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Characterization of interface structures in nanocrystalline germanium by means of high-resolution electron microscopy and molecular dynamics simulations

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Abstract. The atomic structure of nanocrystalline particles formed by vapor deposition and subsequent annealing of amorphous thin films of germanium was studied by high resolution electron microscopy (HREM). The HREM images revealed a strongly varied multiply twinned structure. In some regions of adjacent twins contrast features were detected which were caused by an overlapping of twin lamellae. It will be shown by HREM contrast simulations that these interface types can be described by $\sum = 3^n$ boundaries. The influence of lattice relaxations is taken into consideration by molecular dynamics simulations of the structure models.

Introduction

Internal interfaces in solids influence and/or even control essential properties of materials. The atomic structure of interfaces and boundaries can be determined by high-resolution electron microscopy (HREM). The different techniques of analytical electron microscopy (energy-dispersive X-ray spectroscopy – EDX, electron energy loss spectroscopy – EELS, and convergent beam electron diffraction – CBED) provide the required information on the chemical composition of the interface regions. In order to determine the equilibrium structure and its energy of an interface atomistic simulations of the interface structure have to be carried out. The relaxed interface structure may be simulated by applying molecular dynamics calculation (MD) and the methods of static energy minimization (MS). All interface calculations require a suitable geometrical model to be generated (construction of the computational cell), and the interatomic interaction process as well as the relaxation process to be taken into consideration.

Nanocrystalline materials are single or multiphase polycrystals, the microstructure of which is in the order of 5 to 20 nm. The atomic structure of nanocrystals is characterized by a large number of interface regions of up to the same order of magnitude as the ordered structure is.

In the present paper, interface structures in nanocrystalline germanium (nc-Ge) are characterized by means of HREM experiments assisted by molecular dynamics calculations as well as HREM contrast simulations.

Experimental

Thin films of amorphous germanium were grown on cleavage faces of NaCl and NaBr crystals by vapor deposition (substrate temperature range between 470 K and 620 K, vacuum of 5×10^{-5} Pa). The deposition was carried out at an evaporation rate of about 0.9 nm $\cdot$ min^{-1} up to film thicknesses between 10 and 30 nm. Within the amorphous films nanocrystalline particles of 5 to 30 nm in size may be formed by choosing an appropriate substrate temperature during deposition and by annealing at elevated temperatures after deposition. The influence of substrate conditions on the formation of crystalline particles in amorphous germanium films was described previously (Hofmeister, Junghanns, 1992, 1993). The structure of nanocrystalline particles in amorphous germanium films was studied in a JEM 4000EX microscope at an acceleration voltage of 400 kV. The generation of appropriate structure models for describing the interface structure of nc-germanium as well as the HREM contrast calculations were carried out using the CERIUS program package (Cambridge Molecular Design). The relaxed structure models were calculated by means of a special modified MD simulation program (Garofalini, 1990; Scheerschmidt et al. 1995).

Observations

The HREM images of the nanocrystalline particles revealed the presence of a variety of multiple coherent twins on (111) planes. Preferential texturing, with ⟨110⟩

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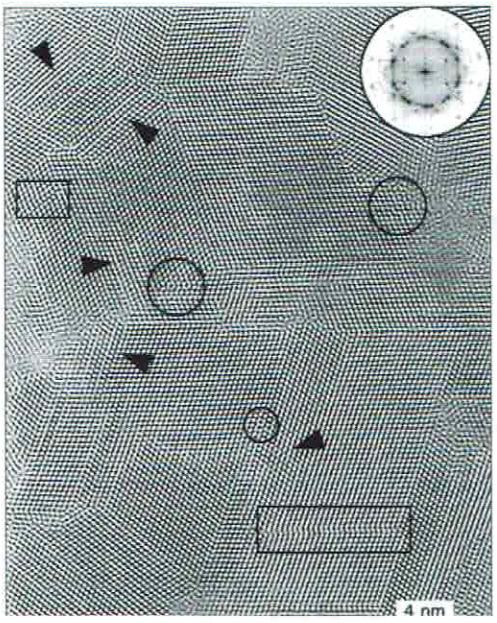

Fig. 1. High-resolution image (taken at 400 kV) of a nanocrystalline (110) oriented germanium film with linear and circular superstructure regions (arrow & insets).

oriented crystallites prevailing, was evidenced. These orientations allow a revealing of the twin interface structure of the nanocrystals. Fig. 1 presents a typical HREM micrograph showing the heavily twinned structure of a nanocrystalline germanium film. The film contains approximately 3.1×10^{12} twin boundaries per cm^2. The Fourier transform of the image (inset of Fig. 1) clearly indicates the pseudo-fivefold symmetry characteristic of multiple twinning.

The most striking features are circular-arranged microtwins which meet in three- or fivefold junctions parallel to the growth direction of the film. Different types of core structures of the intersecting regions are detectable in the HREM image.

The structure images of the coherent (111) twin boundaries in ⟨110⟩ orientation can be interpreted without computer simulations. Since it is known a priori that the (111) twin boundary in the diamond structure falls on a layer of channels (rather than on a layer of atoms), this fact may be used to determine whether the high-resolution micrographs show white channels or white columns of atoms. Under optimum defocus conditions used (near the Scherzer focus) the channels were imaged as bright dots. In addition to the coherent twin boundaries the HREM micrograph shows interface regions of multiple twins exhibiting linear and circular contrast features (especially marked by arrows and circles in Fig. 1) with local non-crystallographic symmetry and stacking faults (encircled by a rectangular box).

The interpretation of these contrast features requires the crystallography of multiple twinning to be taken into consideration.

Crystallography of multiple twinning

The twin boundaries possible in the diamond structure can be classified according to the coincidence site lattice (CSL) theory (Bollmann, 1970, 1982). The coherent primary twin (twinning occurs with {111} as a twin plane) is a $\sum = 3$ boundary. The role of multiple twinning and the specific properties of $\sum = 3^n$ boundaries in crystals with *fcc* and diamond structures were extensively studied. Special computer simulation methods and programs were developed to determine the crystallographic parameters of $\sum = 3^n$ boundaries as well as their topological features (Kopezky, Andreeva, Shukomlin, 1991; Andreeva, Firsova, 1992). The method used allows one to analyze the crystallography of triple and multiple junctions of the *n*-grains. A special group theoretical consideration was developed to describe the symmetry properties of triple junctions of boundaries (Bleris, Karakostas, 1989). In general, the group theory can be used for characterizing and numbering the interface operations that leave the given CSL invariant (Grati, Portier, Fayard, 1979).

The possibility of forming various of multiple twins within a fivefold junction type is demonstrated in Fig. 2 showing a computer simulated fivefold multiple twin consisting of five tetrahedra. The twin boundaries within the ideal pseudo-pentagonal particle are four $\sum = 3$ boundaries with a tilt angle of 70.53°, and one $\sum = 81$ boundary (not shown in Fig. 2) with a tilt angle of 77.88°. The $\sum = 81$ boundary is formed when there is a mismatch of 7.35° between the {111} planes. In the computer model the gap was closed by elastic deformation of the twins. The single tetrahedra were enumerated in the model, with M signifying the matrix and numbers 1 to 4 denoting the order of twins. The adjacent components (as, e.g. matrix/first-order twin, second-/third-order twin) are structurally related by a rotation of 70.53° ($\sum = 3$ boundaries). The various possibilities of combining the matrix with twins of different order lead to superposition structures with coincidence site lattices of types $\sum = 3$, $\sum = 9$, $\sum = 27$, and $\sum = 81$. These interface types will be formed according to the rule $\sum = 3^n$ with *n* as the order of the twins. The symmetry conditions of forming a CSL and the related symmetry of $\sum = 3^n$ twin boundaries are given

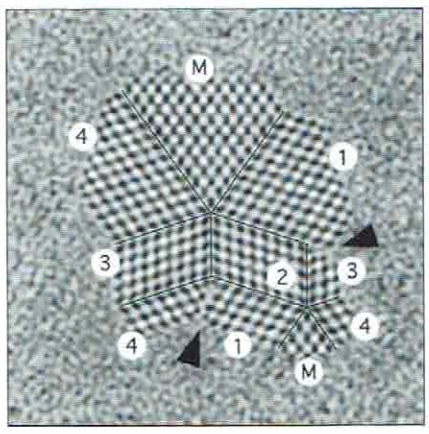

Fig. 2. Computer simulated model of twin quintuplets of germanium in (110) orientation.

Table 1. Crystallography of $\sum = 3^n$ boundaries.

$\sum$	Cubic equivalent $\langle 110 \rangle$ rotations for $\sum = 3^n$ boundaries	Adjacent regions in the quintuplet models	H	$\Phi(\sum)$
3	70.53° 109.47°	M-1, 1-2, 2-3, 3-4	$\bar{3}m$	$6'/m'mm'$
9	38.94° 141.06°	M-2, 1-3, 2-4	$2/m$	$mm'm'$
27	31.59° 148.42°	M-3, 1-4	$2/m$	$mm'm'$
81	77.28°	M-4	$\bar{1}$	$2'/m'$

in Table 1. In general, the conditions of forming a CSL (Bleris, Karakostas, 1989) is given by:

$$\Phi(\sum) = \mathrm{H} + \mathrm{RH}\,, \qquad \mathrm{R} \notin \Phi_1\,, \qquad \mathrm{H} \subset \Phi_1\,. \qquad (1)$$

Here, $\Phi(\sum)$ is the symmetry group of the boundary, H is the sublattice of the matrix phase Φ_1, and R is the CSL 30° operator describing the boundary. In order to describe the symmetry of interfaces and boundaries it is useful to apply the generalized concept of antisymmetry operations W′ leading to the antisymmetry groups also known as black-white groups (see, e.g., Pond, Vlachavas 1983; Pond 1989). The dashes ′ in Table 1 denote the antisymmetry operations of the coincidence lattice of the multiple twins.

Contrast calculations for the CSL models of $\sum = 3^n$ twin boundary interfaces

Image simulations of superimposed (111) twins in [110] oriented germanium yielding to $\sum = 3^n$ boundaries were carried out using the multi-slice programme of CERIUS HRTEM package. Starting point of the contrast calculations was the geometry of the CSL models of $\sum = 3^n$ twin boundaries. The most important experimental parameters influencing the image contrast were specified as follows: accelerating voltage: 400 kV; spherical aberration coefficient C_s = 1 mm; focus spread: 90 Å; beam divergence: 0.65 mrad; objective lens aperture: 0.50 A^{-1}. Under the conditions chosen the optimum defocus value (Scherzer focus) was $\Delta f = -405$ Å. The experimental conditions applied did not allow the imaging of the pair of germanium atoms as separate dots in (110) projection. A supercell of $4 \times 4 \times 1$ units of the (110) mesh was constructed for the contrast calculations. The slice thickness was chosen to equal one period along the [110] axis, i.e. 4.02 Å. The thickness of the twinned regions as well as the depth of the twins within the stacking sequence of the slices were varied. Fig. 3 shows the twin structure superimposed with $\sum = 3$, $\sum = 9$, $\sum = 27$, and $\sum = 81$ interfaces and the corresponding simulated structure images under Scherzer defocus conditions.

In a previous paper (Neumann, Hofmeister, Heydenreich, 1994) it was shown which specific contrast features may arise owing to the different possibilities of the overlapping of twins of different order, and which type of pseudo-symmetry may occur within the HREM images. Respective computer simulations have definitely shown that the local regions of pseudo-symmetry in the HREM images are due to interference effects at the overlapped twins in the germanium particles. Linear superstructures are caused by $\sum = 3$ interfaces whereas most of the circular ones arise from $\sum = 9$ interfaces.

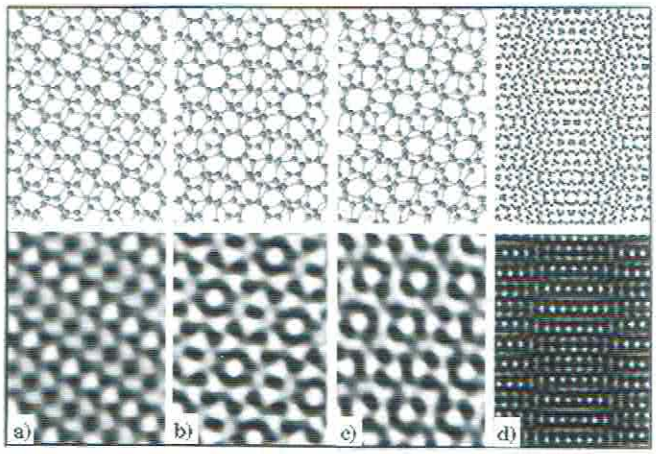

Fig. 3. Superimposed twin structures **a)** $\sum = 3$, **b)** $\sum = 9$, **c)** $\sum = 27$, and d) $\sum = 81$ interfaces) in (110) germanium and the corresponding simulated structure images for the Scherzer defocus.

The contrast calculations of the different types of overlapping of twins enable an image matching of the electron micrographs with the computer simulated ones. However, there are still differences in the intensity distribution between the models and the electron micrographs. Distortions of the circular contrast features may be due to the overlapping of three twins as the previous simulation series revealed (Neumann, Hofmeister, Heydenreich, 1994).

Furthermore, the rigid CSL models did not consider the stress/strain state of the superimposed twinned part. In order to overcome these disadvantages molecular dynamics calculations have been started to determine the relaxed interface structure.

Contrast calculations of CSL models refined by molecular dynamics simulations

In order to obtain the equilibrium structure of the interfaces we perform a molecular dynamics simulation. The interatomic forces are described by the potential first proposed by Stillinger and Weber for silicon (Stillinger, Weber, 1985). The potential is designed to reveal the lattice constant, the melting point and the structure of the liquid phase of silicon. It consists of sums of two- and three-body contributions to the potential energy. Compared with simple pairwise potentials here the important feature is the three-body part: it ensures that the diamond structure is the most stable one. The potential describes sufficiently well a great number of bulk- and defect properties (for an overview, see e.g. Balamane, Halicioglu, Tiller, 1992). According to the fact that both silicon and germanium crystallize in the diamond structure type, a simple rescaling of the energies and lengths scales should yield a reasonable potential for germanium (Ding, Ander-

sen, 1986; Wang, Stroud, 1988). The potential energy V of the system is expanded in the following way:

$$V = \sum_{i<j} f_2(r_{ij}) + \sum_{i<j<k} f_3(r_{ij}, r_{ik}, r_{jk}) \quad (2)$$

with

$$f_2(r_{ij}) = A(Br_{ij}^{-p} - 1)\, e^{\frac{\lambda}{r_{ij}-a}} \quad (3)$$

and

$$f_3(r_{ij}, r_{ik}, r_{jk}) = h_{ijk} + h_{kij} + h_{jki}\,, \quad (4)$$

$$h_{ijk} = \lambda(\cos\theta_{jik} + \tfrac{1}{3})^2\, e^{\frac{\delta}{r_{ij}-a} + \frac{\delta}{r_{ik}-a}}\,, \quad (5)$$

where r_{ij} is the distance between atoms i and j, and θ_{jik} is the angle between vectors r_{ij} and r_{ik}. Here, r is expressed in dimensionless units, with the unit distance being 2.181 Å, i.e. the equilibrium nearest neighbor distance in the crystal. The energies are measured in dimensionless units, with the unit energy being 1.93 eV, i.e. the energy per bond in the crystal. In addition, a cut-off is introduced in such a way that all terms are vanishing for $r \geq a$. The other parameters are $A = 7.096$, $B = 0.6022$, $p = 4.0$, $\lambda = 21.0$, $a = 1.8$, $\gamma = 1.0$, and $\delta = 1.2$ such that the cohesive energy and the lattice constant are accurately reproduced (Ding, Andersen, 1986). The classical equations of motion were integrated using a fifth-order Gear's algorithm. We extended the code used for studying glasses (Garofalini, 1990) by the potential described above and by implementing the linked cell algorithm proposed (Grest, Dünweg, Kremer, 1989). In all simulations the initially atomic sites were randomly distorted, all atoms were assigned to random velocities according to a system temperature of 300 K. The system was prepared in such a way that the interface was parallel to the xy-plane ((001) plane of the supercell). Periodic boundaries were used in x and y direction, whereas in z direction the system experiences free surfaces. However, owing to the thickness of the slab, the surfaces had no influence on the interface properties. A conventional NVE (i.e. with particle number N, volume V, and total energy E kept constant) dynamics was performed in 80000 time steps of 1.0×10^{-15} s each. In order to find out the equilibrium positions and the equilibrium potential energy, the whole system was cooled down to 0 K.

The relaxed structure model of a $\sum = 3$ interface in germanium is shown in Fig. 4. The supercell chosen contains 1152 atoms of germanium. The superposition of the adjacent twin parts is oriented in such a way that the (001) orientation of the supercell (Fig. 4a) is parallel to the (110) plane of the initially twinned germanium particles shown in Fig. 1. The atomic arrangement of the relaxed $\sum = 3$ boundary (Fig. 4b), i.e. the structure of the interface plane energy minimized, obviously shows the generation of "linear channels" similarly to the unrelaxed superimposed structure. However, the atomic arrangement between the channels clearly exhibits deviations from the unrelaxed CSL model. The defocus series of the unrelaxed as well as relaxed structures of the $\sum = 3$ boundary given in Fig. 5 clearly reveal the linear contrast features of the channels in the structure over the whole defocus range. Comparing the simulated HREM images of the relaxed and unrelaxed structures reveals differences

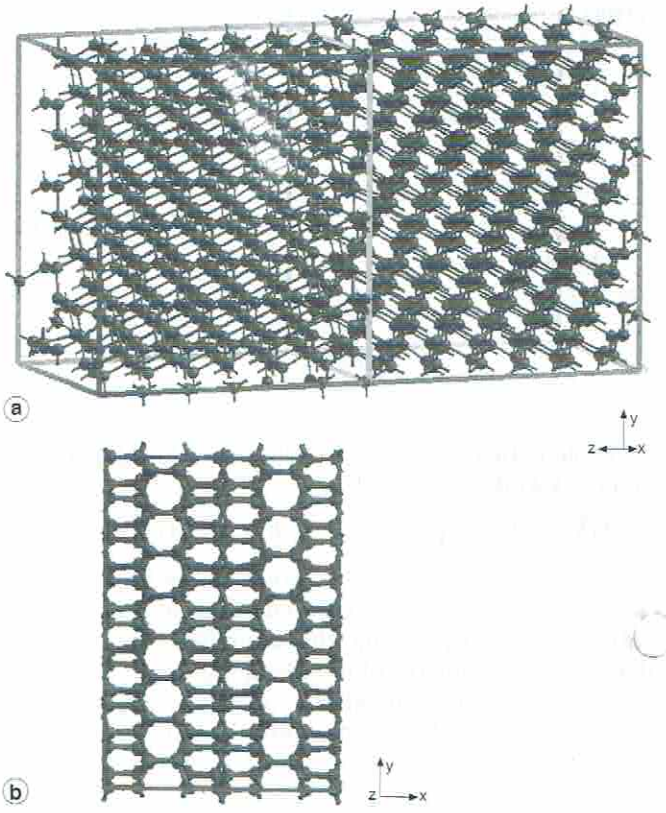

Fig. 4. Relaxed structure model of a $\sum = 3$ interface in germanium. a) Supercell containing 1152 atoms (interface plane marked). b) Calculated atomic structure of a $\sum = 3$ superimposed twin ((001) projection of the supercell).

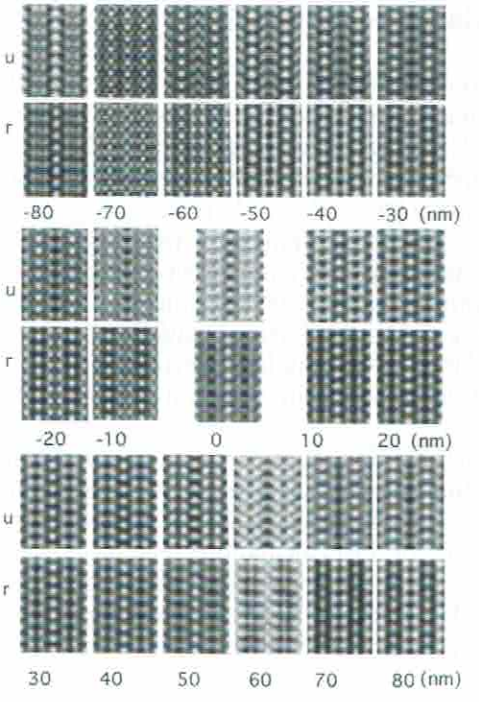

Fig. 5. Calculated defocus series (Δf in nm) of HREM images of a superimposed twin structure of germanium in (110) orientation with a $\sum = 3$ interface (u – unrelaxed structure; r – relaxed structure).

in both geometry and contrast of the basic pattern of the images. The structure is much more relaxed in parallel direction to the interface plane, e.g. in (010) orientation.

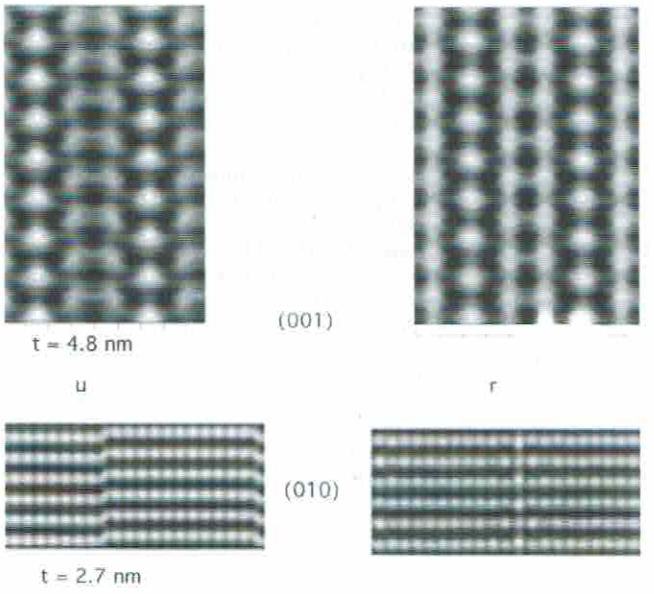

Fig. 6. Calculated HREM images (Scherzer defocus) of a superposed twin structure ($\sum = 3$ interface) in germanium for the (001) and (010) projection referred to the orientation of the supercell (u – unrelaxed structure, r – relaxed structure).

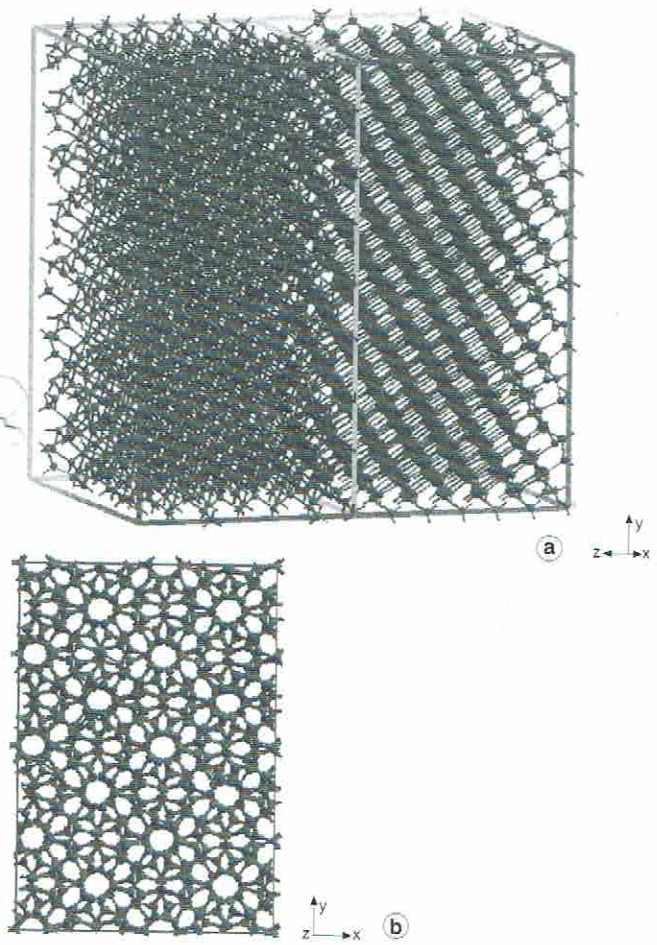

Fig. 7. Relaxed structure model of a $\sum = 9$ interface in germanium. a) Supercell containing 3456 atoms (interface plane marked); b) Calculated atomic structure of a $\sum = 3$ superimposed twin ((001) projection of the supercell).

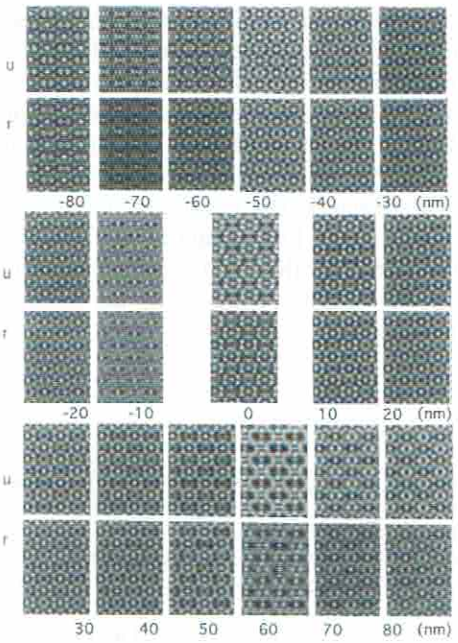

Fig. 8. Calculated defocus series (Δf in nm) of HREM images of a superimposed twin structure of germanium in (110) orientation with a $\sum = 9$ interface (u – unrelaxed structure; r – relaxed structure).

The simulated structure images for optimum defocus conditions (Scherzer focus) of the (001) and (010) orientations of the unrelaxed and relaxed structures are shown in Fig. 6. The (010) structure image of unrelaxed model clearly exhibits a step between the two crystal parts. The lattice relaxation leads to a "smoothing" of the rigid CSL model as shown in the simulated image of the relaxed structure.

The MD simulated structure of a $\sum = 9$ interface in germanium is shown in Fig. 7. The supercell (Fig. 7a) contains 3456 atoms of germanium. The atomic arrangement of this superimposed twin structure, i.e. the structure of the interface plane, exhibits "circular structure regions". The defocus series of the unrelaxed as well as the relaxed structure of the $\sum = 9$ boundary in Fig. 8 obviously show these circular contrast features in the structure over the whole defocus range. Comparing the simulated images near the Scherzer defocus (−40.5 nm) hardly proves any differences within the basic pattern of the images. This means in this projection, the differences between the relaxed and unrelaxed structures are so small that they are not detectable in the HREM images.

Concluding remarks

High-resolution electron microscopy was applied to determine the atomic structure of interfaces and boundaries in (110) oriented nc-germanium. The interpretation of the experimental micrographs requires the application of image modelling procedures as well as the computer simulation of the HREM images. The nature of multiple twins experimentally observed was determined by contrast calculations of superimposed twin structures. The multiple twins in germanium form $\sum = 3^n$ boundaries. Mainly $\sum = 3$ and $\sum = 9$ boundaries were observed. For a quantitative image matching of the electron micro-

graphs with the computer simulated ones the CSL models of the $\sum = 3$ and $\sum = 9$ boundaries were refined by molecular dynamics simulations. The best fits of the experimental micrographs and the simulated ones of the relaxed structures allow the conclusion to be drawn that the MD calculated models describe the atomic structure of the multiple twin interfaces in a good approximation. Further calculations using, for instance, the Tersoff potential (Tersoff, 1988) for the MD simulations will follow to clarify if this implies changes in the atomic arrangement at the interface.

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