LETTER TO THE EDITOR

The study of microstructure in iron- and sulphur-doped InP crystals by means of HREM and computer simulation

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Abstract. The microstructures in iron- and sulphur-doped InP crystals were studied using both electron microscopy and electron diffraction. A modulated structure has been found in S-doped InP crystal, where the commensurate modulations corresponded to periodicities of 0.68 nm and 0.7 nm in real space and were related to the reflections of the cubic lattice in [111] and [1$\bar{1}$3] directions; they were indexed as $q^*_{111} = \frac{1}{3}(a^* + b^* + c^*)$ and $q^*_{\bar{1}13} = \frac{1}{4}(-a^* - b^* + 3c^*)$, respectively. Single atomic layers of iron precipitate were observed, with preferred orientations along which precipitates are formed. Simulated calculations by means of the dynamical theory of electron diffraction using models for the precipitate structure were in good agreement with our experimental results. The relation between the modulated structure and the precipitates is also discussed.

Indium phosphide (InP) crystal as a substrate material has been widely applied in microwave and optoelectronic devices, with increasing demands on the structural properties of this crystal. An important goal is the reduction of the defect density [1, 2]. One of the reduction methods, as suggested by past theoretical and experimental work, is to introduce dopants during crystal growth. There are different densities of defects in the crystals resulting from the different percentages and species of dopants [3, 4]. The investigation of the mechanism and physical properties in the doped crystal has become an important issue. A lot of research on doped InP crystal has been performed by means of TEM techniques [5–7]. In this letter, we report a high-resolution electron microscope (HREM) study of the microstructures and the mechanism in iron- and sulphur-doped InP crystal. These experimental results are in good agreement with computer simulation.

InP has a cubic zinc sulphide structure with the space group $F\bar{4}3m$. The single crystal doped with 0.03 wt% Fe or S was grown by the liquid encapsulation Czochralski (LEC) method, pulling along the [111] crystal axis. The specimens examined in the present work were prepared by crushing the crystals. The electron microscope images were obtained from a JEM-4000EX instrument with point-to-point resolution of 0.19 nm ($Cs = 1$ mm) at 400 kV.

In figure 1 the bright-field image of the Fe-doped InP crystal is shown, with an incident beam along the [1$\bar{1}$0] direction, where all of the precipitates are lying parallel to (111) and (113) lattice planes. Because the atomic sizes in the precipitates and the matrix are not equal, contrast is observed from elastic strains generated near the
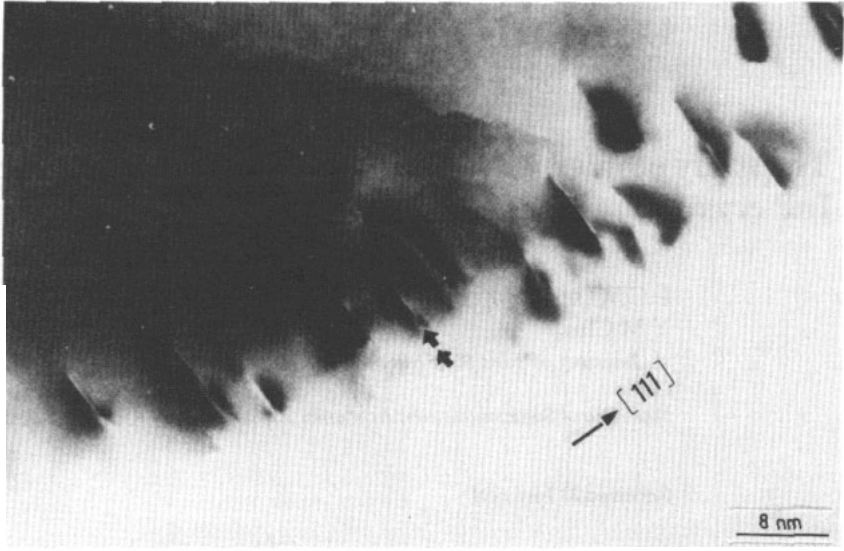
Figure 1. A bright-field image of Fe-doped InP crystal aligned on [1$\bar{1}$0].
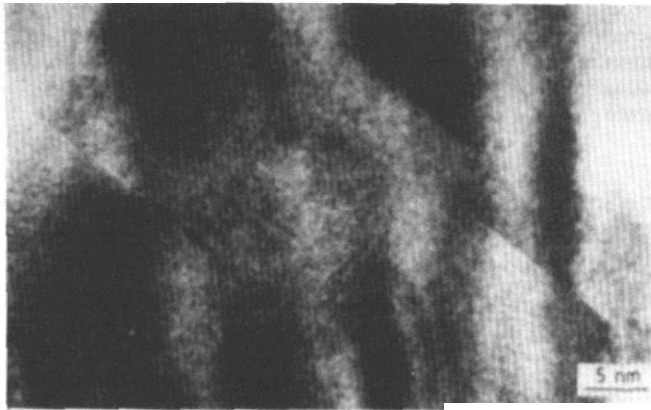
Figure 2. A HREM image of the Fe-doped InP crystal corresponding to figure 1.

interfaces between precipitates and the matrix. The precipitated dopants have preferred orientations which are related to the direction of crystal growth along [111]. Figure 2 shows the HREM image of iron-doped InP crystal, where the bright lines correspond to the precipitate contrast in figure 1 and are indicated by black arrows. The thickness and length of the bright lines were determined to be about 0.2 nm and 5 nm, respectively. It is deduced that the structure of the precipitates consists of one layer of iron atoms sandwiched between two layers of phosphorus along the [111] direction, where the contrast of the bright lines is attributed to the difference in structure factor between FeP and InP layers. This was confirmed by computer simulation based on the multislice
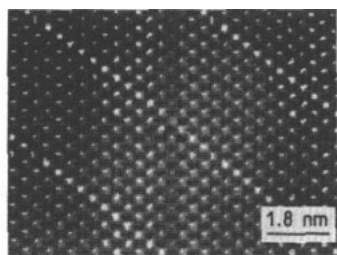
Figure 3. Computer simulation of Fe-doped InP crystal with thickness ≈ 8 nm and defocus ≈ 36 nm.
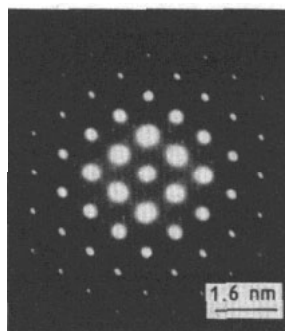

Figure 4. The diffraction pattern of S-doped InP crystal aligned on $[1\bar{1}0]$.
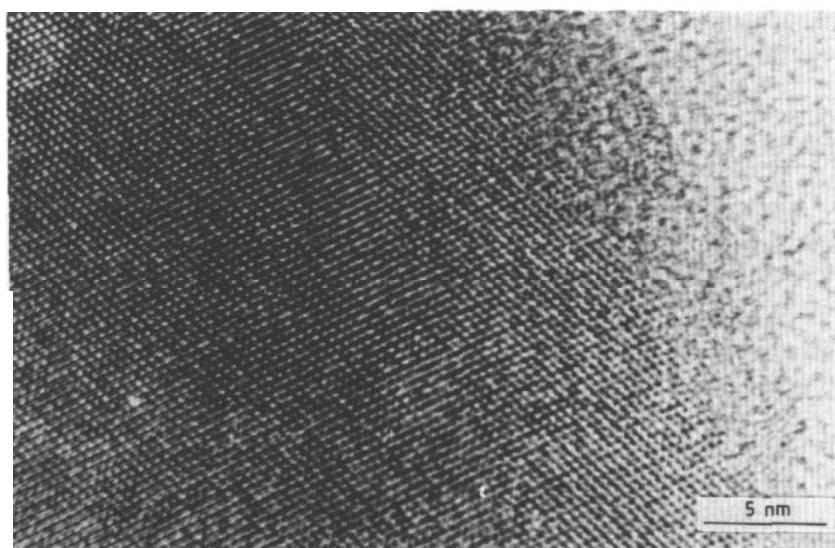

Figure 5. A HREM image of the S-doped InP crystal from the same area as in figure 4.

method for dynamical electron diffraction and image formation. The computer-simulated image of iron-doped InP in figure 3 is in good agreement with our experimental result.

The diffraction pattern of S-doped InP for the $[1\bar{1}0]$ zone axis is shown in figure 4. The superlattice reflections due to the commensurate modulation are clearly visible in the figure. The direction of the structural modulations was along [111] and $[\bar{1}\bar{1}3]$ with the wavelengths of 0.68 nm and 0.7 nm, and the reciprocal-lattice vectors are $q^*_{111} = \frac{1}{2}(a^* + b^* + c^*)$ and $q^*_{\bar{1}\bar{1}3} = \frac{1}{4}(-a^* - b^* + 3c^*)$, respectively. In this area, the diffraction pattern reveals the ordered arrangements of sulphur atoms along (111) and $(\bar{1}\bar{1}3)$ planes. It is considered that the commensurate modulation was due to the displacement of indium atoms by sulphur atoms. However, it was difficult to observe the contrast of the structural modulations in the HREM image (figure 5) with the corresponding diffraction
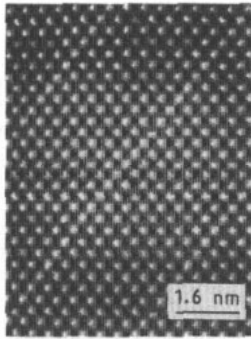
Figure 6. Computer simulation for S-doped InP crystal with thickness ≈ 0.8 nm and defocus ≈ 29 nm.

pattern of figure 4. The result of computer simulation indicates that when the specimen thickness is about 8 nm, with a defocus of 29 nm, the sulphur atomic contrast cannot be clearly observed. In figure 6, the computer simulation image for a model in which the structural modulation contains sulphur atomic-ordered arrangements shows good correspondence with the HREM image of figure 5.

According to the theory of crystal defects [8–11] the planar defects are easily produced at close-packed planes due to thermal stress fields generated during the growth process. In doped crystals, the dopants usually coalesce near the planar defects, and so the number of prismatic dislocation loops is reduced.

In this letter, HREM and computer simulations were carried out in order to reveal the microstructure in iron- and sulphur-doped InP crystal. From the observed and computed results, the following conclusions were obtained.

(i) In sulphur- or iron-doped InP crystal, the dopants were arranged on close-packed planes, both sulphur and iron atoms causing displacements of indium atomic positions, forming FeP or SP atomic bonds.

(ii) In iron-doped InP crystal, single atom layers of iron precipitates were formed between two layers of phosphorus along the [111] direction.

(iii) In sulphur-doped InP crystal, a modulated structure was found.

(iv) In doped InP crystal grown with the LEC method, there are preferred orientations along which precipitates are formed. These may be related to the direction along which the crystal is grown.

(v) This analysis was supported by the computer simulation.

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