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Effect of Yb concentration on the resistivity and lifetime of CdTe:Ge:Yb codoped crystals

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The resistivity and electron lifetime of CdTe:Ge:Yb crystals are reported, demonstrating that the effect of Yb concentration is crucial for accurate electrical compensation. It is also demonstrated that the codoping of CdTe with Ge as deep donor and with Yb as rare-earth element could be a promising way to obtain semiinsulating CdTe crystals with good transport properties. High resistivity ($5 \times 10^9 \Omega \text{ cm}$) and lifetime ($9 \mu\text{s}$) were obtained, thus confirming the beneficial effect of rare-earth doping. © 2007 American Institute of Physics. [DOI: 10.1063/1.2815644]

Substantial efforts are being made to improve important physical properties of a number of different materials by doping with rare-earth elements, ytterbium in particular. Several recent examples are the studies of Yb doping in soft-glass fibers,¹ ceramics,² nonorganic compound nanocrystals,³ garnet crystals,⁴ phosphors,⁵ proton conductors,⁶ etc.

In III-V compound semiconductors doped with rare-earths (for example, GaAs doped with Yb and Er), a significant increase of photoluminescence efficiency and carrier lifetime has been observed.⁷ This effect is probably related with the new defect levels formed by rare-earth dopants and with the ability of rare-earth elements to react with residual impurities in semiconductor lattices (the so-called “cleaning” process). In II-VI semiconductors, the effects of rare-earth doping on magnetic and optical properties have been reported (see for example Refs. 8–11). However, the electrical and transport charge properties of these materials, in particular CdTe, have not been thoroughly studied.

There is an increasing interest in the development of large semi-insulating CdTe single crystals with excellent transport charge properties (high $\mu\tau$ product) for their application as x- and gamma-ray detectors as well as in the optoelectronic field.^{12–15} Unfortunately, stoichiometrically grown undoped CdTe crystals exhibit a low p -type resistivity due to the presence of native acceptor defects (Cd vacancies) and to the group I residual impurities like Na, Li, Cu, and K. One of the possible ways to increase CdTe resistivity is the compensation of native acceptors by doping with deep donors like Ge, Sn, or V.^{16–20} The main drawback is that these dopants introduce fast recombination centers (the so-called S -centers), thus deteriorating the transport charge properties of CdTe crystals.¹² Nowadays, this is one of the major factors that constrain the development of CdTe-based x- and gamma-ray detectors.

In our opinion, the codoping of CdTe with deep donors and rare-earth elements could be a promising way to over-

come this difficulty and obtain semi-insulating CdTe crystals with good transport charge properties. In this work, the resistivity and electron lifetime of CdTe:Ge:Yb crystals are reported, demonstrating that the concentration of Yb is crucial for a precise electrical compensation.

Ge and Yb codoped CdTe crystals were grown by the vertical Bridgman method using the standard conditions reported elsewhere.²¹ Based on previous results on the growth and properties of Ge-doped CdTe and considering the theoretical simulation results reported below, the nominal Ge concentration was kept constant at $5 \times 10^{17} \text{ cm}^{-3}$ in all CdTe:Ge:Yb crystals whereas the Yb concentration varied in the range from 10^{17} to 10^{19} cm^{-3} . The $10 \times 10 \text{ mm}^2$ area 1 mm thickness characterized samples were cut perpendicularly to the crystal growth axis and subsequently chemomechanically polished. A scanning electron microscopy inspection of the samples was made using a Philips XL30 microscope equipped with an EDX 4i analyzer in order to identify possible formations of third phases. The current dopant and residual impurity concentrations were measured using inductively coupled plasma mass spectroscopy with a mass spectrometer ELAN-6000 (PE-Sciex). After electrochemical gold contact deposition, the I - V characteristic curves of the samples were measured using a high voltage source NHQ-105L and a Keithley 6840 electrometer. Applying the setup reported elsewhere,²² room temperature quadrature frequency resolved photoconductivity measurements were performed using a Stanford SR830 lock-in amplifier and a 780 nm diode laser (Lablaser) as excitation light.

Previous to the experiments, we made a theoretic simulation for the electrical resistivity of CdTe:Ge:Yb crystals using the compensation model developed for GaAs^{23,24} and adopted for CdTe.²⁵ The resistivity behavior was examined as a function of the concentrations of both dopants, assuming the presence of two deep donor levels corresponding to $\text{Ge}^{+2/+3}$ at $E_C - 0.8 \text{ eV}$ (Ref. 12) and $\text{Yb}^{+2/+3}$ at $E_C - 1.2 \text{ eV}$.²⁶ A first set of simulations was made fixing the Ge concentration at $5 \times 10^{17} \text{ cm}^{-3}$, which is the typical value to obtain the

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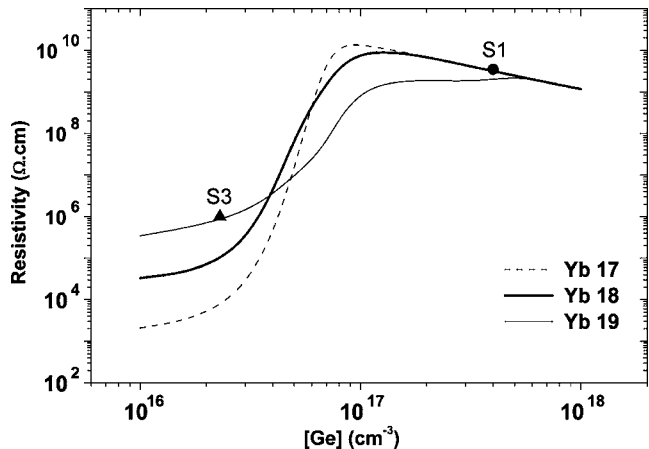


FIG. 1. The theoretic electrical resistivity of CdTe:Ge:Yb crystals as a function of Ge concentration for three different Yb concentrations (Yb 17— $1 \times 10^{17} \text{ cm}^{-3}$, Yb 18— $1 \times 10^{18} \text{ cm}^{-3}$, and Yb 19— $1 \times 10^{19} \text{ cm}^{-3}$). The points marked as S1 and S3 corresponds to the same crystals in Table I.

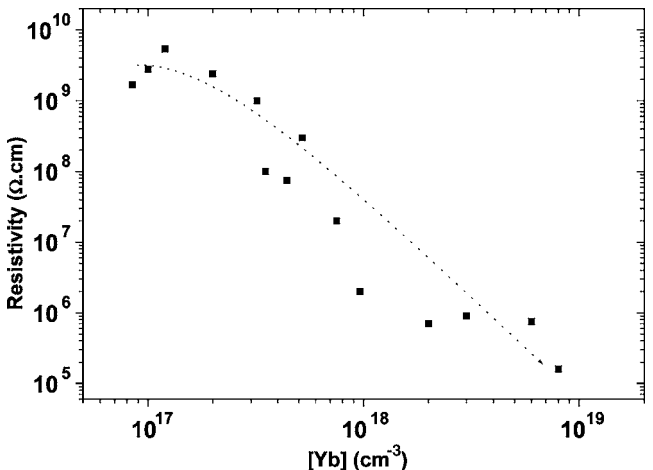


FIG. 2. The experimental resistivity of CdTe:Ge:Yb crystals with the nominal Ge concentration of $5 \times 10^{17} \text{ at./cm}^3$ as a function of Yb concentration (dotted line is only a visual guide).

native acceptor compensation in Ge-doped CdTe crystals,¹² and varying the Yb concentration from 1×10^{17} to $1 \times 10^{19} \text{ cm}^{-3}$. A second set of simulations was made fixing the Yb concentration at three different values and varying the Ge concentration from 1×10^{16} to $1 \times 10^{18} \text{ cm}^{-3}$. The simulation results are shown in Fig. 1.

It has been seen that the resistivity of CdTe:Ge:Yb crystals strongly depends on the Ge concentration, increasing drastically in the range 5×10^{16} – 10^{17} cm^{-3} and slowly above 10^{17} cm^{-3} . According to the simulations, the maximum resistivity is obtained at the lowest Yb concentration. In addition, the simulations point out that resistivity has a lower dependence on Ge concentration at larger Yb concentrations.

Resistivity has a weak dependence on the Yb concentration at Ge concentrations around $5 \times 10^{17} \text{ cm}^{-3}$, varying less than half an order of magnitude in all the studied range. This is an expected result since Yb introduces a very deep donor level that is barely ionized at room temperature and, consequently, not affecting the CdTe:Ge:Yb resistivity. It is also worth noticing that these simulation features could be experimentally observed in CdTe:Ge:Yb crystals only when the inclusion of Yb does not affect the Ge concentration.

The experimental results in Table I show the nominal (i.e., introduced intentionally at the growth) and actual (measured) concentrations of Ge and Yb dopants as well as the concentrations of acceptors and donors in CdTe:Ge:Yb crystals. It can be seen that the Yb doping affects the solubility of codopant Ge and the concentrations of electrically active residual impurities and native defects. When the Yb concentration increases, both the Ge concentration and the total acceptor and donor concentrations decrease. The latter effect could be explained by the high reactivity of Yb dopants that act as

cleaning agents, reacting with the group I residual impurities and segregating them to the top of the CdTe:Ge:Yb crystal ingot; in a similar way as it was reported for III-V semiconductors.²⁷ The decrease of Ge concentration with an increase of Yb concentration could be due either to the reaction between both codopants or to the fact that Ge and Yb occupy the same position in CdTe lattice, i.e., both substitute Cd. The Yb atoms might preferentially occupy this position since Yb is chemically more similar to Cd than Ge.

Figure 2 shows the resistivity of CdTe:Ge:Yb crystals with the nominal Ge concentration of $5 \times 10^{17} \text{ at./cm}^3$ as a function of Yb concentration. Contrary to the theoretical data of Fig. 1, the experimental data reveal the drastic reduction of resistivity up to $10^6 \Omega \text{ cm}$ with an increase of Yb concentration. Only in a narrow Yb concentration range from 1×10^{17} to $3 \times 10^{17} \text{ cm}^{-3}$, the CdTe:Ge:Yb crystals keep a semi-insulating behavior similar to that of CdTe:Ge, with resistivity values larger than $10^9 \Omega \text{ cm}$. This resistivity behavior could be understood only by taking into account the data of Table I. Note that sample S1 (the low Yb concentration sample in Table I) has an experimental resistivity of $5.5 \times 10^9 \Omega \text{ cm}$, which is in agreement with the corresponding theoretical value in Fig. 1 ($4 \times 10^9 \Omega \text{ cm}$). In this case, CdTe:Ge:Yb is very similar to CdTe:Ge because the Yb concentration is low and its influence is almost negligible. When the Yb concentration increases, the resistivity falls with the decrease of actual Ge concentration due to substitution of Ge atoms by Yb in the Cd sublattice. Thus, a resistivity reduction is linked to a lower Ge concentration.

Figure 3 presents the evolution of electron lifetime as a function of the Yb concentration in CdTe:Ge:Yb crystals. Results for undoped and Ge-doped CdTe crystals are also

TABLE I. Nominal (i.e., introduced intentionally at growth) and actual (measured) concentrations of the Ge and Yb dopants and the concentrations of acceptors and donors in CdTe:Ge:Yb crystals.

Sample	Nom. (Ge) (at./cm ³)	Nom. (Yb) (at./cm ³)	(Ge) (at./cm ³)	(Yb) (at./cm ³)	(N _A) (at./cm ³)	(N _D) (at./cm ³)
S1	5×10^{17}	1×10^{17}	4×10^{17}	1.2×10^{17}	3.3×10^{16}	1×10^{16}
S2	5×10^{17}	1×10^{18}	7×10^{16}	8.8×10^{17}	2.5×10^{16}	1.6×10^{16}
S3	5×10^{17}	1×10^{19}	2.3×10^{16}	6×10^{18}	2.1×10^{16}	9.7×10^{15}
S4	5×10^{17}	0	3.7×10^{17}	N.D.	6×10^{16}	2.2×10^{16}

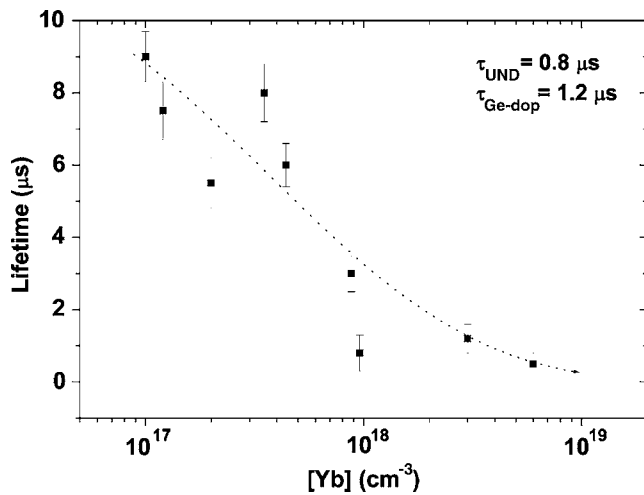


FIG. 3. The evolution of electron lifetime as a function of the Yb concentration in CdTe:Ge:Yb crystals (dotted line is only as visual guide). τ_{und} is the electron lifetime of a typical undoped CdTe crystal. $\tau_{\text{Ge-dop}}$ is the electron lifetime of a typical Ge-doped CdTe crystal (S4 in Table I).

presented for comparison purposes. The most remarkable feature is that the CdTe:Ge:Yb lifetime increases to the values from 5.5 to 9 μs in the Yb concentration range where the crystals are semi-insulating. A further increment in the Yb concentration leads to a decrease of lifetime. This behavior could be explained by two possible mechanisms acting in different ways. The first one, and presumably most important, is the cleaning process due to the interaction of Yb dopants with residual impurities (e.g., see Ref. 27). Note in Table I that the major reduction of the impurities concentration is detected when the Yb concentration is low. The second possible mechanism is related with changes of the defect level structure in CdTe:Ge:Yb crystals in comparison to that of the undoped and Ge-doped CdTe crystals. This mechanism has been considered for CdTe crystals doped with deep donors as a possible explanation for improving transport charge properties.²⁸

In summary, we demonstrated that the codoping of CdTe with Ge as deep donor and Yb as rare-earth element could be a promising way to obtain semi-insulating CdTe crystals with good transport properties. High resistivity ($5 \times 10^9 \Omega \text{ cm}$) and lifetime (9 μs) have been obtained, thus verifying the beneficial effect of the rare-earth doping that seems to be generic for many different materials.

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