HREM STRUCTURE CHARACTERIZATION OF RELAXED INTERFACES IN COVALENTLY BONDED MATERIALS

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ABSTRACT

Multi-layer semiconductor structures (quantum wells and grain boundaries) grown by molecular beam epitaxy (MBE) as well as precipitates in glasses are investigated by high resolution electron microscopy (HREM) providing local atomic information at the relaxed interfaces. The interpretation of the micrographs requires methods of image analysis and the computer simulation of the HREM contrast by calculating the electron beam specimen interaction of a theoretical structure model, and by subsequently considering the electron-optical process. The relaxed atomic structures of the interfaces are modelled by molecular dynamics and energy minimization with the bonding forces and the parameters of the pair and three-body potentials being varied. Possibilites will be discussed of revealing the compositional variations and the elastic deformations at the interfaces by HREM imaging under special imaging conditions.

INTRODUCTION

Some of the most important properties of materials in high-technology applications are strongly influenced or even controlled by the presence of solid interfaces. Therefore the structural characterization of their atomic arrangements and of defects related to the misfit at the boundaries are of great importance. The influence of the interfaces is based on the inhomogeneity of their mechanical, chemical and electrical activity, with the gradients very often being extended over only a few atomic layers.

Three types of interfaces were investigated by HREM, and in the present paper some selected examples are used to discuss the relevance of the molecular dynamics (MD) model generation for the structure analysis applying HREM image simulations: First, silver particles in sodium-silicate glasses are investigated which are generated after sodium-silver ion exchange by thermically activated migration [1-3]. Second, HREM micrographs dealing with the relaxations at tilt grain boundaries in Ge [4,5] are discussed. The grain structure in this covalently bonded material is compared with very similar boundaries in non-bonded metallic films of Au [6]. The third group of investigations is related to high resolution electron microscope imaging of multilayer structures in the binary systems based on GaAs and GaSb containing In and Al (AlAs/GaAs, AlSb/GaSb, InAs/GaSb, GaAs/GaSb, InSb/GaAs, InAs/AlSb). The systems are characterized by different misfits and varying scattering factors resulting in different elastic behaviour at the boundaries and the corresponding imaging effects. Furthermore, quantum wells in the ternary compounds as e.g. $In_xGa_{1-x}As/Al_yGa_{1-y}As$ on (100) oriented GaAs substrates are of interest because of their small misfits but high stoichiometric variability [7,8].

EXPERIMENTAL AND COMPUTATIONAL PROCEDURES

The semiconductor samples are grown by molecular beam epitaxy (MBE). Cleaved 90° wedge-shaped specimens, planar and cross-sectional samples are used in HREM investigations. The tilt grain boundaries are observed by a two-step epitaxial growth on preorientated bicrystals. The sodium-silicate glass investigated consists of approximately 70%SiO_2-30%Na_2O as well as stabilizing and reducing components. Ion exchange in a $NaNO_3/AgNO_3$ melt and subsequent annealing creates Ag particles with different diameters according to the distance from the surface and the temperature regime. The majority of the HREM experiments are carried out in a JEOL-JEM 4000 EX at 400 kV and near the Scherzer focus (Δ≈50nm) to transmit a broad

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band of $\pi/2$-phase shifted spatial frequencies. Image analysis is applied, consisting of on- or off-line digitization, Fourier-space diffraction and filtering as well as real-space image processing to enhance details of the contrast features like edges, characteristic periodicities and distortions. This enhancement is always achieved reducing or avoiding image information.

The HREM image contrast is mainly determined by two processes: First, by the electron interferences owing to the interaction process of the electron beam with the almost periodic potential of the matter and, second, by the interference of the plane waves leaving the specimen and being transferred by the microscope. Images are modelled by calculating both processes and then fitted by trial and error to the experimental contrast. Both the CERIUS (Molecular Simulations Incorporation, Cambridge) and the EMS multi-slice software [9] are applied to simulate the image contrast. The assumptions made for the microscope parameters are related mostly to the experiments, i.e. U=400kV accelerating voltage, C_S=1mm spherical aberration, δ=10nm defocus spread, α=0.5mrad semiangular beam divergence, α'=16nm^{-1} diffraction aperture.

MOLECULAR DYNAMICS STRUCTURE MODELLING

The relaxed atomic structures of the multilayers, the grain boundaries and the particles as well as their interfaces are modelled by MD and static energy minimization with the bonding forces and the parameters of the pair and three-body potentials being varied. For the computer-aided generation of structure models the CERIUS program package is applied. The structures of glasses are modelled by relaxing disturbed and topologically rearranged sodium silicate crystals (see Figs.1-3). Different shapes of metallic silver particles are included and the whole system is relaxed again. The crystalline atomic arrangements including grain boundaries and epilayers are modelled owing to the crystallographic space groups and the asymmetric unit. The basic model for grain boundaries is given by the O-lattice coincidence site model (see Fig.4): The rigid-body shift within the image plane is determined extrapolating the corresponding lattice fringes of the experimental micrographs, whereas the rigid body shift in beam direction is varied during the relaxation experiments to fit the image contrast. Similarly, according to the interface geometry described by the lattice misfit of the epilayers and determined by the electron microscope experiments, free surfaces of the models are created and the different epilayers are matched to describe the semiconductor multilayers (see Fig.5).

The total energy therefore has to include the valence bonding, the non-bonded forces as well as constraints owing to restrictions of the model and the topology. The force field of the many particle system is calculated by the energy gradient owing to two-, three- or four body interaction, i.e. distance, angle, torsion and inversion of the bonds. In energy minimization the atomic positions are changed owing to the negative energy gradient up to a relaxed final configuration. The MD simulations start with Boltzmann-distributed particle velocities and solve the equations of motion. Up to now Morse like pair potentials are applied for the bond distance interaction with a Fourier development describing the many body angular term - i.e. the Si-O, Si-Si, Si-Na bonds in the sodium silicate glass and all semiconductor bonds where the parameters are fitted to molecule properties [10] -, and a 12-6 Lennard-Jones interaction for the metallic particle and its interface as well as all non-bonded interactions.

For ionic and pure van der Waals systems two-body potentials alone appear to be sufficient. They are inadequate for properly describing systems which exhibit covalent bonds or metallic interaction. Whereas the latter demands the embedded atomic approximation, special many body interactions are preferred for covalent structures as, e.g., the Tersoff-Potential or the modified Born-Mayer-Huggins pair potential in combination with Stillinger-Weber angular terms. The Morse potential in combination with the 3- and 4-body terms used here is qualitatively equivalent to other potentials preferred in the literature because the steep descent of the repulsive term gives comparable equilibrium crystal structures sufficient for image simulations. It fails, however, in calculating the next neighbour atomic arrangement in glasses and its far field attraction cannot describe the details at surfaces and interfaces. Thus the calculations will be refined using the better potentials and atomic data reproducing more experimentally observed features, enabling the rearrangement of bonds and including semi-coherent interfaces [11]. Some first results are shown in Fig.2 to refine the structure of the glass and to investigate the behaviour of the migrating Ag atoms after the ion exchange.

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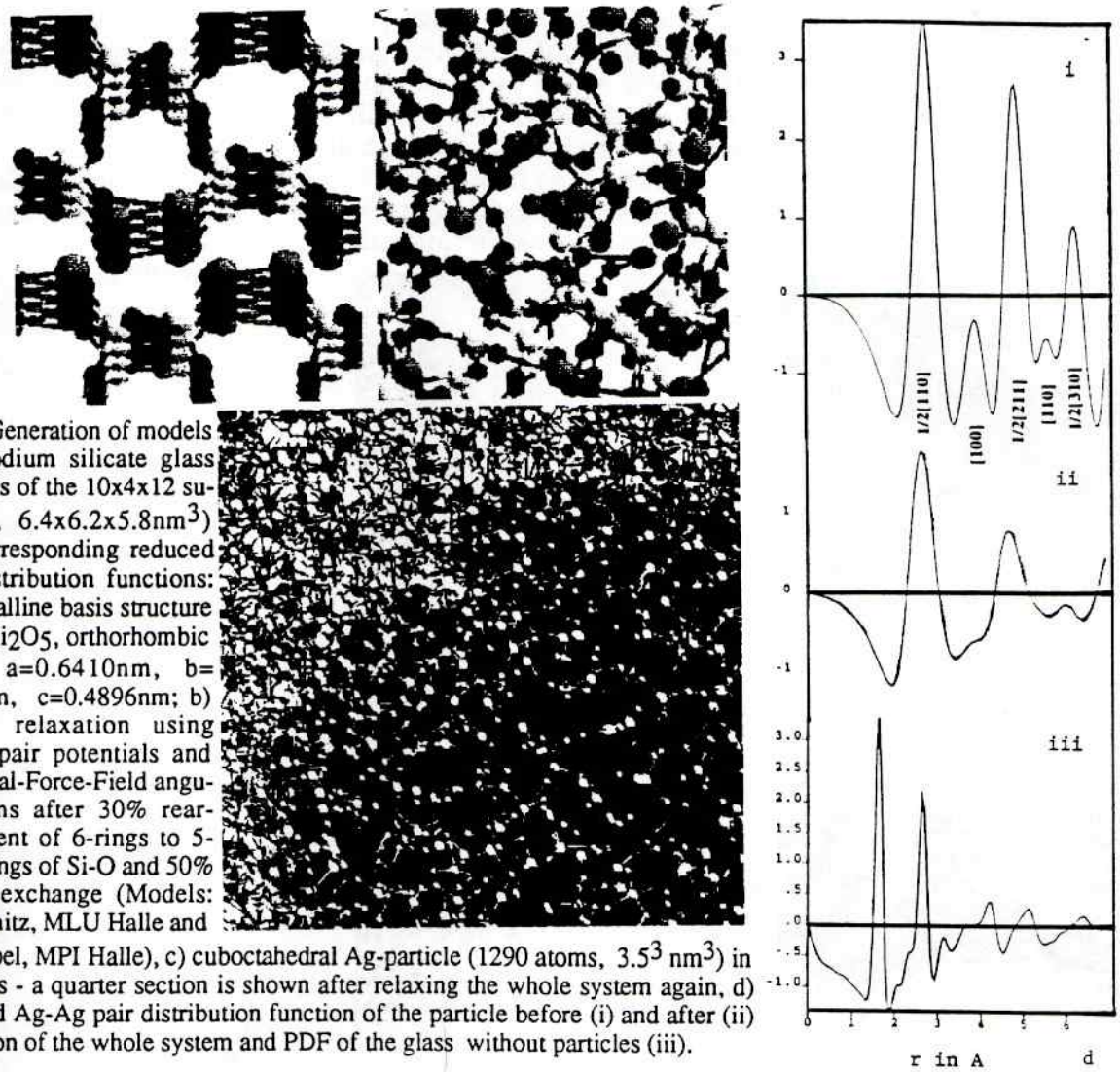

Fig.1: Generation of models of a sodium silicate glass (sections of the 10x4x12 supercell, 6.4x6.2x5.8nm^3) and corresponding reduced pair distribution functions: a) crystalline basis structure α-$Na_2Si_2O_5$, orthorhombic Pcnb, a=0.6410nm, b=1.542nm, c=0.4896nm; b) energy relaxation using Morse pair potentials and Universal-Force-Field angular terms after 30% rearrangement of 6-rings to 5- and 7-rings of Si-O and 50% Na-Ag exchange (Models: R. Schmitz, MLU Halle and D. Timpel, MPI Halle), c) cuboctahedral Ag-particle (1290 atoms, 3.5^3 nm^3) in the glass - a quarter section is shown after relaxing the whole system again, d) Reduced Ag-Ag pair distribution function of the particle before (i) and after (ii) relaxation of the whole system and PDF of the glass without particles (iii).

RESULTS AND DISCUSSION

Fig. 1 shows the MD generation of the structure of the sodium silicate glass starting with a α-$Na_2Si_2O_5$ crystal, rearranging the 6-fold ring structure and randomly replacing Na by Ag atoms according to the experimental ring statistics and ion exchange rate. The MD relaxation for a whole cuboctahedral particle-glass system is given in Fig.1c as displacements of the particles surface atoms which can be characterized by the PDF's before and after the relaxation (Fig.1d i and ii, resp.) as well as in comparison with the PDF of the glass (Fig.1d iii). Fig.2 demonstrates the influence of the relaxations on the HREM image contrast of the small crystalline cuboidal or cuboctahedral shaped silver particles in the sodium silicate glass. Besides the Fresnel fringes at the particle borders and the speckled contrast of the amorphous glass matrix according to the Scherzer imaging, the lattice disturbances at the surface of the particles can be observed. The static relaxation yields an amorphous glass structure sufficient for HREM image simulations, the calculations of Fig. 3 starting with a more realistic sodium silicate glass [11] and assuming different 12-6 LJ forces for Ag and MD-cooling demonstrates the possibility of Ag migration and 3d-coalescence (cf. Si-O and Ag-Ag partial RDF's).

Fig. 4 shows experimental and computer simulated HREM images of grain boundaries in Ge. The theoretical contrast is refined by trial and error by determining the rigid body shift of the atomic columns from the experimental micrographs and calculating the relaxed models by energy minimisation. A sufficient contrast description demands the MD calculations as shown (cf. Figs. 4 e-h). Fig. 5 describes the influence of relaxations on the HREM image contrast due to the misfit at the interfaces and including changes of stoichiometry x/y across the

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semiconductor layers in ternary systems of $In_xAl_yGa_{1-x-y}As$. The lattice relaxation at the boundaries are calculated assuming atomic equilibrium distances of the perfect crystal structure and restricting the atomic positions to those of the crystal far from the defect. In both the experimental example (Fig.5a, Micrographs: S. Ruvimov) and simulated defocus series for the sharp interface (b) with a step in concentration x and the smoothed one (c) the roughness of the interfaces and the influence of strains as well as thickness and orientation fluctuations can be revealed. The misfit of this system is rather low so that solely the random changes of the stoichiometry give inhomogeneous composition resulting in strain effects.

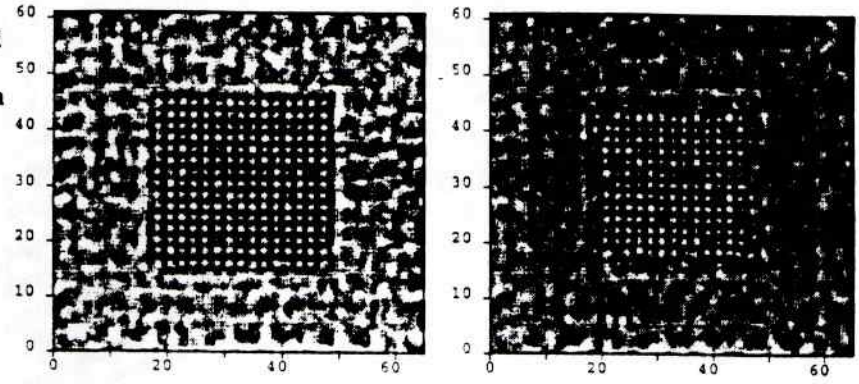

Fig.2: Simulated HREM images for different shapes, diameters and relaxations of the (100) oriented Ag-particle in the 10x4x12 sodium silicate glass matrix (a,b: cuboidal, 1372 atoms; c,d: cuboctahedral, 640 atoms; a,c: nonrelaxed particle; b,d: whole system relaxed) at 400kV, C_S=1mm, δ=10nm, α=0.5mrad, Δ=-70nm

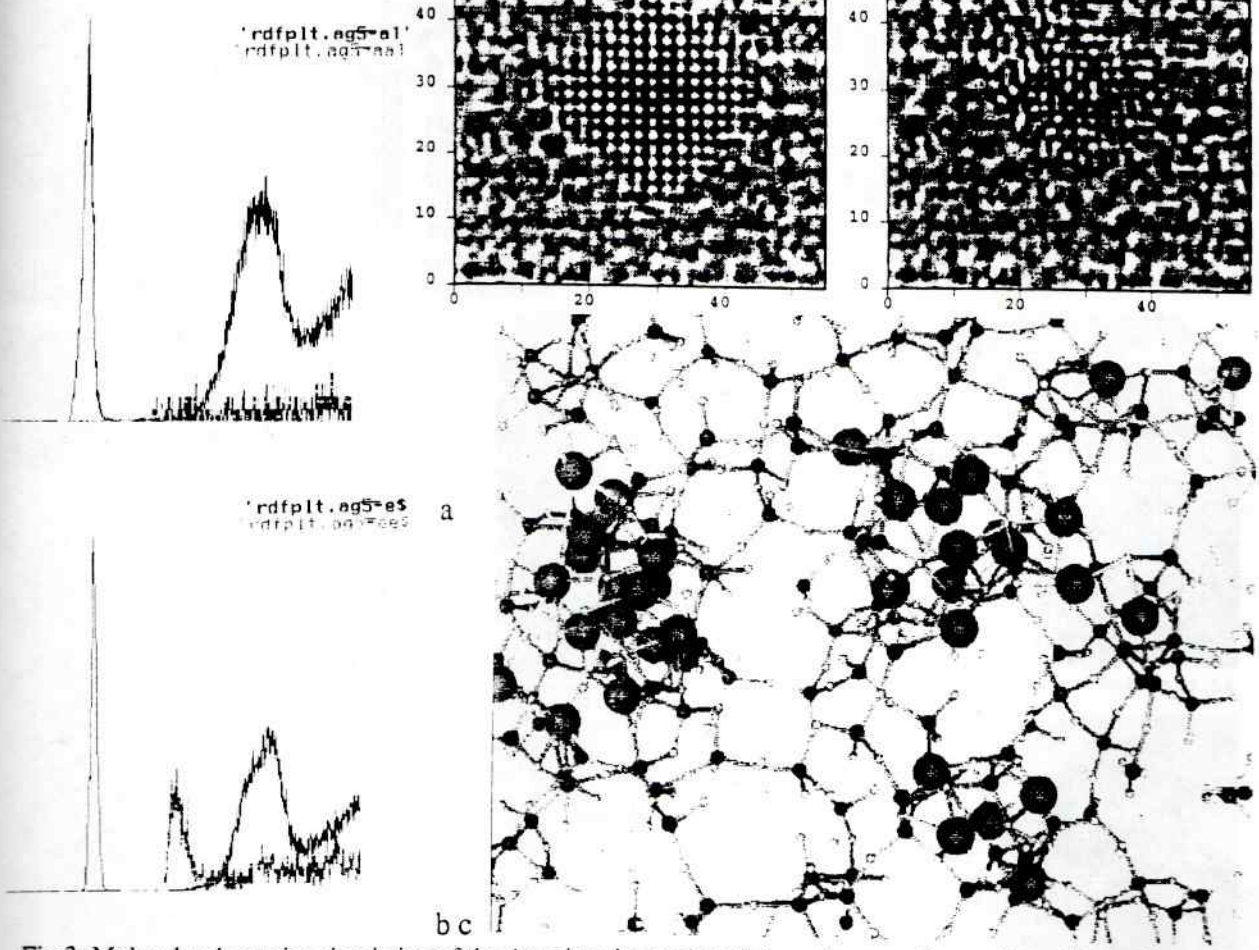

Fig.3: Molecular dynamics simulation of the Ag migration and particle coalescence in a sodium silicate glass: Partial radial distribution functions (RDF) of Si-O (black) and Ag-Ag (grey) of the initial relaxed glass structure after 30%Ag-Na exchange and 100ps relaxation at 2000 K (a) and 50ps/50ps at 1500K/300K (b); Snapshot (c) after 30%Ag-Na exchange, relaxation at 2000 K and nucleation of Ag at 300K

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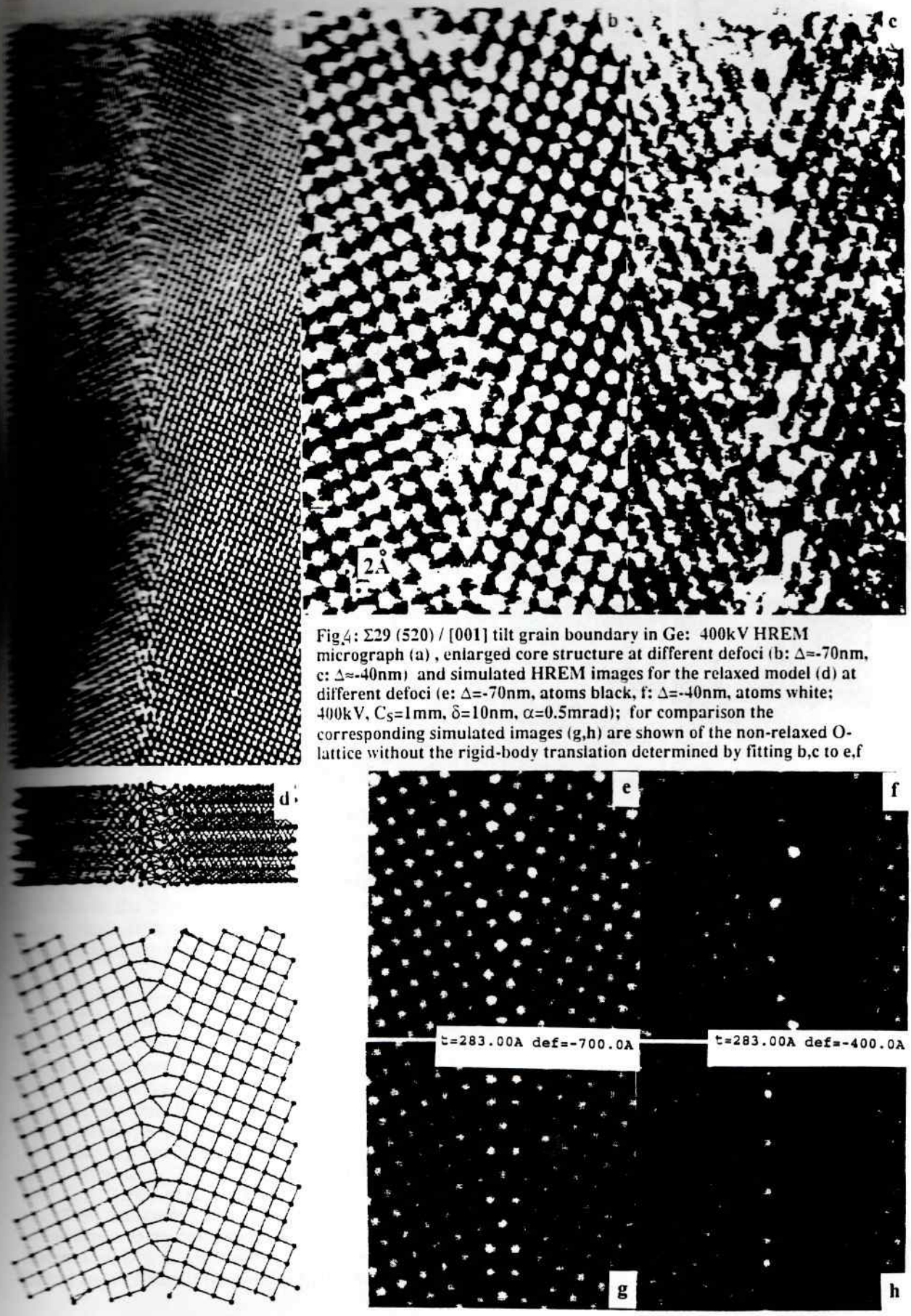

Fig.4: Σ29 (520) / [001] tilt grain boundary in Ge: 400kV HREM micrograph (a), enlarged core structure at different defoci (b: Δ=-70nm, c: Δ=-40nm) and simulated HREM images for the relaxed model (d) at different defoci (e: Δ=-70nm, atoms black, f: Δ=-40nm, atoms white; 400kV, C_S=1mm, δ=10nm, α=0.5mrad); for comparison the corresponding simulated images (g,h) are shown of the non-relaxed O-lattice without the rigid-body translation determined by fitting b,c to e,f

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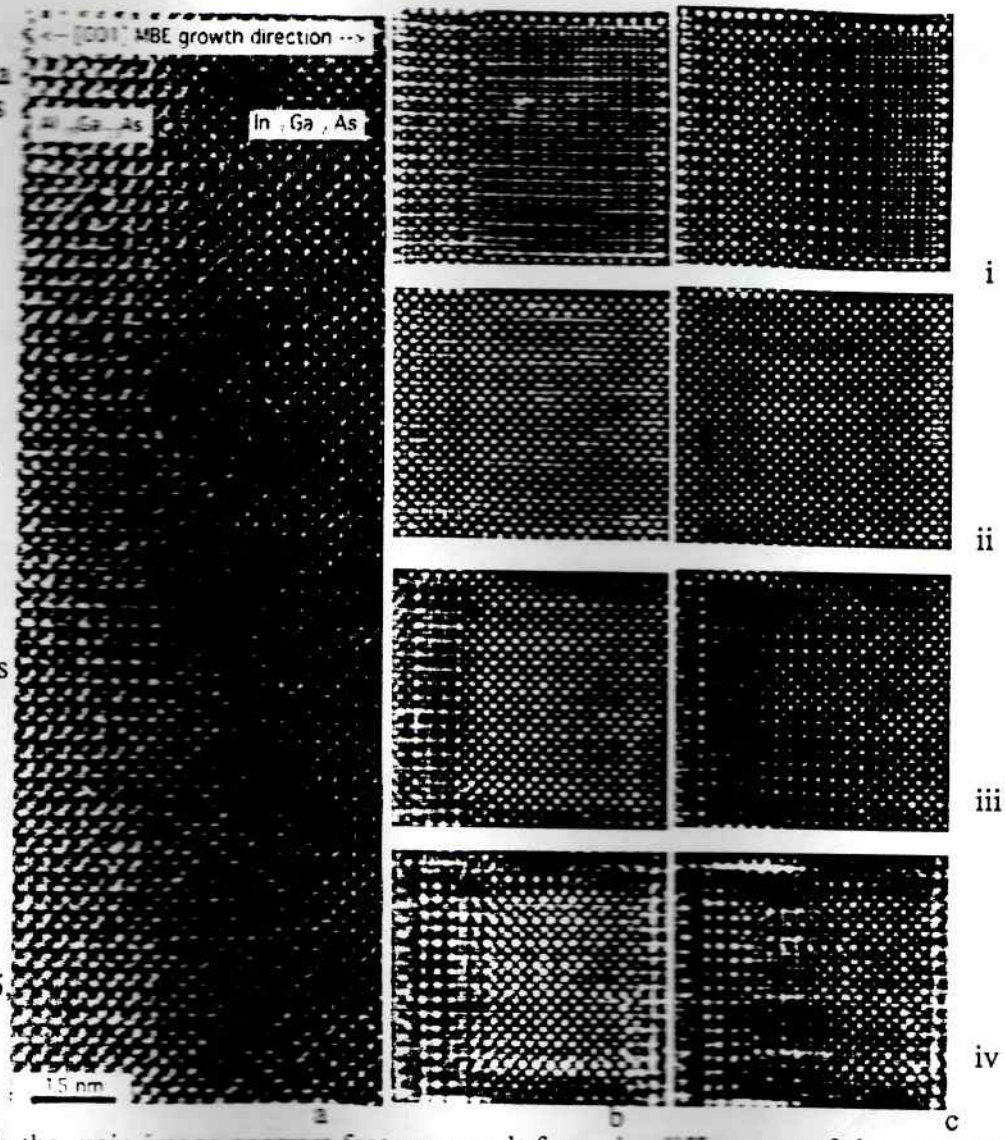

Fig.5: 400kV-(100)HREM of a AlGaAs/InGaAs interface with a gradient of stoichiometry (a; A. Hoepner, MPI Stuttgart) and simulated HREM defocus series (Δ/nm= 70(i), 40(ii), 10(iii), -20(iv), 400k, C_S=1mm, δ=10 nm, α=0.5mrad, α'=16nm^{-1}) for the energy relaxed $In_xAl_yGa_{1-x-y}As$ multilayer structure with different layer geometry on GaAs substrate (b: uprupt interface x/y= 0/0, 0/25 %; c: smooth gradient, x/y=30/25, 20/25, 10/25, 5/25, 0/25 %)

Even though the main image contrast features result from the differences of the structure factors of the projected atoms and the microscope aberrations, the atomic relaxations at interfaces can be discussed in terms of contrast details and in dependence on thickness and focus of the HREM experiments. Thus the compositional variations and the elastic deformations can be revealed at the interfaces by HREM imaging under special imaging conditions. Image processing and simulation are required and enable a more quantitative interpretation of the HREM micrographs and thus the detailed analysis of the interfaces.

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