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Point Defect Clusters in $Pb_{1-x}In_xTe$ Single Crystals Revealed by X-ray Diffuse Scattering Method

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The method of X-ray diffuse scattering is used to characterize the point defect structure in $Pb_{1-x}In_xTe$ ($x = 0.005–0.055$) single crystals. It is found that clusters of both vacancy and interstitial defects are present in all samples, but the ratio of their concentrations varies depending on the doping level. The clusters of interstitial point defects are supposed to be dislocation loops formed from Pb_i and Te_i, while the clusters of vacancy-type defects may be formed from complexes of In atoms and tellurium vacancies.

1. INTRODUCTION

Doping of narrow-gap PbTe compound with some nonisovalent impurities like In and Ga affects significantly the electronic and optoelectronic properties (1). The most characteristic features of In-doped PbTe ($Pb_{1-x}In_xTe$) are the systematic excess of In content in samples over the density of majority carriers (electrons) at $x > 0.004$ and the pinning of Fermi level in the wide range of impurity concentrations. The latter implies that the main part of In impurity atoms is electrically inactive. However, the X-ray photoemission data on the electronic state of In in PbTe (2) show rather that indium atoms incorporate into PbTe in their acceptor configuration $5s^25p^1$, substituting for lead in octahedra. Then, one can suppose the formation of electrically neutral complexes of In impurity with intrinsic point defects, which may segregrate into extended point defect clusters. Such clusters were recently found in $Pb_{0.99}In_{0.01}Te$ by X-ray diffuse scattering method (3).

In this paper we report on the study of point defect structure in $Pb_{1-x}In_xTe$ single crystals and its evolution with the level of doping.

2. EXPERIMENTAL

Single crystals of $Pb_{1-x}In_xTe$ solid solutions were grown from PbTe–InTe melts by Bridgman technique. The as-grown crystals were single phase; they had *n*-type conduction and nearly the same carrier density $n \sim 7 \times 10^{18}$ cm^{-3}. Crystal composition (Table 1) was established using the lattice constant measurements (4, 5). The samples for diffuse scattering measurements were cut orthogonally to the [111] axis of the boules and chemically polished.

The X-ray diffuse scattering measurements were performed on a triple-crystal diffractometer using the low-dispersion scheme (*n*; $-m$; *n*): Ge(400)–$Pb_{1-x}In_xTe$(400)–Ge(400) with a singlefold reflection in monochromator and analyzer. A detailed description of the experimental technique and procedures of measurement is given in (6). In the present work special attention was paid to the asymptotic component of diffuse scattering (AXDS) (7), as it is more sensitive to clusters of both vacancy-type and interstitial-type defects than the conventional Huang scattering (we will denote further the clusters creating the negative and positive local lattice dilatations as vacancy and interstitial clusters, respectively). In order to heighten the sensitivity to a weak AXDS signal, we did not use the vertical collimation of incident beam, i.e., the collimation along the q_y direction being orthogonal to the diffraction plane. In this case, the measured intensity $I(q_x, q_z)$ can be represented as follows:

$$I(q_x, q_z) = \int_{-\Delta q_y}^{+\Delta q_y} d\sigma(\mathbf{q})\, dq_y, \qquad [1]$$

where $d\sigma(\mathbf{q})$ is the AXDS cross-section, q_x and q_z are projections of vector $\mathbf{q}$ in the diffraction plane, and the range $(-\Delta q_y; +\Delta q_y)$ is determined by the vertical size of the detector window. The q_z and q_x projections are parallel and orthogonal to the diffraction vector, respectively. The AXDS cross-section is proportional to $|\mathbf{q}|^{-4}$, where $\mathbf{q}$ is the deviation of the diffraction vector from the reciprocal lattice vector. Considering Eq. [1], the measured AXDS intensities should be proportional to $|\mathbf{q}|^{-3}$.

3. RESULTS AND DISCUSSION

The asymptotic diffuse scattering can be represented as a set of local Bragg reflections from weakly distorted areas

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TABLE 1
Concentration of In Impurity in the $Pb_{1-x}In_xTe$ Solid Solutions Derived from the Lattice Constant Measurements

Sample	x
1	0.005
2	0.008
3	0.030
4	0.055

close to the point defect cluster. Since the field of atomic displacements induced by the cluster has an inverted symmetry, there are always at least two equidistant points around it that have similar lattice distortion and, hence, would scatter X-rays in phase. Therefore, the resulting AXDS intensity profile should have stationary phase oscillations (8). Such oscillations are usually well developed in the intensity distribution drawn in Iq^3, q coordinates around the point $q = 0$. The angular position of oscillations and their period give unique information on the sign of lattice dilatation created by cluster (i.e., cluster nature), its power, and its average size (9). In this experiment both vacancy and interstitial clusters can be analyzed separately since they contribute to the AXDS intensity profile at $q < 0$ and $q > 0$, respectively.

The experimental data on distribution of diffuse scattering around the (400) reciprocal lattice site in $Pb_{1-x}In_xTe$ single crystals are shown in Fig. 1. The strong oscillations of diffuse scattering arising from both sides of $q = 0$ suggest the presence of vacancy and interstitial clusters in all samples examined, though their ratio varies depending on the doping level. From Fig. 1 it is evident that in samples 1 and 2 ($x = 0.005$, 0.008), the fine vacancy clusters (~ 0.02 μm) are the predominant scattering centers (note the prominent diffuse oscillations at $q < 0$). The concentration of interstitial clusters (AXDS at $q > 0$) is sufficiently lower than that

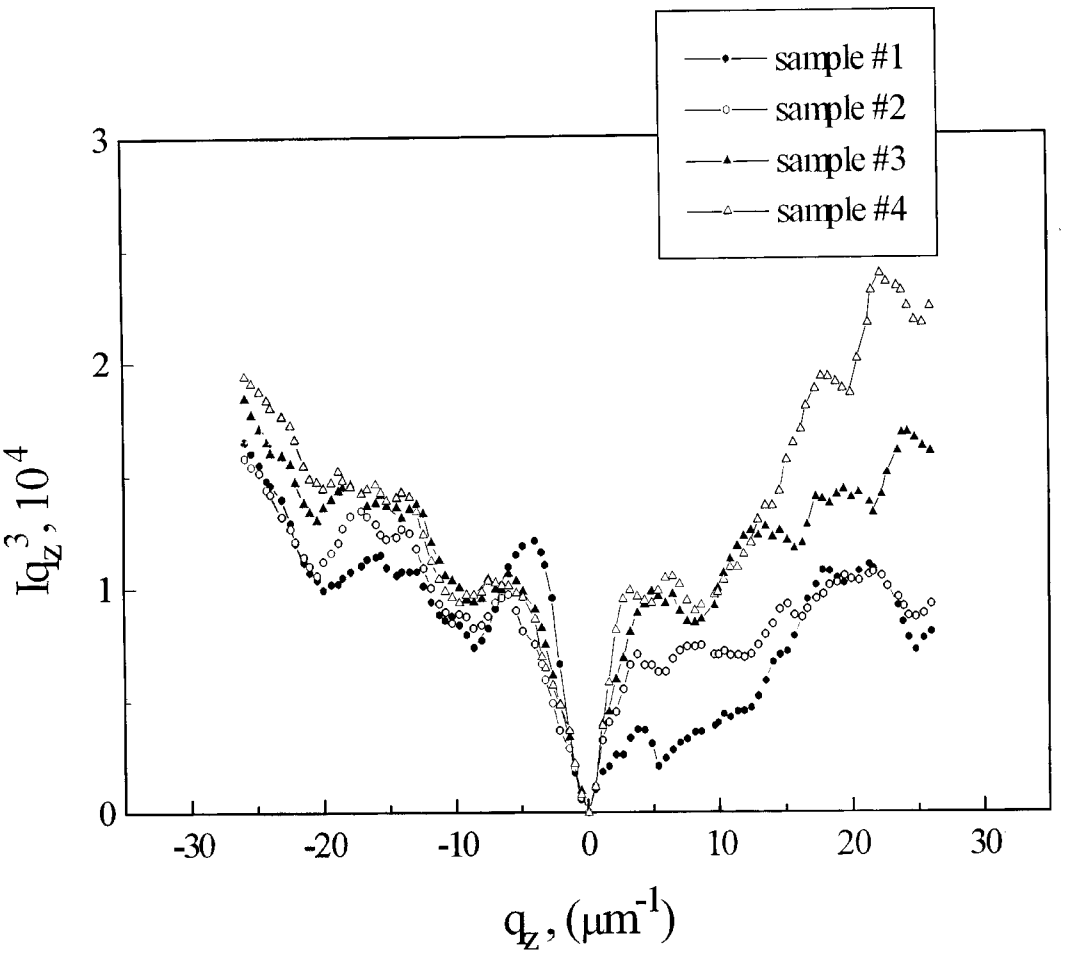

FIG. 1. AXDS intensity profiles taken around (400) reciprocal lattice site in $Pb_{1-x}In_xTe$ single crystals ($q_z \| [100]$).

of vacancy ones. With increasing indium content the interstitial point defect clusters become larger and their concentration goes up rapidly. Therewith, the density of vacancy clusters also increases to some extent, but their size remains practically the same (there are no sufficient changes in the oscillation structure from the $q < 0$ side). Finally, in sample 4, the interstitial scattering centers make the main contribution to the AXDS picture. The character of the diffuse scattering profile at $q > 0$ is associated with planar-type interstitial defects, such as dislocation loops. Considering this model, an average radius of these loops should be ~ 0.2 μm.

On the basis of experimental results, the following picture of point defect cluster formation in $Pb_{1-x}In_xTe$ at $x = 0.005$–0.055 may be proposed. The character of the phase diagram (4) suggests the excess of tellurium atoms in the solid solution and presence of acceptor vacancies of lead (V'_{Pb}) may be responsible for p-type conduction in pure and weakly doped PbTe. An increase in In concentration should shift the figurative point of the corresponding solid solution to the excess of the metallic component (Pb). Considering the almost linear decrease in the lattice constant with increasing indium content (5) and photoemission data (2), we suppose the formation of electrically neutral complexes of $(In'_{Pb}–V^{\bullet}_{Te})^0$ type in the solid solution. When indium concentration goes above a certain threshold, these complexes may form clusters of the vacancy type, giving rise to the diffuse scattering background at $q < 0$ (Fig. 1). This conclusion is also supported by our SIMS measurements: the total In content in samples is nearly twice as large as in the solid solution. On the other hand, doping with indium should increase the number of lead interstitials (Pb_i). These lead interstitials and surplus Te atoms may form the interstitial dislocation loops. Therefore, the interstitial clusters observed in the X-ray diffraction experiment may have a composition close to that of PbTe.

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