (1987). *Philos. Mag. B*, **56**, 15-30.
KATO, N. (1952). *J. Phys. Soc. Jpn*, **7**, 406-414.
LYNCH, D. F., MOODIE, A. F. & O'KEEFE, M. A. (1974). *Electron Microscopy* 1974. *Proc.* 8*th Int. Congress on Electron Microscopy, Canberra, Australia*, 1974. Australian Acad. Sci. Publ. pp. 222-223.
NONOYAMA, M., NAKAI, Y. & KAMIYA, Y. (1973). *J. Electron Microsc.* **22**, 231-241.

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The Development of *In Situ* High-Resolution Electron Microscopy

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Abstract

Progress in introducing high-resolution electron microscopy at controlled elevated temperatures is described. Initial work involved the study of dynamic events in materials like cadmium telluride which can be heated to a sufficient degree by the imaging beam. However, for reproducible experiments the temperature must be carefully controlled and measured, and this involves a heating specimen holder. Results achieved recently this way on a variety of substances including CdTe, GaAs, Si, GaAs–Ti, GaAs–Ni, Si–Mo and Si–Ti, are reported. To derive information pertinent to bulk behavior both the manner of an *in situ* reaction and its kinetics should be compared with those for specimens prepared from macroscopic materials treated *ex situ*. For interface reactions in semiconductor materials it is found that events typical of the bulk can be recorded under high-resolution conditions in a large proportion of cases.

Introduction

Following the first demonstration that the electron microscope is capable of resolving crystal lattices (Menter, 1956) and that images can be interpreted in terms of atomic postions (Cowley & Iijima, 1972), there have been increasing applications of high-resolution electron microscopy (HREM). The recording of dynamic events at atomic resolution is a natural extension of the technique since it presents the possibility that atomic behavior can be seen, and deduced, directly. Several examples are quite well known (Hashimoto, Takai, Yokota, Endo & Fukuta, 1980; Sinclair *et al.*, 1982; Eyring, Dutner, Goral & Holladay, 1985; Iijima & Ichihashi, 1986; Bovin, Wallenberg & Smith, 1986). One drawback of these early works has been that they rely either on the fortuitous occurrence of interesting events during the course of observation and recording, or on the imaging electron beam inducing changes in the sample. It has only recently been appreciated that heating holders have sufficient stability to allow image recording at elevated temperatures (Parker & Sinclair, 1985; Gibson, McDonald & Unterwald, 1985; Sinclair & Parker, 1986), so that natural thermally activated processes can also be studied. Of course this is an important development for fundamental investigations of reactions and transformations in solids. During the past year, we have applied this technique to a variety of interfacial annealing phenomena in semiconductor systems. This article describes some of this research and assesses its prospects for revealing atomic mechanisms in this important class of materials.

Experimental considerations

As with all *in situ* transmission electron microscopy (TEM) experiments (*e.g.* Butler & Hale, 1981), images are obtained following normal procedures, with a special sample holder employed to manipulate the specimen temperature. For high-resolution imaging one critical parameter is the crystal orientation with respect to the incident beam, which generally requires use of a double-tilt specimen holder. Currently no such holder with heating capability is commercially available but we circumvented this problem by using cross-section specimens which are prepared with one low-index crystallographic direction easily identifiable macroscopically (Sinclair, Parker & Kim, 1987). In this case with a side-entry high-resolution TEM a single-tilt axis is sufficient for correct orientation.

Observations can be recorded continuously on videotape using an image pick-up system. The quality, especially with the new medium-voltage microscopes, is sufficiently good that atomic-level changes are easily seen without recourse to image processing. Micrographs for analysis or publication can be photographed from a video display either during playback

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(which averages several frames) or from a single 'freeze' frame. Alternatively, if image drift is minimal, conventional image plates can be employed. While it is often thought that images at elevated temperatures would be too blurred for HREM, it is our experience on a range of substances that no real impediment exists.

It is important to consider the influence of the thin-foil specimen and the TEM environment on the observations. If one is concerned (as we are) with reactions representative of bulk behavior, then the close proximity of the specimen surfaces and the microscope 'vacuum' must be taken into account. We currently assess the reliability of our results by several procedures: (i) by comparing the microstructural changes occurring in the high-resolution areas with those in thicker parts of the same specimen; (ii) by comparing results of the *in situ* experiment with those in bulk material treated *ex situ* and subsequently thinned for TEM examination; (iii) by measuring the kinetics of a specific reaction as a function of temperature during the *in situ* experiment and comparing such data with their equivalent in bulk. Such work also allows estimation of the influence, if any, of the electron beam itself since we can monitor both irradiated and non-irradiated areas. Naturally there are instances when the thin foil effects dominate and the changes are quite different from those in the bulk experiment. They do not yield direct information about the bulk reaction, although it might be possible that some insight can still be derived from the results. However, we have found that there are sufficient instances where bulk behavior is achieved in the HREM specimen that the technique appears to be profitable. In those cases one can expect to use the unique observations provided by HREM to understand material behavior at the atomic level. For our particular current interest in interface reactions, there need only be a few atomic jumps on either side of the reaction zone to bring about interpretable changes of significance.

Alternatively the TEM situation (thin foil, electron irradiation, non-UHV atmosphere) can be used to advantage actually to study such phenomena as surface mobility, radiolysis and specimen oxidation or reduction. Once again quite useful understanding is provided about the behavior of solids, as exemplified by the atomic rearrangements seen in small metal particles (Iijima & Ichihashi, 1986; Bovin *et al.*, 1986) and research such as that by Kang & Eyring (1987) reported in Smith & Barry (1987).

The determination of specimen temperature in the field of view has always been problematic for *in situ* work. If the heating holder has large thermal mass it might be expected that the temperature specified by the attached thermocouple is reasonably reliable. However, one of the more important practical considerations in our experience is the efficiency of the specimen mounting in the holder (*i.e.* the degree of thermal contact between specimen and holder) which can vary, especially for fragile thin foils. One way to identify the absolute temperature is to apply a correction factor to the thermocouple reading by comparing observations *in situ* with equivalent changes produced *ex situ* (*e.g.* Raaijmakers, Reader & Van Houtum, 1987). An alternative, suggested by Parker (1988), is to incorporate a well known standard material as part of the HREM specimen and to follow its reaction, as well as that of the unknown, over the course of the *in situ* experiment. This is probably the most effective method. It also allows quantitative determination of electron beam effects by comparing data with the beam off (using the beam only to record occasional images) with those obtained during continuous imaging. Parker (1988) terms these as 'time-lapse' and 'real-time' *in situ* imaging, respectively.

The microscopy reported here was carried out on a Philips EM 400ST (120 kV) or on a Philips EM 430ST (300 kV) instrument, unless otherwise indicated. Heating was achieved with the standard Philips heating holder, PW6592, which is capable of reaching about 1270 K.

Results

1. *Early observations of cadmium telluride*

Figs. 1–3 show some of the changes which can be induced in cadmium telluride during HREM observation, and serve to illustrate the importance of controlled experiments. These results were obtained during the course of routine HREM imaging, without the use of a heating holder. It is thought that the specimen reaches a temperature of about 370 K since the relatively low thermal conductivity of CdTe does not allow heat dissipation from the imaged area.

In Fig. 1 conventional micrographs, taken about one minute apart, reveal that a defect rearrangement has occurred in the vicinity of an extra $\{111\}$ plane in the material. The nature of the fault and the identity of its associated partial dislocation can be easily determined from the image spot positions and they turn out to be an extrinsic stacking fault bounded by a Frank dislocation in this example. The continuous lattice distortion at the end of the fault is replaced by a discontinuous intrinsic stacking fault along an intersecting $\{11\bar{1}\}$-type plane. Presumably some reaction has taken place whereby a Shockley partial dislocation emanated from the Frank dislocation at the end of the extrinsic fault, leaving behind a Cottrell-type dislocation (Hornstra, 1958). However, because the micrographs were taken conventionally, the actual event itself was not recorded and so the above interpretation is ambiguous. For instance, a dislocation might have been created at the edge of the crystal and slipped into the fault, not out of it. Thus it is clear that continuous recording (*e.g.* by videotaping)

is necessary to capture the essence of such occurrences. Indeed, they would be completely missed if there were no recording at all, and it is quite fortuitous that even 'before' and 'after' micrographs were obtained in this case.

Fig. 2 gives an example where a successful video recording is achieved. A dislocation, originally dissociated on a $\{11\bar{1}\}$-type plane (Fig. 2*a*), suddenly recombines (Fig. 2*b*), dissociates again on an intersecting $\{111\}$ plane (Fig. 2*c*), and finally slips out of the crystal, leaving it defect-free in the original location. The sequence takes about 14 s and demonstrates a coordinated event, involving hundreds of atoms and reminiscent of a cross-slip mechanism in f.c.c. crystals. We believe that thermally induced stresses are responsible for 'driving' the reaction. Important steps can be isolated from the video recording and subsequently studied in detail. The dislocations themselves can be identified from a Burgers circuit carried out on the individual images (Yamashita & Sinclair, 1983*a*) although there is always some ambiguity since only projected lattice displacements can be seen. In

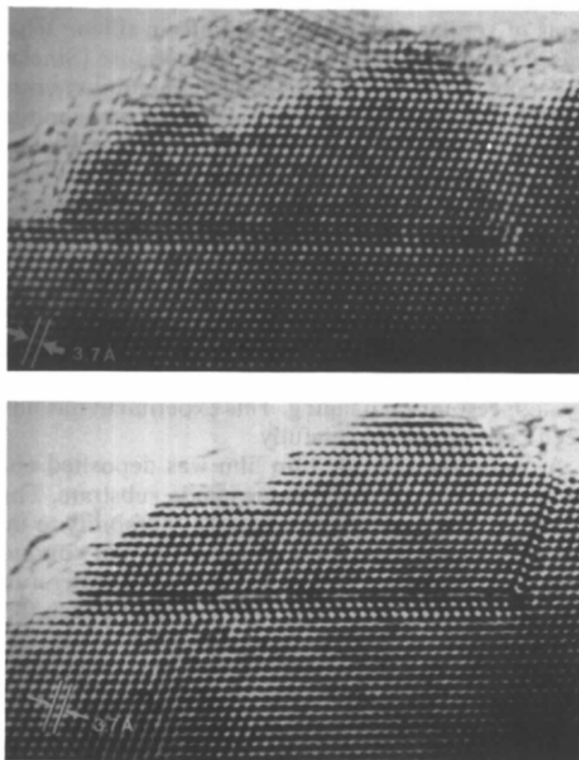
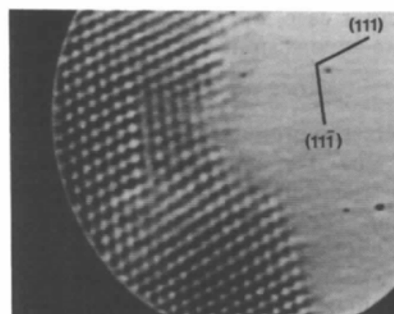
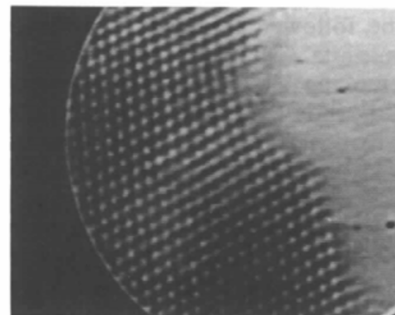


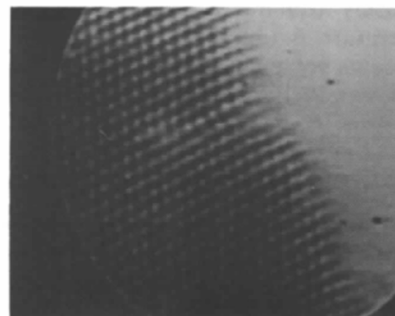
Fig. 1. Conventional electron micrographs, taken about one minute apart, of a CdTe specimen heated by the imaging beam. A dislocation event near the end of an extrinsic attacking fault (horizontal) converts a continuous lattice strain field into a discontinuous intrinsic stacking fault. Burgers circuits performed on the images are consistent with the dislocation reaction $\frac{1}{3}[111] \rightarrow \frac{1}{6}[110] + \frac{1}{6}[112]$. Note also changes in the edge of the specimen due to high surface atomic mobility. (Taken on JEOL 200 CX at Lawrence Berkeley Laboratory, USA.)



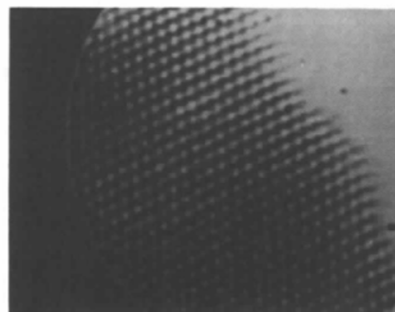
(*a*)



(*b*)



(*c*)



(*d*)

Fig. 2. A sequence of individual video frames, image processed by noise reduction and four-frame averaging, showing the steps in the rearrangement of CdTe during the removal of a dissociated dislocation. The approximate time intervals between the frames are 2 s for (*a*)-(*b*) (recombination of partials), 1 s for (*b*)-(*c*) (expansion of partials on inclined $\{111\}$ plane), and 10 s for (*c*)-(*d*) (final dislocation disappearance). The imaging direction is $[1\bar{1}0]$.

this particular case, the original dissociation on the $\{11\bar{1}\}$ plane is consistent with the reaction

$$\tfrac{1}{2}[10\bar{1}] \rightarrow \tfrac{1}{6}[1\bar{2}\bar{1}] + \tfrac{1}{3}[11\bar{1}],$$

which reverses to produce a perfect $\frac{1}{2}[10\bar{1}]$ 60° dislocation (Fig. 2*b*). The latter now undergoes the well known dissociation into Shockley partials on the $\{111\}$ plane (*i.e.* $\frac{1}{2}[10\bar{1}] \rightarrow \frac{1}{6}[11\bar{2}] + \frac{1}{6}[2\bar{1}\bar{1}]$), one of which has slipped out of the crystal in Fig. 2(*c*), the other doing so by the time of Fig. 2(*d*). Both mechanisms were first described by Hornstra (1958) for diamond-cubic-related structures. Even individual atomic displacements produced by a moving dislocation can be followed this way (*e.g.* Sinclair *et al.*, 1982; Yamashita & Sinclair, 1983*b*) so long as the defect is moving slowly compared to the rate of recording. It should be noted, however, that using the beam to bring about changes in the sample is rather haphazard and an inefficient use of observation time.

The disappearance of a bulk defect over a period of several minutes is seen in Fig. 3. The region of the image which is devoid of lattice fringes is gradually filled in. This can only occur by a diffusional mechanism. The kinetics of this reaction can be determined quite precisely from the recording. However, because the temperature is unknown, the absolute reaction rate represents somewhat limited information. More significant would be how the reaction varies as a function of temperature, which would yield knowledge of the activation energy (from an Arrhenius plot) as well as the mechanism (from the direct observation of the atomic changes).

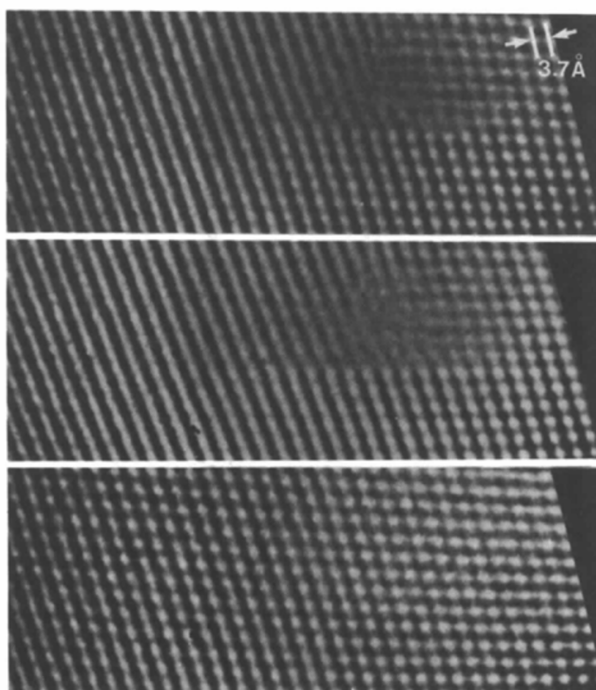


Fig. 3. The gradual disappearance of a small defect cluster in CdTe over a period of several minutes during observation. (Taken on the 600 kV HREM at Cambridge Univ., England.)

These examples therefore demonstrate the great power of *in situ* HREM observations but indicate the necessity for controlled heating experiments. Disadvantages of using the beam to induce reactions include lack of precise control and reproducibility of specimen temperature, limitation on the samples to be studied to those which can be affected by the beam, limited information on the absolute temperature and reliance on haphazard occurrences.

2. *Recent heating experiments on* CdTe

It has always been our interpretation that the changes in CdTe, such as those described above, were induced by the heating effect of the electron beam. The arguments for this suggestion are presented elsewhere (Sinclair, Yamashita & Ponce, 1981) and they appear to be borne out by subsequent results of others on equivalent behavior in more benign specimens (*e.g.* small metal particles) and by our own observations of similar dislocation reactions in silicon when raised to an appropriately high temperature (Sinclair & Parker, 1986). However, dislocation mobility under stress is enhanced at low temperatures in semiconductors under SEM and TEM imaging conditions, which is thought to arise from additional activation due to electron–hole recombinations (Maeda, Sato, Kubo & Takeuchi, 1983; Maeda, Suzuki, Ichihara & Takeuchi, 1984). This phenomenon might therefore play a role in our early work. It is necessary to assess its importance since it may influence kinetic measurements when it is predominant. One approach lies in heating CdTe samples themselves and following the results by high-resolution imaging. This experiment has now been carried out successfully.

A cadmium telluride thin film was deposited epitaxially on a $\{111\}$ gallium aresenide substrate. This at once provides greater mechanical durability to the CdTe TEM specimen and a higher thermal conductivity support than CdTe itself. At room temperature the HREM imaging current was minimized such that there were no observed changes fcr up to 20 min. The temperature was quickly raised to 770 K whereupon both dislocation reactions and atomic surface rearrangements were seen to take place quite rapidly. These are the direct counterparts of the earlier observations, including the recent results described by Lu & Smith (1987). Since the present temperature is well above that for recombination-enhanced motion in GaAs and InP (~570 K for SEM and ~470 K in a TEM) (Maeda, Sato, Kubo & Takeuchi, 1983; Maeda, Suzuki, Ichihara & Takeuchi, 1984; Maeda & Takeuchi, 1983) and there were no changes in the present case before *in situ* heating, we strongly

believe that heating alone is providing the primary activation for the behavior.

Fig. 4 shows a sequence of images during the dissociation of the CdTe at this elevated temperature. For the most part, the material decomposes by removal of successive {111} planes, normally involving a ledge mechanism. However, there are many instances in which the reaction fluctuates, back and forth as it were. Thus image spots migrate both ways along the ledges, and disappear and reappear several times before their ultimate removal. One has a real impression of a 'dynamic equilibrium' state rather than a steady inexorable progress of the reaction.

In addition, it can be appreciated that there is no question about the image quality at this temperature being acceptable for high-resolution interpretation.

3. *Solid-phase epitaxial regrowth (SPE) of silicon*

The most detailed *in situ* study we have carried out so far concerns the epitaxial regrowth of amorphized silicon (Parker, 1988). This is an important procedure in microelectronic applications for the fabrication of high-quality single-crystal silicon following ion implantation. A series of kinetic measurements of the rate of regrowth shows that the reaction is interface controlled (*i.e.* it proceeds linearly with time) and that the activation energy [2·52(22) eV] is similar to that derived from bulk experiments [*e.g.* Rutherford back-scattering spectroscopy, 2·85(23) eV] on the same batch of material and to values quoted in the literature, the average of which is 2·65 eV (Parker, 1988). By using standard well characterized material as half of the cross-section sample, the local temperature can be established reasonably accurately (say ±10 K) within a few micrometers of the area of interest. Furthermore, experiments can be carried out in the time-lapse mode so as to determine the influence of the imaging beam, which for silicon (a reasonably good thermal conductor) under typical 120 kV HREM imaging conditions turned out to be equivalent to a 20 K rise in temperature. The activation energies for the time-lapse and real-time observations are also quite close [2·52(22) and 2·33(15) eV respectively]. Whether this difference is real or not is difficult to say, but there clearly is not a large effect. Thus thermal activation and bulk kinetics are indicated to be dominant by these results. The good correlation between *in situ* and bulk data can be appreciated by reference to the graphs presented by Sinclair, Parker & Kim (1987).

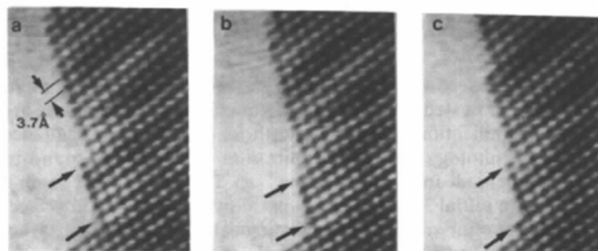


Fig. 4. Individual consecutive video frames (unprocessed) showing the disappearance (*b*) and reappearance (*c*) of individual atomic columns at {111} plane ledges during the dissociation of CdTe at a nominal temperature of 770 K. The time interval between the frames is approximately one thirtieth of a second.

The HREM observations also provide new insight into the mechanism of SPE. Although the interface moves forward slowly there are occasions on which a sudden burst of crystallization occurs, involving many atoms simultaneously. This led us (Parker, 1988) to develop a revised kinetic model for SPE based on the necessity for some 'catalytic' species (*e.g.* a vacancy) to bring about the reaction. Sometimes there is even a reversal of the reaction (Sinclair & Parker, 1986) equivalent to that seen in the dissociation of CdTe, implying also a dynamic state. In addition, the stresses set up at the reaction interface are sufficiently high to bring about dislocation reactions in the silicon crystal. We had previously estimated from our CdTe work at 'room temperature' (Sinclair, Yamashita & Ponce, 1981) that such events would take place at about 870 K in Si, and this prediction appears to be supported by the results.

The importance of this particular research therefore lies in the demonstration that worthwhile kinetic measurements of an interface reaction can be made by *in situ* HREM. Furthermore, a method to determine local temperature was derived and the atomic-scale observations were used to develop a model for regrowth.

4. *Interdiffusion in silicon–metal multilayers*

Following the discovery that interdiffusion of amorphous silicon into crystalline titanium renders the resultant Ti–Si 'alloy' amorphous (Holloway & Sinclair, 1987), *in situ* HREM was carried out to elucidate the associated atomic mechanism. Direct comparisons were made with the microstructure developed at equivalent stages by heat treatment of bulk samples followed by thinning for TEM. Both *in situ* and *ex situ* annealing are characterized by planar growth of the amorphous alloy, despite the presence of many Ti grain boundaries (*e.g.* Figs. 5, 6). Because Si predominantly diffuses into the titanium, Kirkendall voids are produced by net diffusion in the opposite direction of vacancies, or their equivalent in amorphous Ti–Si, an effect first reported for Co–Zr multilayer interdiffusion by Schroder, Samwer & Koster (1985). Both the *in situ* and *ex situ* experiments show the appearance of such Kirkendall voids. We believe this is direct proof that bulk diffusion behavior is reproduced even in the TEM thin foil. Nucleation of crystalline silicides occurs first at the Kirkendall voids (Holloway & Sinclair, 1988*a*). This event was

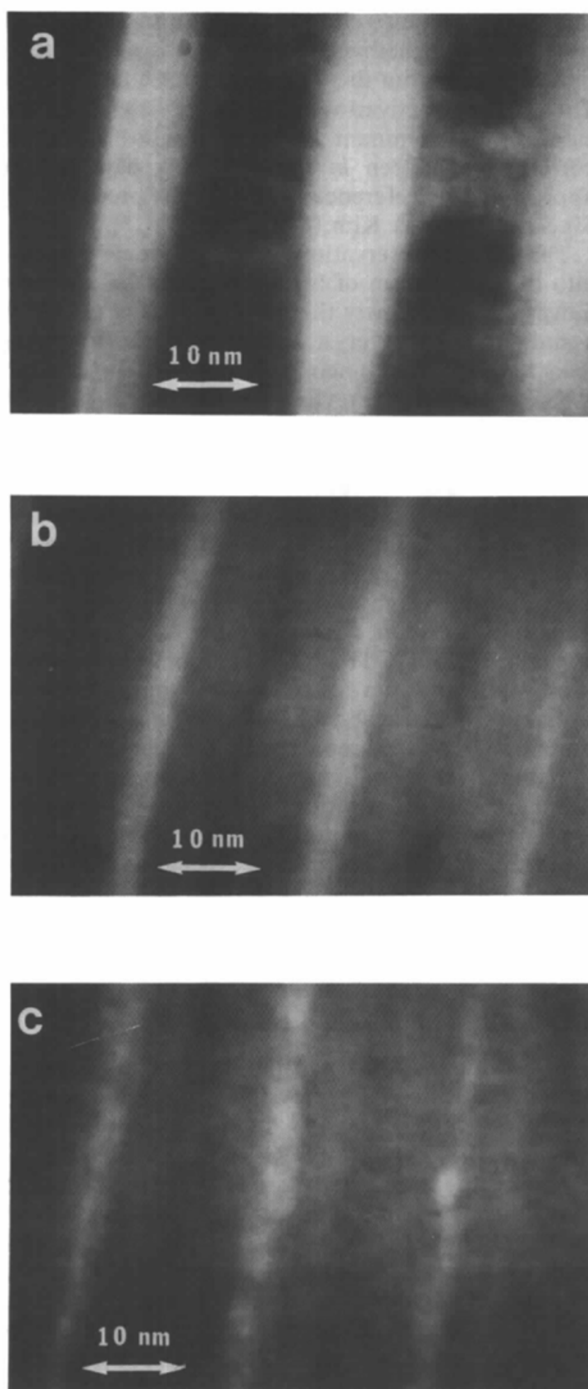


Fig. 5. Cross-section TEM video photographs of Ti–Si multilayers at various stages during an *in situ* annealing experiment: (*a*) before annealing, an initial 3·0 nm amorphous alloy layer is apparent at each interface. The crystalline α-Ti region is distinguished in the darker layers by the various diffracting conditions of the titanium grains; (*b*) at a nominal temperature of 780 K, the interface between the amorphous Si (lighter) and the amorphous alloy shows a roughened appearance; and (*c*) at a nominal temperature of 800 K, Kirkendall voids are forming between neighboring layers. A band of crystalline titanium remains in the centers of the layers.

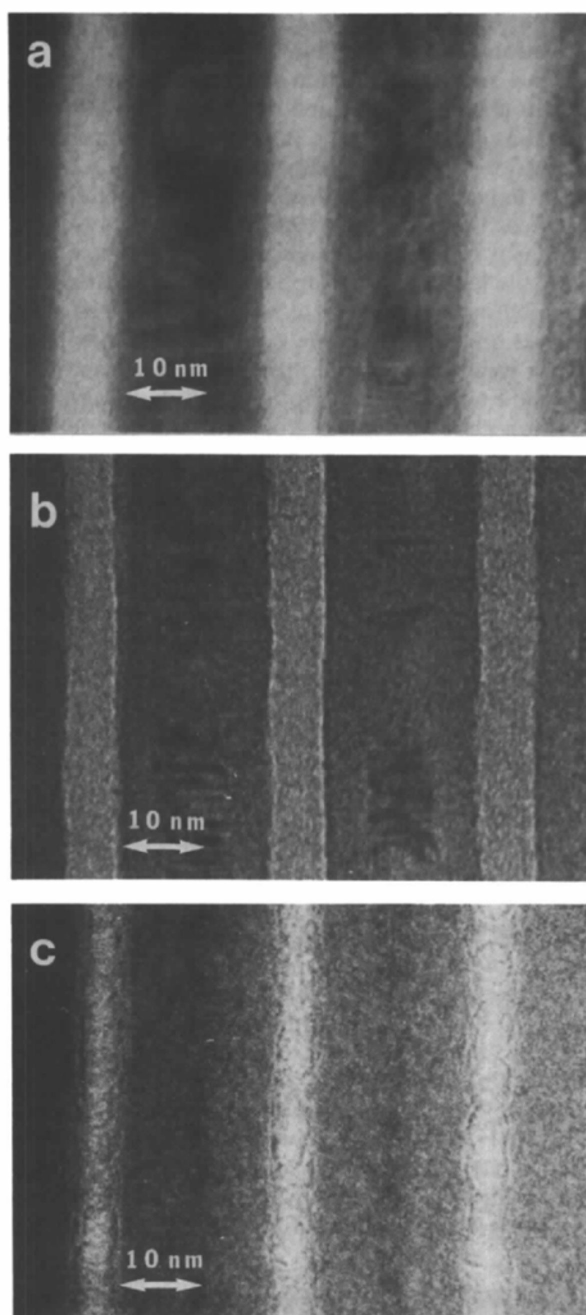


Fig. 6. Cross-section TEM micrographs of Ti–Si multilayers rapid thermal annealed in bulk and subsequently sectioned. These are at a magnification comparable to those in Fig. 5. The sequence and morphology of the amorphization reaction correspond to that observed on *in situ* heating. (*a*) The unannealed sample shows an initial 3·0 nm amorphous alloy layer at each interface. The crystalline α-Ti region is distinguished in the darker layers by the various diffracting conditions of the titanium grains. (*b*) After rapid thermal annealing at 648 K for 30 s, the amorphous alloy layer thickness has grown to about 4·0 nm. The reaction is planar, and does not occur preferentially along Ti grain boundaries. (*c*) After rapid thermal annealing at 720 K for 30 s, the amorphous alloy layer is now 7·5 nm thick. The amorphous Si has been consumed and rows of Kirkendall voids take their place.

unclear in the bulk experiment since the nucleation stage was missed. Continuous recording of the *in situ* reaction allows such a straightforward deduction.

Conversely, annealing of Mo–Si multilayers does not result in the extension of the amorphous layers formed during multilayer deposition. Instead, it is observed in both *in situ* and *ex situ* specimens that a crystalline silicide nucleates first in the amorphous material, and that no Kirkendall voids are created (Holloway & Sinclair, 1988*b*). Once more the equivalence of *in situ* and *ex situ* experiments is demonstrated, in this case by microstructural appearance. A correlation of kinetic data as a function of temperature is problematic, since the interdiffusion layer is somewhat limited and the annealing temperatures are quite low (*e.g.* 570–770 K). Sometimes the measured heating holder temperature is significantly higher (~100 K) than that necessary to bring about the bulk reaction: this is currently thought to arise from poor thermal contact of the TEM specimen in the holder itself.

5. *Metal–gallium arsenide reactions*

Most elemental metals are thermodynamically unstable in contact with gallium arsenide (Beyers, Kim & Sinclair, 1987) and so will react with it on annealing. Titanium, for example, interacts with gallium arsenide and forms two binary compounds, Ti_xGa_{1-x} ($x = 0{\cdot}35 \pm 0{\cdot}05$) and TiAs (Kim, Kniffin, Sinclair & Helms, 1988). Nickel, although it finally forms two binary compounds, NiGa and NiAs, does so by first producing an Ni_xGaAs ($x = 2$–3) ternary compound (Ogawa, 1980; Lahav, Eizenberg & Komem, 1985; Sands, Keramidas, Washburn & Gronsky, 1986). In addition these elements develop a different morphology. Titanium forms a layered structure of Ti_xGa_{1-x}/TiAs/GaAs whereas nickel produces an agglomerated type of structure of NiGa and NiAs. Furthermore, GaAs has a fairly high vapor pressure, even at intermediate temperatures, and so will readily dissociate on heating. This material therefore provides a rich source for studying *in situ* behavior, although the technical motivation lies in developing stable metallic Ohmic and Schottky contacts to the semiconductor.

Fig. 7 shows a sequence at the edge of a GaAs specimen heated to a nominal temperature of 920 K. The local surface orientations are {110} and {111} type. Over a period of several minutes we observed dissociation of the specimen. The {110} behavior was most interesting since a clear $1 \times n$ reconstruction can be seen [similar to that described previously for {110} surfaces in gold (Marks, 1983)], even though the surface is not under UHV conditions. Surface reconstructions observed by HREM profile imaging have also been reported for Au (Marks & Smith, 1983), Si (Gibson *et al.*, 1985) and CdTe (Lu & Smith, 1987).

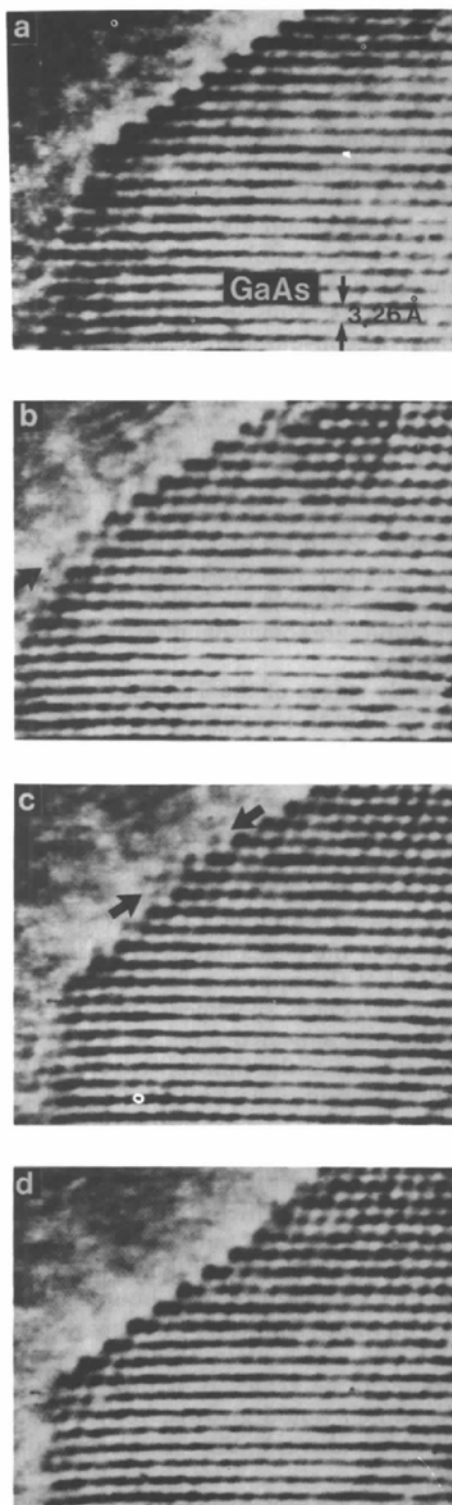


Fig. 7. The dissociation of gallium arsenide from a {110} plane surface at 920 K (nominal) occurs by the successive removal of atomic columns. Although the individual image spots are unstable in position and intensity for several seconds, no distinct disappearance and reappearance occurs as for the CdTe {111} planes (Fig. 4). The time interval for the present sequence is approximately 30 s.

Evaporation occurred by removal of successive atom columns along the {110} plane starting from the ledge corner. The image spots which were in the process of removal were unstable in intensity and position for several seconds, suggestive of a delicate balance before their final disappearance. This is quite difficult to illustrate in still frames but is quite clear during the original observation and in the video recording.

When the GaAs crystal becomes quite thin its disappearance can be rapid, and can also illustrate dynamic reversals. Thus in Fig. 8 we show photographs from the consumption of GaAs in contact with the TiAs layer formed by reaction with titanium. In one instant the GaAs crystal seems to have disappeared, then it suddenly reappears and finally it disappears for good. Whether this is due to changes in orientation of the GaAs crystal [similar to those in small gold particles heated by an imaging electron beam (Smith, Petford-Long, Wallenberg & Bovin, 1988)] or whether the GaAs has evaporated and recondensed is difficult to decide, but nevertheless the observations are somewhat unexpected and therefore intriguing.

In the early stages of the Ti–GaAs and Ni–GaAs reactions, the GaAs is consumed near the original interface and the product phases are formed in its place. This directly demonstrates that metal elements are prominent diffusing species for both reactions. The microstructures are then similar to those of bulk specimens implying that the initial reaction can be followed by *in situ* HREM. Upon prolonged annealing some unusual results are found (Fig. 9). Holes are produced at the GaAs interface for the Ti–GaAs reaction, and at the upper surface of the metal thin film for the Ni–GaAs specimens. Neither has been observed in bulk annealed samples. We believe that these are artifacts of the thin-foil experiment. In the Ti case, the reaction of Ti with the GaAs first forms TiAs and releases Ga. In bulk, the Ga diffuses through the TiAs layer to produce a Ti_xGa_{1-x} ($x = 0{\cdot}35 \pm 0{\cdot}05$) intermetallic compound. In the thin foil, we suggest that Ga accumulates at the top and bottom surfaces of the sample because of surface energy and alternately produces elemental gallium, which is liquid at the annealing temperature. The liquid composition which is thermodynamically in equilibrium with GaAs at 870 K can contain about 3 at.% As. This composition can be achieved by dissolving some of the GaAs, which would give rise to the appearance of voids and disrupt the metal-semiconductor interface.

In the nickel case, the Ni_xGaAs ternary compound is known to break down during high-temperature annealing (620–770 K) to NiGa and NiAs phases. In addition, the NiAs phase disappears at even higher temperatures (>770 K) in vacuum by the sublimation of As from the surface (Lahav, Eizenberg & Komem, 1987). In the cross-section sample, this behavior would result in voids at the upper surface where the specimen is thinner.

In summary, the mechanism of the initial reaction can be followed by *in situ* HREM. Upon prolonged annealing thin-foil effects can influence the resulting

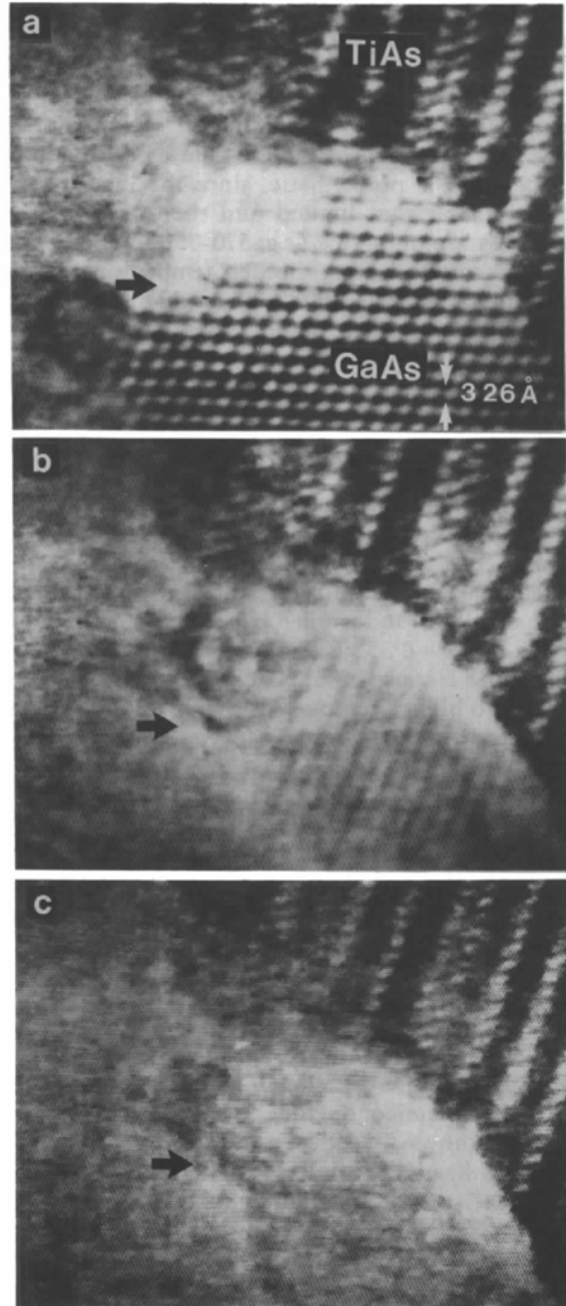


Fig. 8. A sequence of video images showing the consumption of GaAs in contact with the TiAs layer formed by *in situ* reaction of the semiconductor with metallic titanium. The whole GaAs area shown momentarily 'disappears' from the image, then partially reappears for about 1 s manifested by faint {111} lattice fringes, and finally disappears for good.

morphology although their interpretation is consistent with the bulk behavior and indeed can provide evidence for the atomic mechanisms suggested. This confirms the caution which must be exercised in applying the *in situ* TEM approach. On the other hand, when the experiment is proceeding satisfactorily the results are quite dramatic. Fig. 10 shows a sequence from the Ni-GaAs reaction in which the advance of the Ni_xGaAs product phase into the GaAs substrate is noticeable. By following the recording it is conclusive that GaAs image spots are replaced upon reaction by new Ni_xGaAs material, thus proving that the reaction occurs at the GaAs interface (*i.e.* nickel diffuses in, not gallium and arsenic out). This conclusion has been deduced by others from 'bulk' results (Lahav *et al.*, 1985; Sands, Keramidas, Yu, Gronsky & Washburn, 1987). Also, although there is gradual encroachment of the product into the GaAs,

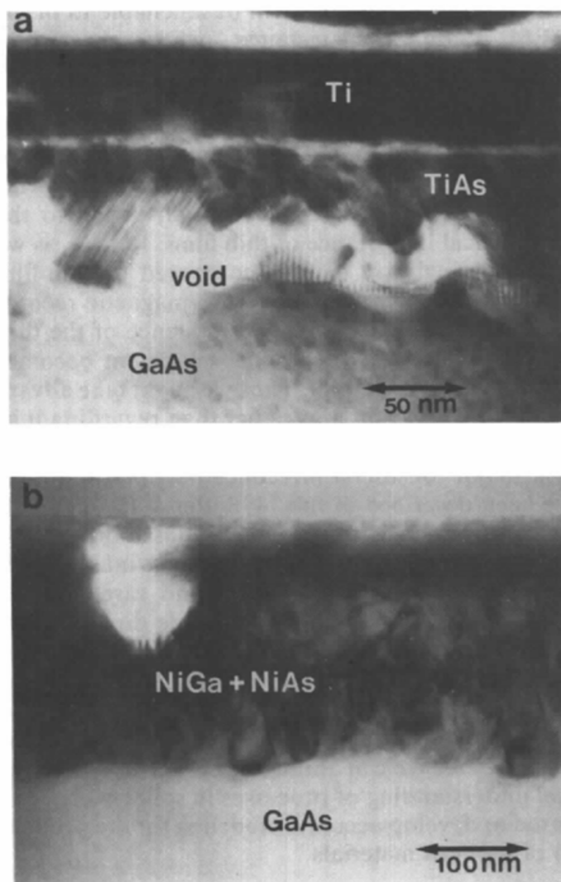


Fig. 9. Upon prolonged *in situ* reaction of titanium (*a*) and nickel (*b*) with gallium arsenide, voids are created in the TEM thin foil. Their location yields some insight into the reaction events.

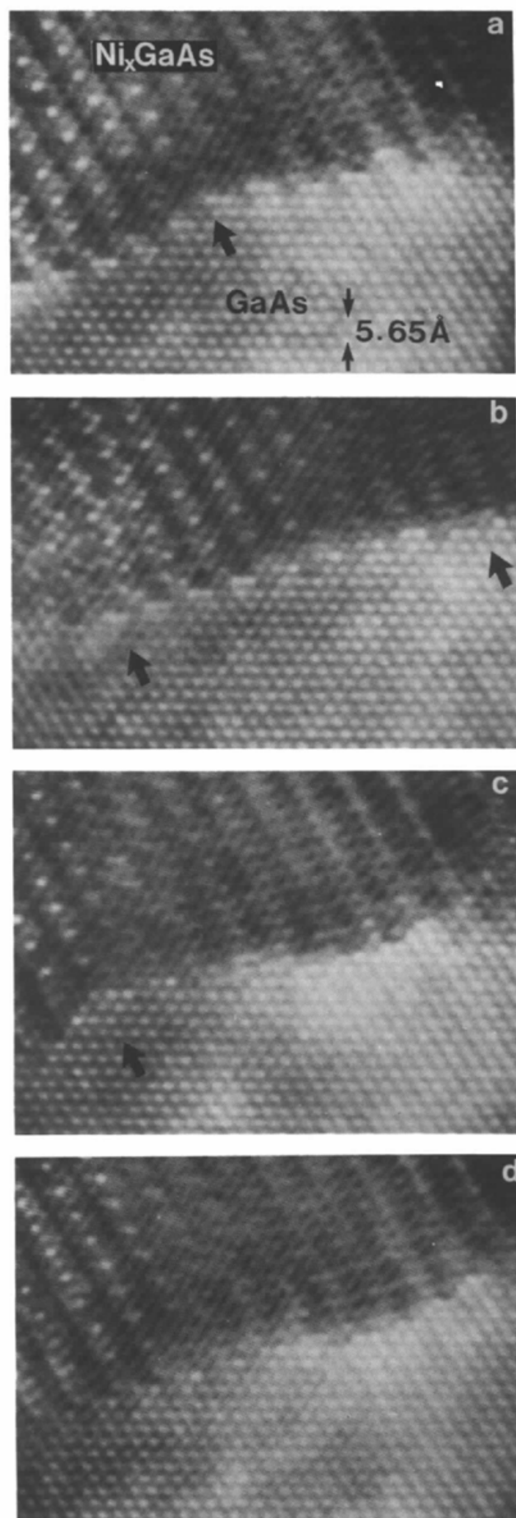


Fig. 10. A sequence of video images showing the gradual advance of the Ni_xGaAs-GaAs interface into the GaAs during reaction of the latter *in situ* with nickel at 720 K (nominal). By following the progress of the reaction with reference to specific atom columns, it can be seen definitively that GaAs is consumed at the interface and is replaced by new Ni_xGaAs material, proving that the chemical reaction takes place at this location. Occasional reaction bursts [(*a*)-(*b*), (*c*)-(*d*)], to planarize the interface, occur in addition to a progressive advance of the interface.

reaction bursts often occur, as we have seen in the silicon SPE. However, we did not observe any reaction reversals in this system, presumably since it is more difficult to break the stronger Ni–Ga–As chemical bonds once they are formed.

6. *Solid-phase epitaxial regrowth in* GaAs

Unlike silicon, regrowth of amorphized GaAs results in a highly defective crystal (Opyd, Gibbons, Bravman & Parker, 1986). We undertook preliminary *in situ* studies of this reaction in an attempt to clarify the origin of the lattice defects. During the *in situ* experiment regrowth occurred upon heating to 520–570 K, but not in the area under continuous TEM observation (*e.g.* Fig. 11). Thus it was not possible to follow the reaction as it occurred. We presume that the 300 kV imaging beam created point defects in the GaAs which essentially poison the regrowth mechanism. While this is interesting in itself, it is of course unfortunate for the experimenter and illustrates that the beam itself can adversely influence the results. Whether this is a problem unique to GaAs regrowth, or is applicable to other semiconductors, is unknown at present.

Discussion

We have described in this article the use of a heating holder to bring about atomic arrangements while imaging under HREM conditions. In a substantial proportion of cases behavior representative of bulk material is observed. Consequently we can conclude that *in situ* atomic-level experiments are possible in the TEM, despite the nature of the thin-foil specimen and the microscope environment. Of course the holder need not be confined to being the heating type, and indeed various *in situ* studies should be feasible, so long as the sample is stable during observation.

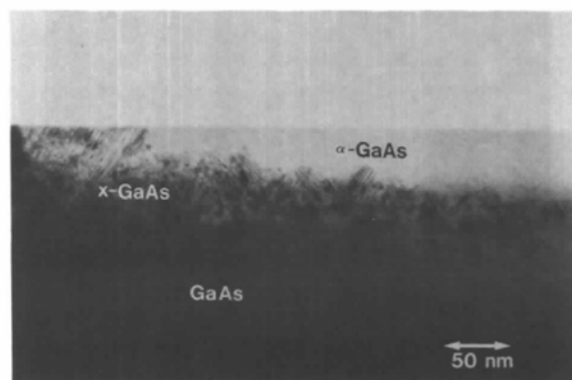


Fig. 11. Solid-phase epitaxial regrowth of amorphized gallium arsenide is slowed down by the 300 kV HREM imaging beam. Thus, the area on the left of the micrograph was outside the area under *in situ* observation and has regrown in the normal manner, containing a high density of stacking faults and microtwins. The area to the right was under HREM investigation. (Specimen courtesy of Y. Nissim.)

Having said this, the precautions one must take to ensure bulk reactions should still not be underestimated. We have suggested several procedures which can be adopted, involving either quantitative measurement of kinetic data both *in situ* and *ex situ* or qualitative comparison of microstructural development, supplemented by observations in non-irradiated areas. A combination of these provides the greatest degree of certainty, although this is often difficult and time consuming. Nevertheless, the opportunity actually to observe reaction mechanisms at the atomic level is not provided by alternative techniques and so the effort is certainty worthwhile.

Not all transformations will be amenable to *in situ* HREM study. For instance, whenever surface nucleation competes with bulk nucleation, as often occurs in martensitic phase changes, information about the bulk behavior would be lacking. Likewise, if surface diffusion were to dominate we would learn about this effect, not about the bulk mechanism. This in itself may not be inconsequential, owing to the technological importance of thin films. Indeed, as we rely increasingly on devices composed of thin-film parts (*e.g.* microelectronic devices, magnetic recording media), study of the actual influence of the thin film itself on microstructural development becomes important in its own right. Thus we might take advantage of the TEM thin film rather than regarding it as an unfortunate necessity.

The major considerations concerning *in situ* studies have been described in full by Butler & Hale (1981). Our contribution is to extend the possibility to the high-resolution regime. The experiments must be performed with the utmost thought and care, but the results which can be obtained provide direct insight into atomic behavior during microstructural development. New unexpected information is likely to be uncovered, such as the occasional reversibility of a reaction and the occurrence of transformation 'bursts' reported here. We can anticipate deeper and perhaps novel understanding of processes in solids which can be used to develop accurate modeling for the production of modern materials.

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References

BEYERS, R., KIM, K. B. & SINCLAIR, R. (1987). *J. Appl. Phys.* **61**, 2195-2202.
BOVIN, J. O., WALLENBERG, R. & SMITH, D. J. (1986). *Nature (London)*, **317**, 47-49.
BUTLER, E. P. & HALE, K. F. (1981) *Practical Methods in Electron Microscopy*, Vol. 9, edited by A. M. GLAUERT, pp. 1-457. Amsterdam: North-Holland.
COWLEY, J. M. & IIJIMA, S. (1972). *Z. Naturforsch. Teil A*, **27**, 445-449.
EYRING, L., DUTNER, C., GORAL, J. P. & HOLLADAY, A. (1985). *Ultramicroscopy*, **18**, 253-274.
GIBSON, J. M., MCDONALD, M. C. & UNTERWALD, F. C. (1985). *Phys. Rev. Lett.* **55**, 1765-1767.
HASHIMOTO, H., TAKAI, Y., YOKOTA, Y., ENDO, H. & FUKUTA, E. (1980). *Jpn. J. Appl. Phys.* **19** L1-L4.
HOLLOWAY, K. & SINCLAIR, R. (1987). *J. Appl. Phys.* **61**, 1359-1364.
HOLLOWAY, K. & SINCLAIR, R. (1988*a*). *J. Less-Common Met.* **140**, 139-148.
HOLLOWAY, K. & SINCLAIR, R. (1988*b*). *Proc. Mater. Res. Soc.* **103**, 167-172.
HORNSTRA, J. (1958). *J. Phys. Chem. Solids*, **5**, 129-141.
IIJIMA, S. & ICHIHASHI, T. (1986). *Phys. Rev. Lett.*, **56**, 616-618.
KANG, Z. C. & EYRING, L. (1987). *Ultramicroscopy*, **23**, 275-281.
KIM, K. B., KNIFFIN, M., SINCLAIR, R. & HELMS, C. R. (1988). *J. Vac. Sci. Technol.* **A6**, 1473-1477.
LAHAV, A., EIZENBERG, M. & KOMEM, Y. (1985). *Proc. Mater. Res. Soc.* **37**, 641-646.
LAHAV, A., EIZENBERG, M. & KOMEM, Y. (1987). *J. Appl. Phys.* **62**, 1768-1777.
LU, P. & SMITH, D. J. (1987). *Phys. Rev. Lett.* **59**, 2177-2179.
MAEDA, K., SATO, M., KUBO, A. & TAKEUCHI, S. (1983). *J. Appl. Phys.* **54**, 161-168.
MAEDA, K., SUZUKI, K., ICHIHARA, M. & TAKEUCHI, S. (1984). *J. Appl. Phys.* **56**, 554-556.
MAEDA, K. & TAKEUCHI, S. (1983). *Appl. Phys. Lett.* **42**, 664-668.
MARKS, L. D. (1983). *Phys. Rev. Lett.* **51**, 1000-1002.
MARKS, L. D. & SMITH, D. J. (1983). *Nature (London)*, **303**, 316-318.
MENTER, J. W. (1956). *Proc. R. Soc. London Ser. A*, **236**, 119-129.
OGAWA, M. (1980). *Thin Solid Films*, **70**, 181-189.
OPYD, W. G., GIBBONS, J. F., BRAVMAN, J. C. & PARKER, M. A. (1986). *Appl. Phys. Lett.* **49**, 974-976.
PARKER, M. A. (1988). *In Situ High-Resolution Transmission Electron Microscopy of Solid-Phase Epitaxy in Silicon and Silicon on Sapphire.* PhD thesis. Stanford Univ., USA.
PARKER, M. A. & SINCLAIR, R. (1985). *Proc. Electron Microsc. Soc. Am.* **43**, 358-359.
RAAIJMAKERS, I. J. M. M., READER, A. H. & VAN HOUTUM, H. J. W. (1987). *J. Appl. Phys.* **61**, 2527-2532.
SANDS, T., KERAMIDAS, V. G., WASHBURN, J. & GRONSKY, R. (1986). *Appl. Phys. Lett.* **48**, 402-404.
SANDS, T., KERAMIDAS, V. G., YU, A. J., GRONSKY, R. & WASHBURN, J. (1987). *J. Mater. Res.* **2**, 262-275.
SCHRODER, H., SAMWER, K. & KOSTER, U. (1985). *Phys. Rev. Lett.* **54**, 197-200.
SINCLAIR, R. & PARKER, M. A. (1986). *Nature (London)*, **322**, 531-533.
SINCLAIR, R., PARKER, M. A. & KIM, K. B. (1987). *Ultramicroscopy*, **23**, 383-396.
SINCLAIR, R., PONCE, F. A., YAMASHITA, T., SMITH, D. J., CAMPS, B. A., FREEMAN, L. A., ERASMUS, S. J., NIXON, W. C., SMITH, K. C. A. & CATTO, C. J. C. (1982). *Nature (London)*, **298**, 127-131.
SINCLAIR, R., YAMASHITA, T. & PONCE, F. A. (1981). *Nature (London)*, **290**, 386-388.
SMITH, D. J. & BARRY, J. C. (1987). *Ultramicroscopy*, **23**, 255-478.
SMITH, D. J., PETFORD-LONG, A. K., WALLENBERG, L. R. & BOVIN, J. O. (1986). *Science*, **233**, 872-875.
YAMASHITA, T. & SINCLAIR, R. (1983*a*). *Proc. Electron Microsc. Soc. Am.* **41**, 112-113.
YAMASHITA, T. & SINCLAIR, R. (1983*b*). *Proc. Mater. Res. Soc.* **14**, 295-298.

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Signal Processing of High-Resolution Transmission Electron Microscope Images Using Fourier Transforms

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Abstract

Interpretation of images obtained by high-resolution transmission electron microscopy (HRTEM) can be aided by the use of processed signals. Images are recorded digitally or are digitized from a photograph, and then these data are Fourier transformed and treated. The low- and high-frequency signals are removed, and a variety of circular and elliptical (anisotropic) apertures or screens are applied to explore and highlight features of special interest. A minicomputer can be used to perform such image processing rapidly, interactively, and with high precision. Elliptical filters are of special interest for the examination of linear or planar features such as the distribution of stacking faults or the presence and distribution of superstructures. Some superstructures themselves contain defects, and these can similarly

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