Identification of Cl and Na impurities in inclusions of a vapor-grown CdTe doped with Zn and Cl

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Morphology and analysis of composition of inclusions were done by secondary electron microscopy and spatially resolved energy-dispersive analysis of x-ray on semiintrinsic CdTe:Cl and CdTe:Zn:Cl crystals grown from the vapor phase by the modified Markov technique and on undoped CdTe crystals grown from the melt by the Bridgman method. In CdTe:Cl and CdTe:Zn:Cl crystals nonstoichiometric inclusions of about 10–20 μ m were found, which contain high concentrations of Cl and Na impurities. The Cl is concentrated in small precipitates of 1–2 μ m inside these inclusions. After short-time low-temperature annealing (600 °C), the inclusions mostly disappeared.

I. INTRODUCTION

Potential industrial application of room-temperature x-ray detectors based on semiinsulating cadmium telluride requires the homogeneity of electrical properties and low concentration of native defects and impurities.¹ In many cases Te-rich precipitates and inclusions enriched with impurities are the main sources of inhomogeneity of CdTe-based materials,^{2–4} which creates the problem of resistivity control at the postgrowth heat treatment and during the operational period.

As it was earlier shown,^{5,6} in CdTe crystals grown from the melt, tellurium precipitates are formed from native defects (V_{Cd} Te_i) during the cooling process due to the strong retrograde character of Te solubility in solid CdTe, while the Te-rich inclusions are originated by melt droplet capture on the growth surface. This phenomenon leads to inhomogeneous distribution of impurities due to segregation. Moreover, taking into account that the solubility of many impurities in liquid Te is higher than in solid CdTe, the concentration of residual impurities in Te-rich defects can be considerably higher than in bulk material.⁷

Commercially available semiintrinsic CdTe has always a high concentration of the doping impurity, particularly chlorine,⁸⁻¹⁰ and it is well known that the

main Cl-related defects are a shallow donor (Cl_{Te}) and acceptor-like complex $(Cl_{Te}-V_{Cd})$.^{11,12} It is also known that the nonuniformity of the Cl distribution leads to deterioration of the resistivity uniformity,¹³ but so far a limited study of Cl precipitation has been done¹⁴ and to the best of our knowledge this problem is important both for the melt- and vapor-grown CdTe materials.

This paper presents the results of the chemical analysis of inclusions in CdTe:Cl and CdTe:Zn:Cl grown from the vapor phase and CdTe grown from the melt for the comparison following our previous study of Te-rich inclusions and the deviation from the stoichiometry in the boundary regions.^{15–17} The annealing of the samples was carried out by taking into account the possibility to reduce the concentration of inclusions^{15,16} and to increase the Cl solubility in the bulk.^{11,18}

II. EXPERIMENTAL

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CdTe:Cl, CdTe:Zn:Cl monocrystals were grown from the vapor phase by the modified Markov technique¹⁰ under controlled vapor pressure $P_{Cd}/P_{Te2} = 2$ with a nominal concentration of chlorine of 5×10^{18} cm⁻³ and zinc of 2.5×10^{18} cm⁻³ in the feed material added to the melt as CdCl₂ and ZnCl₂. The crystals have high structural quality and are twin-free, with an average dislocation density lower than 10^3 cm⁻² and with a resistivity up to $10^9 \Omega$ cm, which was measured by the Van der Pauw

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method.^{8,9} Undoped high-resistivity CdTe crystals considered as reference samples were grown by the Bridgman method as it has been reported elsewhere.¹⁹

Oriented (111) wafers of about $20 \times 10 \times 1.5 \text{ mm}^3$ or cleaved (110)-oriented samples were taken from the asgrown ingot for comparison. The wafers were mechanically polished (Al₂O₃ powder of 5 µm), followed by a micropolish with 1.0 and 0.3 μ m α -alumina in ethylene glycol. Afterward, the samples were free etched in Br/ methanol solution (2% Br), followed by chemopolishing with Br/ethylene glycol (0.5% Br) which gives a Te-free surface as it was shown by Raman scattering analysis.^{15,16} All samples were treated in the same way, prior to being analyzed by energy-dispersive x-ray analysis (EDAX) measurements. On the cleaved (110) surface EDAX analyses were done without chemical treatment of samples. These precautions were undertaken to avoid the influence of the surface contamination by Al or Br on the EDAX results.

The annealing processes were carried out in evacuated and sealed off quartz ampules at 600 °C for 4 h under a Cd vapor atmosphere. After annealing, the ampules were withdrawn from the furnace and cooled rapidly in air. Afterward, the samples were again chemically polished to remove the surface layer at the depth of about 10 μ m.

The samples were studied by EDAX with a Philips XL30 equipment combined with secondary electron microscopy (SEM) after deposition of a thin Au layer (10 nm). Corrections for absorption, fluorescence, and atomic number were performed with DX4i EDX software. Influence of the Au layer was taken into account by comparison the EDAX signal with that from the low-resistivity CdTe sample without Au coverage. The homogeneity of each sample was checked by SEM image overview, followed by EDAX analysis in high spatial resolution when some inclusion was found.

III. RESULTS AND DISCUSSION

Figures 1(a) and 2(a) present the SEM images of typical precipitates in as-grown CdTe:Cl and CdTe:Zn:Cl samples concentrated inside of relatively big inclusions of 10–15 μ m. Such precipitates have either a seedlike or oval shape and a length of about 1 μ m. These precipitates mainly disappear after the annealing process as it is shown in Fig. 1(b) for the CdTe:Cl sample.

Figure 2(b) shows the detail of one of the oval-shaped precipitates present in Fig. 2(a). The EDAX maps of Cl and Na distribution on this precipitate are shown in Figs. 2(c) and 2(d) with the same scale for presentation. It is clearly seen that Cl is concentrated in the precipitates, while Na is distributed uniformly throughout the group of precipitates.

The results of the EDAX composition analysis made in the inclusion shown in Fig. 2(b) are presented on Table I, column 1A, where it can be seen that Cl and Na





(b)

FIG. 1. SEM image of precipitates in the (a) as-grown and (b) annealed CdTe:Cl samples.

are accumulated in a high concentration (up to 30 at.% for Cl and 10 at.% for Na). The measurements carried out in other inclusions (columns 2A and 4A) show that the Cd concentration is larger than the concentration of Te, but this situation is not a general rule (see column 3A). In this way, we can suggest that the small precipitates would contain the CdCl2-CdTe phase, which was earlier found by Magee et al.¹⁴ Furthermore, the Zn concentration detected in some inclusions up to a value of 3 at.% (column 4A) is relatively high compared with the nominal doping of the feed of 2.5×10^{18} cm⁻³. For the comparison with these results, measurements of Cl, Na, and Zn concentrations at a distance of 30 µm from the inclusion are presented in column 5A, which practically reflect the concentrations in the bulk taking into account that these data can be interpreted with some precaution because they are at the limit of the EDAX sensitivity. All data from the columns 1–5A correspond to the inclusions revealed on the chemically treated (111) surface, while data from column 6A reflect the case on the cleaved (110) surface. Comparing these results, one must conclude

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that the impurities revealed on the chemically treated surface are substantially the same as the one which can be seen on the cleaved surface, but the composition of different inclusions can significantly differ being enriched with Cl or with Na in a different proportion. After the annealing it was still possible to find inclusions, but the presence of Cl, Na, and Zn atoms is lower pronounced than in inclusions of as-grown samples (Table I, columns 1–4B).

The data of the compositional analysis on inclusions for undoped CdTe samples grown from the melt are shown in Table II, for as-grown and annealed samples



FIG. 2. (a) SEM image of the inclusion in as-grown CdTe:Zn:Cl crystal. (b) Detail of the inclusion, which is marked in Fig. 2(a) by the arrow. EDAX mapping of (c) Cl and (d) Na distribution in this inclusion.

TABLE I. EDAX data (at.%) in different inclusions of CdTe:Zn:Cl samples: columns 1A-4A for (111), 5A for an inclusion-free area, and 6A for (110) surface.

	As-grown						Annealed			
Atom	1A	2A	3A	4A	5A	6A	1B	2B	3B	4B
Cd	29.85	42.83	41.51	41.27	46.84	38.41	47.19	48.22	47.10	48.46
Те	28.14	41.82	43.79	39.52	49.02	38.07	46.81	47.12	47.32	48.63
Zn	1.48	1.46	0.75	3.32	0.85	1.54	0.64	1.12	0.58	1.32
Cl	30.24	11.29	10.49	15.89	1.42	13.80	3.30	2.51	4.21	0.98
Na	10.29	2.60	3.46	0.00	1.87	8.18	2.06	1.03	0.79	0.61

TABLE II. EDAX data (at.%) in different inclusions of as-grown and annealed p-CdTe samples.

	As-grown				Annealed					
	1A	2A	3A	4A	5A	1B	2B	3B	4B	5B
Cd	50.67	48.45	49.65	48.01	49.45	52.04	51.10	50.47	49.67	49.31
Те	48.14	47.32	47.06	50.67	48.32	46.37	47.32	48.00	48.22	48.91
Na	0.00	0.59	1.25	0.00	0.59	0.78	0.53	0.58	0.66	0.49
Si	0.57	2.04	1.04	0.51	1.04	0.50	0.63	0.40	0.91	0.81
Al	0.62	1.60	1.00	0.81	0.60	0.31	0.42	0.55	0.54	0.48

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Inclusions with an average dimension of about 10–20 μ m were found similar to those in the vaporgrown crystal. Some enrichment of the inclusions with Na, Si, and Al and deviations from the stoichiometry up to 2 at.% of excess either of Cd or Te were registered at the limit of EDAX error (columns 1–5A). After annealing, the Te-rich inclusions disappeared, while Cd-rich inclusions still remained probably due to the influence of the Cd atmosphere conditions (columns 1–5B). Nevertheless, lower concentration of impurities such as Na, Si, and Al was detected, while other usual impurities for CdTe Bridgman growth like Fe, K, Ca, and Ag⁷ were below the EDAX limit.

The comparison of the EDAX data for vapor-grown CdTe:Zn:Cl with those for the reference CdTe grown from the melt shows that the composition of inclusions differs depending on the growth method. Na is present in very small concentrations in both cases, the concentration being higher in the vapor grown sample whereas Al and Si were only detected in the melt-grown sample. This difference can be explained by taking into account the growth temperature, which is higher for the Bridgman method than for the modified Markov technique, and the quartz ampule used in the Bridgman method, which can be a source of other additional impurities. In fact Al was registered only in the reference sample, which means that the misinterpretation of the Al, K, and Br L lines due to their overlapping in EDAX analyses must be excluded due to the fact that all samples were chemically treated in the same way.

One must take into account that the EDAX data reported in this paper reflect the impurity concentrations in the inclusions but not in the bulk. Nevertheless, using the data of the impurity concentration present on inclusions, one can estimate the role played for the segregation on a given impurity. Considering as one example the case of Cl segregation, the total quantity of Cl atoms (N_{Cl}) in inclusions shown in Fig. 2 can be estimated in a similar way to the calculation made in Ref. 4, using the formula

$$N_{\rm Cl} = V_i N N_{\rm A} \rho_{\rm Cl} (1/A_{\rm Cl})$$

where V_i is the volume of the "i" inclusion, N is the density of inclusions, N_A is Avogadro's number, ρ_{Cl} is the density of the CdCl₂–CdTe phase, and A_{Cl} is the relative atom mass of Cl. In consequence, taking into account the shape and the size of the inclusions shown in Fig. 2(a) and if the etch-pits density $N = 10^2-10^3$ cm⁻³, one can calculate the value of N_{Cl} as high as 10^{14} – 10^{15} cm⁻³, while the nominal doping concentration in the feed is 5×10^{18} cm⁻³. This means that an increase of N up to 10^5-10^6 cm⁻³ is needed to make the concentration of Cl atoms in inclusions comparable with the total Cl concentration in the bulk, which in turn means that the segregation of Cl can influence significantly the concentration of Cl in the bulk. But if the concentration of Cl in the vapor-grown material is much lower than in the feed, the influence of precipitates is larger. The estimation made by Fiederle *et al.*¹³ shows that real concentration of electrically active Cl can be around 5×10^{15} cm³, and in this way the inclusions would have served for "self-cleaning" of the bulk crystal during the cooling process, which is an important factor for obtaining high-resistivity crystals.

One can also roughly estimate the Cl distribution into the bulk during the annealing process in the following way. Using the calculation of the impurities diffusion length from inclusions in $CdTe^7$ and taking into account the diffusion coefficient for Cl^{20}

$$D (\text{cm}^2 \text{ s}^{-1}) = (0.071 \text{ to } 2.4) \exp(-1.6 \text{ eV}/kT)$$

and the parameters of our annealing process (T = 600 °C and t = 4 h), the obtained diffusion length can be as much as 30 μ m. This means that the homogenization of the Cl distribution can be really reached during the annealing process.

The latest experimental results obtained with the lowtemperature photoluminescence study²¹ show an increase of the Cl- and Na-related LT PL bands after the annealing process due to the Cl and Na impurities diffusion into the bulk. The earlier results of Saminadayar *et al.*¹¹ and Tanaka *et al.*¹⁸ are in good agreement with our results. Furthermore, the confirmation of the Cl-rich inclusions dissolution in CdTe:Cl during annealing can be also found in Ref. 14. More work is currently being done on the analysis of the kinetics of Cl-rich inclusion dissolution with the help of the spatially resolved cathodoluminescence and Raman scattering methods, in the same way as it was published for undoped CdTe.^{15,16}

IV. CONCLUSIONS

Morphological SEM study of the typical inclusions in semiintrinsic CdTe:Cl and CdTe:Zn:Cl samples grown by the modified Markov technique was carried out combined with the composition measurement of inclusions by EDAX. Reference undoped Bridgman-grown CdTe samples were used. In CdTe:Cl and CdTe:Zn:Cl crystals typical inclusions of 10–15 μ m containing Cl and Na impurities were found. The Cl is concentrated in 1–2 μ m small seedlike or oval-shaped inclusions up to 30 at.%. The annealing of the samples in Cd-vapor atmosphere has been found to be fruitful to obtain more uniform samples with a Cl concentration at the level of the EDAX sensitivity.

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