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PART I

Atomic Imaging of Defects

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SOLVING THE STRUCTURE OF INTERFACES BY HIGH RESOLUTION ELECTRON MICROSCOPY

ALAIN BOURRET
Service de Physique,S. CEN-Grenoble, 85 X, 38041 Grenoble Cédex, France

ABSTRACT

This paper reviews some of the new advancements made in solving the structure of planar interfaces in a wide range of materials and interface types. The main contributions of the HREM technique are the determination of the atomic positions at the interface, the detection of additional defects such as dislocations or monoatomic steps and more recently the chemical composition when crossing the interface. It is concluded that quantitative results obtained by image processing and pattern recognition will in the future greatly improve the knowledge of interfacial structures at an atomic scale.

INTRODUCTION

Numerous observations of interfaces between two similar or dissimilar materials with high resolution electron microscopy (HREM) have been reported in the last few years. Most of the results were obtained on semiconductor materials : grain boundaries, silicon-silicide interfaces, multilayers, quantum wells, semiconductor-metal interfaces were the configurations on which HREM has given significant contributions (for recent reviews, see [1] and [2]). However other metallic or composite systems were recently observed [3]. For instance the product of chemical reactions at surfaces or metallic interfaces as well as metal oxides have been characterized (Cu/Au [4] ; MgOAl [5] ; Cu/O [6]). Similarly the interfaces between a precipitate and the matrix have been observed in few systems such as Al/Ge [7], Al-Cu-Li alloy [8], superalloys [9]. With the improved resolution of modern microscopes (down to 0.16 nm) the possibilities have been greatly extended : more than one zone-axis can be looked at, opening the way to true 3-D HREM and more compact structures can be studied. Most of these observations have been treated qualitatively, the interpretation ranging from a direct read-out of the structure to a visual comparison with computer simulated images of a small number of atomic models. These qualitative approaches were sufficient to give some insight into the overall characteristics of interfaces. One can deduce for instance i) the periodicities at the interface, ii) the coherency or the loss of coherency with or without interfacial dislocations iii) the rotation of the material iv) the presence of steps or facets as small as a monolayer, v) the presence of additionnal extrinsic defects such as dislocations or impurities seggregated at the interface. However more subtle details are also accessible although they are more demanding for the technique. For instance the following items are of remarkable interest : i) determination of the atomic position at the interface particularly when large distortions of the bonds (or change of the coordination number) are likely to occur. This is the case for grain boundaries separating two disoriented but similar crystals, for epitaxial layers at vicinal surfaces, or for interfaces between two very different structures - ii) determination of the chemical composition at the interface or close to it ; this includes the determination of the stacking sequence when crossing the interface in the case of compounds - iii) measurement of the amount of residual strain induced by the interface structure - iv) determination of the number of structural variants.

This paper will review some of these topics concerning the interface characterization and discuss on several examples the potentialities and limitations of HREM.

DETERMINATION OF THE PERIODICITY AT THE INTERFACE

When two periodic semi-infinite media are present on each side of a completely general interface they form a quasi-periodic interface structure [10]. This structure can be approached locally by a pattern which is characteristic of a periodic coincident structure. In specific cases of orientation relationship and/or interface plane, and/or lattice parameter ratio the interface is strictly periodic (commensurate case).

Therefore a first step towards a complete crystallographic analysis of the interface is to describe the periodic or quasiperiodic relaxed structure. The diffraction techniques are well suited for this purpose [11] but large areas of homogeneous interfaces are not always available. Moreover the signal coming strictly from the interface is sometimes difficult to recognize from double diffraction. As a complement the HREM technique on end-on interfaces has been successfully applied to the determination of the interface 2-D unit cell. For instance the structure of a $(11\bar{2})$ $\Sigma=3$ grain boundary in germanium is a c(2x2) supercell of the geometrical coincidence lattice [12]. At least two observation axes are necessary because the projection of an end-on surface transforms the 2-D structure in a 1-D pattern (figure 1).

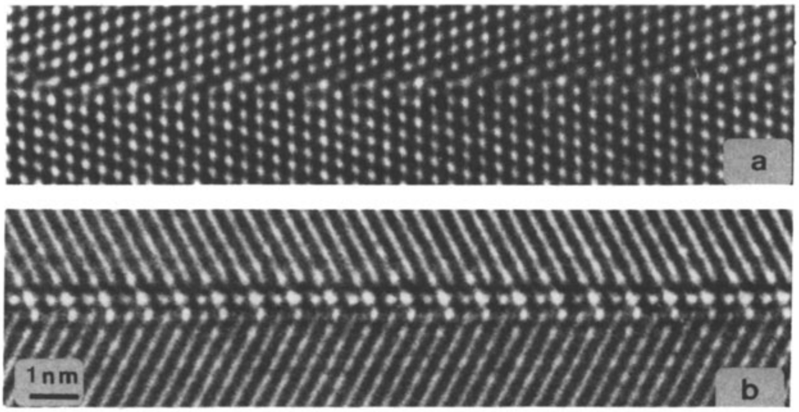

Fig. 1. HREM of a $(11\bar{2})$ $\Sigma=3$ twin observed at 200 keV along a) <011> axis, defocus - 70 nm, atoms are bright - b) <231> axis, defocus - 55 nm, atoms are dark. Note the periodicities along the interface (200 kV).

Similarly the periodicity of a Si-Al interface is very nearly commensurate with four aluminum planes matched with three silicon planes [13]. On epitaxially grown material a 2-D periodic unit cell of 2.8 x 2.8 nm^2 has been measured in (100)(Cd,Hg)Te/(100)GaAs system [14] and of 5x5 nm^2 in the (100)ZnTe/(100) GaAs system [15].

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It should however be noted that in most of the systems studied so far and especially on epitaxial layers with very large mismatch or different structures, the unit cell of the relaxed interface (or its first approximation) is not yet available and has not been systematically looked for. For instance the $BaF_2/(111)$ Ge has been described as being incoherent while the $BaF_2/(100)$InP is coherent [16] on the basis of HREM observations. This description is clearly insufficient and as the epitaxy is possible in both systems, there should be an organized periodic or quasi periodic 2-D medium at the interface. The main difficulty in this case originates from the atom relaxations along the <011> observation axis and several other viewing axes are needed in order to provide more quantitative informations on the unit cell.

Very often interfaces between very different materials do exhibit small but systematic deviations from the exact epitaxial relationship. This is for instance the case of the silicon sapphire system with approximate relationship (100)Si⫽$(0\bar{1}12)$ Al_2O_3 [17] as well as on the fluoride-Ge system [18]. These rotations are not fortuitous and are related to the unit cell of the periodic (or quasi-periodic) structure at the interface. A detailed study in the V_5Si_3/V_3Si system has been performed for instance by Bonnet et al. [19], showing that these deviations are due to the formation of a pseudo-coincident lattice at the interface. Such an analysis based on HREM results has to be applied more generally on other systems.

Of special interest, but not yet considered is the case where one (or eventually two) medium cannot be considered as a semi infinite medium. Strong deviations from the equilibrium bulk unit cell are possible giving rise to strained structures. One may distinguish between i) completely coherent structures inducing a loss of some symmetry elements present in the bulk, ii) and partially relaxed structures which have generally ill-defined unit cells. Examples of coherent structures with cubic to tetragonal transformation are numerous : for instance the Si/Ge multilayers [20], the CdTe/HgTe multilayers [21] or CdTe/ZnTe quantum wells [22] (figure 2).

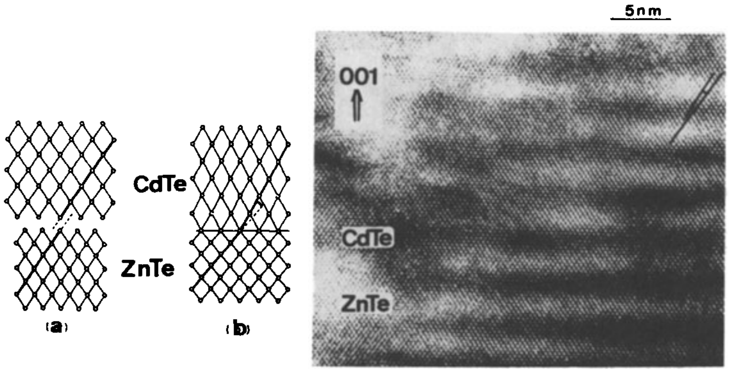

Fig. 2. A (001)ZnTe/(001)CdTe strained layer superlattice observed along the [110] axis with a scheme of a) relaxed and b) strained lattices. The substrate being $Cd_{0.5}Zn_{0.5}Te$ the successive layers are alternately under tension and under compression (200 kV) (courtesy G. Feuillet).

The unit cell at the interface is generally given by the substrate itself when no misfit dislocations have been produced. If partial relaxation has occured a complete determination of the dislocation density and their Burgers vector enable to calculate the residual strain and hence the unit cell in the strained layer. The HREM technique is of great interest in the case of a relatively high misfit dislocation density for which more conventional techniques fail. The dislocation distance specially for 2-D arrays should however not be smaller than 2-5 nm - otherwise the contrast of the dislocations running perpendicular or inclined to the observation axis blur the contrast of end-on dislocations.

The strain itself is difficult to deduce directly on the HREM pictures at least for 2-D strained structures. A large relaxation occurs along the observation axis in a thin foil as prepared for electron microscopy observation. Therefore, although the coherency could be checked on HREM, direct lattice measurement and unit cell determination has to be corrected, to be representative of the original layers [23].

Non-planar interfaces in one dimension or even two dimensions are frequently observed. HREM, applied along 1-D facet edges, is possible and allows to extract the structure [24]. For 2-D facetting HREM images are more difficult to interpret in a straighforward manner because of the superposition problem when projected along one axis. Systems like (010) PtSi⫽(111)Si have been shown to exhibit regular atomic steps in order to minimize the interfacial energy [25]. Similarly the (100) (Cd,Hg)Te/(100)GaAs is not flat and seems to exhibit a polypyramidal shape [26] but has not yet been fully modelized.

DETERMINATION OF THE 2D-SPACE GROUP AT THE INTERFACE

A first step towards the 2-D space group determination is to measure the relative position between the two materials on each side of the interface. This positioning has a meaning for strictly periodic interfaces and has been measured at commensurate grain boundaries. For instance at a <001> (310) Σ=5 grain boundary in germanium there is a large translation along the common <001> axis equal to 1/5 of the 001 distance [27] (fig. 3). An accuracy of the order of 0.01 nm in measuring this distance is now possible on HREM images. In the heterophase case, one could also measure the rigid body translation at least if the interface is periodic.

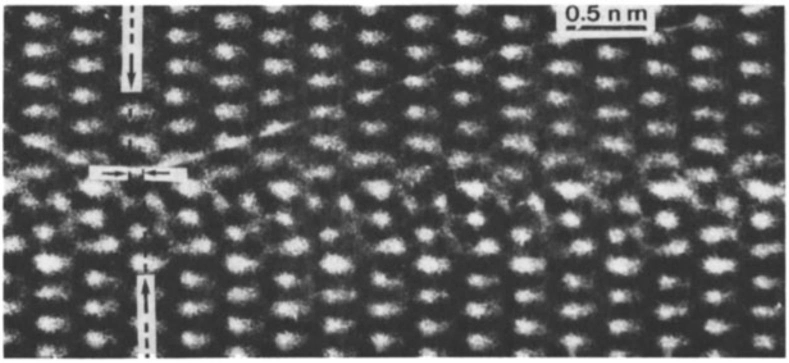

Fig. 3. Determination of the rigid body translation along the <001> axis in a (310) Σ=5 grain boundary in germanium. Atoms are white (400 kV). The observation axis is $[1\bar{3}0]$. (Courtesy J.L. Rouvière).

The relative position is not random and its determination is important although this measurement has not yet been performed. Planar view of the interface observed with high resolution could give valuable insight into this problem : the detailed pattern appearing into the moiré pattern [26] is characteristic of the translation and rotation state between the two crystals. A constant pattern would be the sign of a very close periodic approximation and a constant relationship at the interface. This property has not yet been exploited but it ought to be.

A complete 2-D space group determination of a relaxed interface has only been performed in very few cases. Special grain boundaries such as $(112)\Sigma=9$ [28], (510) $\Sigma=13$ or (310) $\Sigma=5$ [29] were completely determined by a combination of HREM and electron diffraction technique. Facetted structures with a mirror glide symmetry are often favoured when the grain boundary plane is vicinal to a low index plane (fig. 4). However special care should be taken with the HREM technique when looking for symmetry relations in an image : symmetry elements are very easily affected by small optical or crystal misalignement and results should always be checked by diffraction (electrons or X-rays).

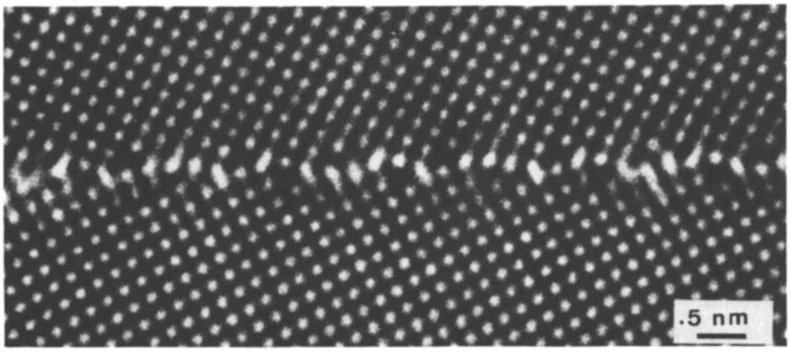

Fig. 4. The structure of a $(11,3,0)$ $\Sigma=65$ observed along [001] Defocus - 42 nm. 400 kV. Atoms are black. Note the long period and the mirror glide symmetry along the interface (courtesy J.L. Rouvière).

ATOMIC MODELING AND POSITIONING AT THE INTERFACE

At completely coherent interfaces, for which the structure is continuous when crossing the interface, modeling is simplified. In this case the measurement of the relative position of the two crystals enables to build an atomic model. This method has been currently employed for coherent silicon-silicide interface studies [30]. For more general interfaces atomic positions at the interface are necessary to be determined in order to characterize the structure. The knowledge of the two crystals on both sides is insufficient to deduce the interface structure : local rearrangement do generally occur. Very few cases have been already completely solved and examples are limited to pure tilt grain boundaries. The model of <001> (310) $\Sigma=5$ belongs to the Shubnikov layer group $p2'_1$ and the core structure is described by a zigzag sequence of $\frac{1}{2}[110]$ and $\frac{1}{2}[1\bar{1}0]$ dislocation cores. Two observation axes were necessary to deduce this structure. Simulated images from computer relaxed configurations exhibit a complete agreement with the experimental images (fig. 5). The white (or black) dots can be completely superimposed within the accuracy of the numerical calcu-

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lation (~ 0.01 nm) . It should be noted however that the dots do not correspond to the exact atomic projection and that direct visual interpretation results in large errors in measuring the atom locations [29]. Therefore solving the structure still relies on a tedious trial-and-error procedure. Many other grain boundary structures were proposed involving more complex configurations including structures having two or more variants. The most characteristic multiple structure is the <001> (510) $\Sigma=13$ in germanium : it has a variant which is asymmetric but has a mirror glide symmetry, while the other variant is symmetric (fig. 6). In addition

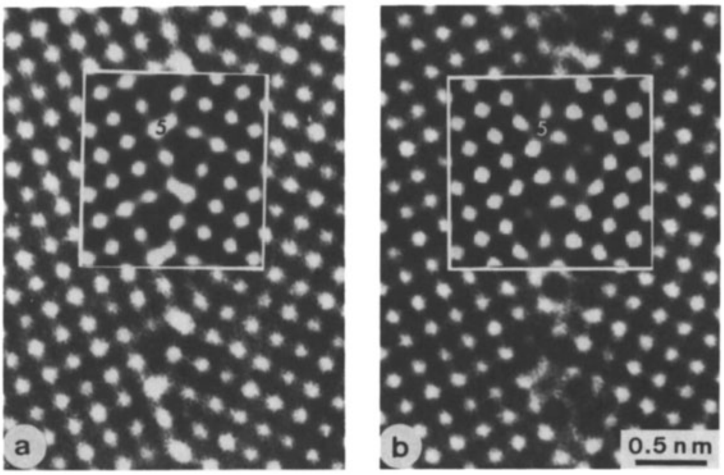

Fig. 5. Comparison between simulated and experimental images of a (310) $\Sigma=5$ in germanium a) black atoms b) white atoms (400 kV) (courtesy J.L. Rouvière).

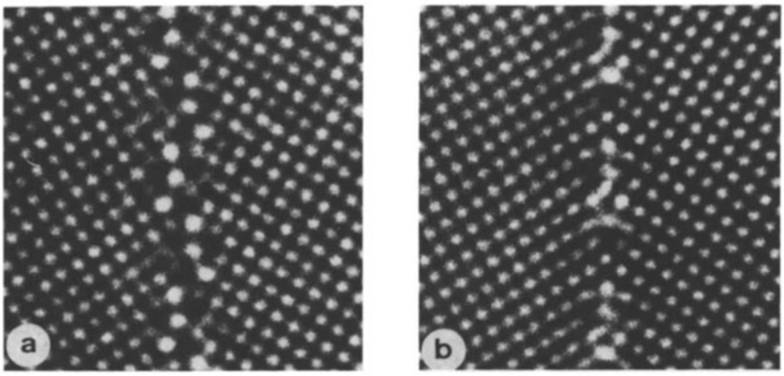

Fig. 6. Two possible structures of the same interface, a (510) $\Sigma=13$ in germanium : a) with a mirror glide symmetry and b) symmetric. Both variants coexist in the same as-grown bicrystal. Germanium. Atoms are black (courtesy J.L. Rouvière).

small variations occur from one period to the following which were explained by side view observations along <150> : the structure is not the same everywhere along the dislocation cores [31].

The extension of such an analysis to more complicated structures in heterophase systems is not straightforward. There is in general a 2-D relaxation of the atoms at the interface contrary to the case of pure tilt grain boundary. Moreover the chemical type of the atoms adjacent to the interface should be previously determined. Special situations could include a quasi 1-D relaxation. A classic example is the (111) CdTe//(001) GaAs interface which has a very small lattice mismatch along the $[11\bar{2}]$ CdTe and the [110]GaAs direction (~ 0.7 %) and can be considered as being relaxed only along the perpendicular directions (fig. 7). This example is a good candidate for further analysis by HREM.

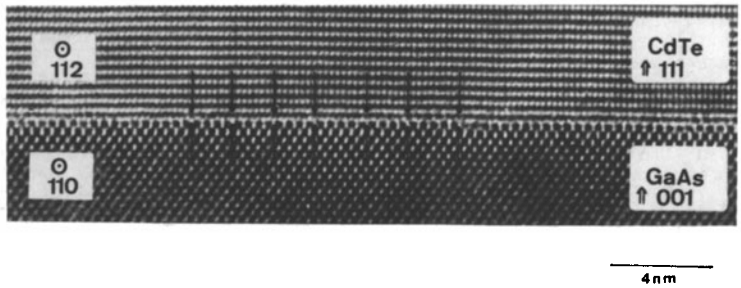

Fig. 7. (111)CdTe/(001)GaAs interface observed along the <110>GaAs axis (200 keV). (Courtesy G. Feuillet).

DETERMINATION OF THE CHEMICAL COMPOSITION

An important preliminary remark has to be made : the HREM technique is not a spectroscopic technique and recognizing atomic species relies on differentiating atomic structure factors through intensity measurement in the image. This fact has several consequences :

i) close atomic number species could be difficult to differentiate. However dynamical interactions between electron and matter is so strong that even small differences can be enhanced by a careful choice of specimen thickness and imaging conditions.

ii) the information collected in the HREM mode is always integrated along the specimen thickness. Therefore at best the chemical composition will be an average along an atomic column

iii) as the intensity collected in the image plane is generally not linearly related to the projected potential, linearity with the chemical composition is also generally lost.

Therefore indirect and a-priori informations on the atomic species present in the sample are always necessary.

This determination is generally of great importance in heterophase systems as well as in grain boundaries. Although numerous HREM observations of impurity precipitation were performed at grain boundaries, direct evidence for seggregated impurity monolayer has not yet been obtained. Preliminary results on sulphur seggregated at grain boundaries in nickel have been recently reported showing the potentialities of HREM [32].

However it is on semiconductor epitaxial layers that most results have so far been published. In compound semiconductors the contrast between atomic columns of different atomic numbers is very well pronounced and characteristic for InP, ZnTe, HgTe along <001> and <013> axis [33]. The same is true for AlAs or GaAs along <001> [34] or InP and InGaAs along <001> [35]. In <110> InAs [36] or even <110> GaAs the fine details visible in HREM images at 400 kV, which occur as a result of multiple interactions can be exploited in order to detect the crystal polarity and hence to specify where the different atomic species are. However the closer the atomic numbers are, the less reliable are the results : the image critically depends on thickness and exact orientation : small asymmetries in the detailed pattern could arise as well from slightly misorientated crystal or optical misalignement. A good agreement between experimental and simulated images over a wide range of defoci and thickness is the best reliability test for a correct interpretation.

The optimum defocus and thickness for chemical differentiation has to be explored by computer simulation in each specific case. These conditions themselves are conditioned by the specific questions one has to address : locating the interface or determining the chemical nature at the interface itself.

As a first example one may consider an interface with four different chemical species : (100)InP/(100)GaAs. The interface has two possible structures with either a In/As stacking (a) or a P/Ga stacking (b). Simulated images with a <001> observation axis show that both structures should be recognizable (fig. 8) at a defocus - 65 nm and a thick specimen (17 nm). The phosphorus atomic columns are marked by a strong white spot and serve as markers to recognize the gallium atomic column at the interface. An intensity profile through the phosphorus atomic sites gives for the two interfaces a transition region which is different for type (a) and (b). It is also important to note that the image is characterized by three different patterns : two are characteristic of the bulk layers and one of the interface. The interface pattern is at least three atomic planes wide, which means that, due to the formation of Fresnel fringes at the interface, spurious effects appear and no direct

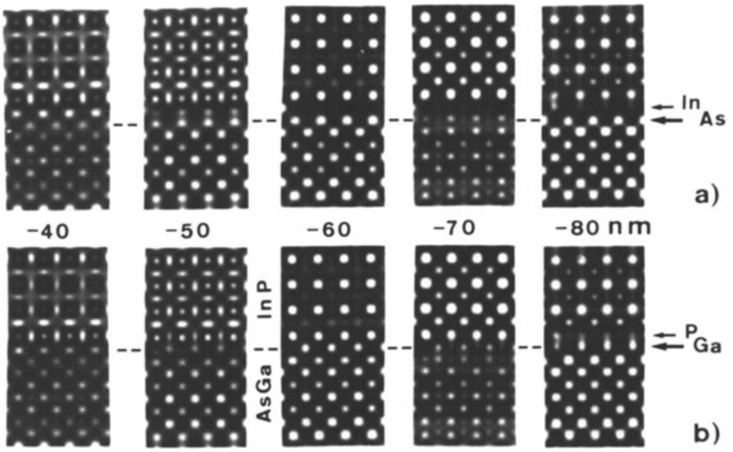

Fig. 8. Simulated images of the (100)InP/(100)GaAs interface with the two possible structures. a) In/As stacking and b) P/Ga stacking at the interface (400 kV). Thickness 17.3 nm.