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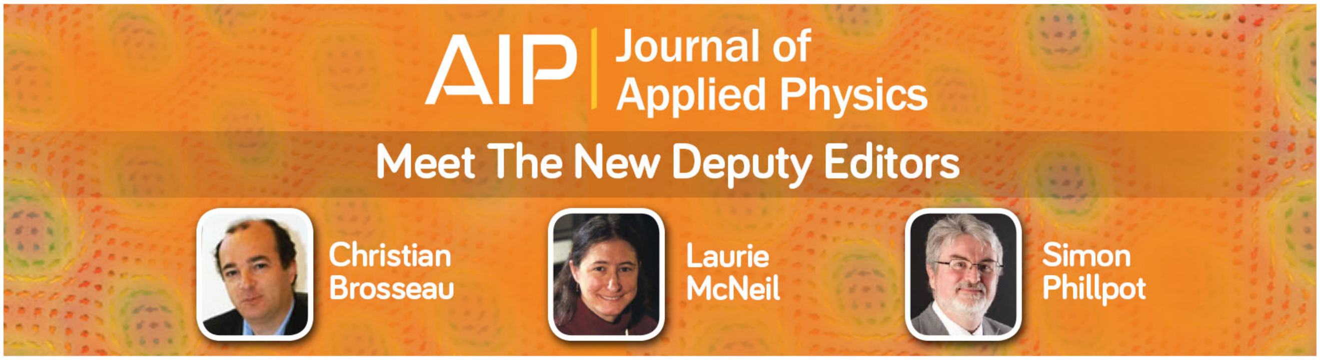

Deep levels in GaTe and GaTe:In crystals investigated by deep-level transient spectroscopy and photoluminescence

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Deep levels of undoped GaTe and indium-doped GaTe crystals are reported for samples grown by the vertical Bridgman technique. Schottky diodes of GaTe and GaTe:In have been fabricated and characterized using current-voltage, capacitance-voltage, and deep-level transient spectroscopy (DLTS). Three deep levels at 0.40, 0.59, and 0.67 eV above the valence band were found in undoped GaTe crystals. The level at 0.40 eV is associated with the complex consisting of gallium vacancy and gallium interstitial (V_{Ga}-Ga_i), the level at 0.59 eV is identified as the tellurium-on-gallium antisite (Te_{Ga}), and the last one is tentatively assigned to be the doubly ionized gallium vacancy (V^*_{Ga}). Indium isoelectronic doping is found to have noticeable impacts on reducing the Schottky saturation current and suppressing the densities of Te_{Ga} and V^*_{Ga} defects. The peak which dominated the DLTS spectrum of GaTe:In is assigned to be the defect complex consisting of V_{Ga} and indium interstitial (In_i). Low-temperature photoluminescence (PL) spectroscopy measurements were performed on GaTe and GaTe:In crystals. A shallow acceptor level at 140 meV corresponding to V_{Ga} was measured in undoped GaTe. Two shallow acceptor levels at 123 and 74 meV corresponding to V_{Ga} and indium-on-gallium antisite In_{Ga} were observed in GaTe:In samples. The PL results suggested that the indium atoms could occupy gallium vacant sites during GaTe crystal growth period and thereby change the electrical and optical properties of GaTe crystal. © *2009 American Institute of Physics*. [DOI: 10.1063/1.3080157]

I. INTRODUCTION

The layered III–VI semiconductor crystal GaTe has potential application in photoelectronic devices; its optical and electrical properties have been studied for decades.[1–12] The band-gap energy of GaTe at room temperature is around 1.7 eV. This value is ideal for room-temperature x-ray and gamma-ray radiation detector applications. For this application, the band gap of the material is required to be high enough to achieve high resistivity, but low enough to keep electron-hole pair ionization energy small. Undoped GaTe is *p*-type with low resistivity (20 $\Omega\cdot$cm) and low mobility (15 $cm^2/V\cdot s$).[2] To meet radiation detector application requirements (resistivity $>1\times10^9$ $\Omega\cdot$cm, mobility $\sim 1\times10^3$ $cm^2/V\cdot s$), the material should possess deep levels near the middle of the band gap,[13] and dopants have to be introduced into the material to compensate the native shallow acceptors. The type and intensity of both intrinsic and extrinsic defects have influence on the fundamental properties of GaTe; it is important to study defect levels between the valence and the conduction bands of GaTe crystals.

Deep-level transient spectroscopy (DLTS) and low-temperature photoluminescence (PL) techniques are two sensitive techniques to identify defects. Free-exciton, bound-exciton, and edge emissions of undoped GaTe crystal have been well investigated,[7–12] and a shallow acceptor level around 0.15 eV has been reported and identified to be gallium vacancy V_{Ga}. Undoped GaTe Schottky diodes were fabricated and tested,[3–6] and one DLTS measurement conducted at room temperature and above was reported.[4] GaTe crystal has a monoclinic structure with space group $C2/m$,[7] while the well-studied GaSe crystal has a hexagonal structure with space group P$\bar{6}$2m; it is interesting to study the defects of GaTe in comparison with those of GaSe.[14] In this article, we have grown GaTe and GaTe:In crystals, fabricated and characterized GaTe and GaTe:In Schottky diodes using current-voltage, capacitance-voltage, and DLTS. Three deep acceptor levels associated with gallium vacancy, at least two of them had never been reported, have been found and identified. One shallow acceptor level associated with indium antisites In_{Ga} has been obtained from low-temperature PL measurement of GaTe:In. We found that the indium isoelectronic doping could decrease the intensities of defects associated with V_{Ga} significantly and thereby improve GaTe diode quality noticeably.

II. EXPERIMENT

Undoped GaTe and GaTe:In crystals doped with 400 ppm indium were grown at EIC Laboratories and Fisk University by the vertical Bridgman method. The typical sample sizes of undoped GaTe and GaTe:In grown at EIC Laboratories and undoped GaTe at Fisk University were $16.3\times6.6\times0.9$, $14.0\times3.9\times0.4$, and $10.0\times5.0\times0.5$ mm^3, respec-

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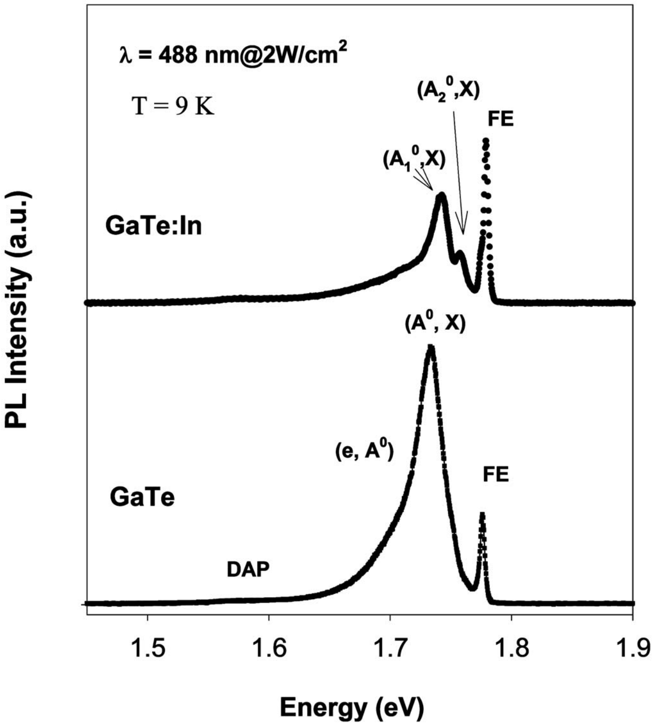

FIG. 1. Low-temperature photoluminescence spectra of GaTe and GaTe:In crystals grown at EIC Laboratories.

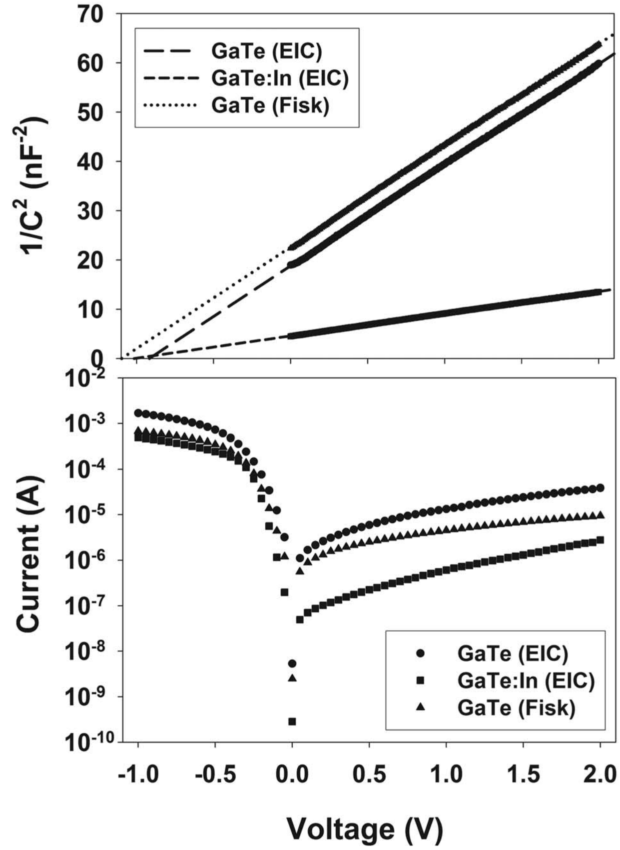

FIG. 2. The I-V curve (down) and the plot of $1/C^2$ vs voltage (up) for GaTe and GaTe:In Schottky diode tested at room temperature. The Au contact was grounded. The diameter of Sn contact was 1.0 mm.

tively. Sn metal spots with diameter of 1.0 mm were sputtered onto the fresh-cleaved GaTe (001) surfaces to create Schottky contacts; Au layers with area around 16 mm^2 were then sputtered to the opposite surfaces to form Ohmic contacts.

Current-voltage, capacitance-voltage, and DLTS measurements were carried out on the Schottky diodes to analyze their characteristics. Details of DLTS and PL measurements have been reported elsewhere.[14] Briefly, DLTS capacitance varied from 140 to 360 K was measured at 1 MHz using a Boonton 7200 capacitance meter; PL signals at 9 K were collected with a SPEX 1877D Triplemate spectrometer, and the samples for PL measurement were illuminated with the 488-nm argon-ion laser with intensity of 2.0 W/cm^2.

III. RESULTS AND DISCUSSION

The low-temperature PL spectra of GaTe and GaTe:In differed noticeably, although indium and gallium belonged to the same IIIA family. Typical PL spectra of GaTe and GaTe:In crystals at 9 K are shown in Fig. 1. The peak energies of ground state free exciton (FE) emissions of GaTe and GaTe:In samples are located at 1.776 and 1.779 eV, respectively. The band gaps of GaTe and GaTe:In are thereby estimated to be 1.794 and 1.797 eV, respectively, if the binding energies of FEs are taken to be 18 meV.[12] The dominant PL peak of undoped GaTe located at 1.734 eV is the bound exciton emission, an exciton bound to an acceptor (A^0, X). The edge emissions including donor-acceptor pair (DAP) transition located at 1.57 eV and free electron to neutral acceptor transition (e, A^0) at 1.69 eV are very weak. The activation energy of acceptor A (E_A) can be estimated by using the Haynes factor (0.3) which was given in Ref. 12. The energy required to free the bound exciton from the acceptor is 42 meV; the energy E_A required to free a carrier is thereby given as 140 meV. For GaTe:In, it is interesting to see two peaks located at 1.742 and 1.757 eV appeared in the region of (A^0, X) of undoped GaTe. The energy difference of the two peaks is 15 meV; the value agrees well with the optical phonon mode energy (14 meV) obtained in Ref. 9; however, the second peak may not be the phonon replica of the first one. The two peaks are attributed to (A_1^0, X) and (A_2^0, X), and the corresponding activation energies are 123 and 74 meV, respectively. To observe phonon replicas of the bound excitons, the quality of the samples may need further improvement. It is generally accepted that the 140 meV level in undoped GaTe sample originates from gallium vacancy V_{Ga}. Doped with indium, some of the gallium vacancies can be occupied by indium atoms which lead to formation of In_{Ga}. In GaTe:In, the activation energy of In_{Ga} is expected to be shallower than that of V_{Ga} as in GaSe:In crystal.[14] A_1 is attributed to V_{Ga} defect, thus, it is reasonable to identify A_2 as In_{Ga} defect.

Figure 2 shows the current-voltage characteristics and the plot of $1/C^2$ vs voltage for GaTe and GaTe:In Schottky diode measured at room temperature. One can see that good rectification is obtained. The diodes conduct in forward direction when a negative bias is applied to the Sn contact. The reverse current of GaTe:In grown at EIC Laboratories at each applied voltage was one order of magnitude smaller than that of undoped GaTe grown at EIC Laboratories. The result

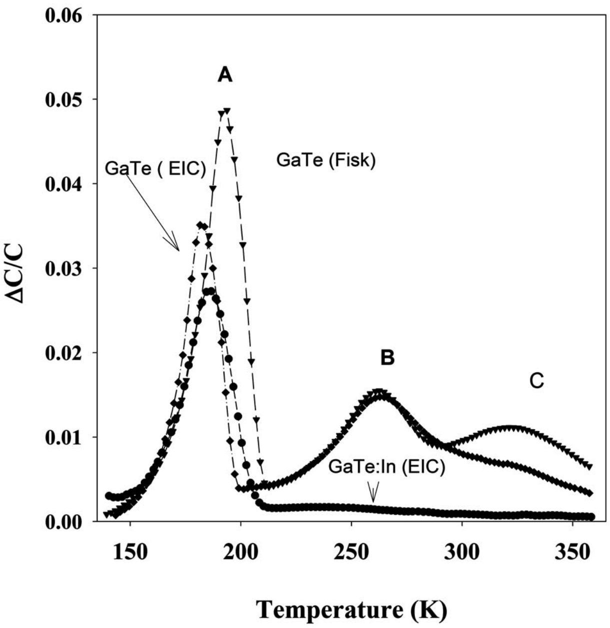

FIG. 3. DLTS spectra of undoped GaTe grown at EIC Laboratories and Fisk University, and GaTe:In grown at EIC Laboratories. The filling pulse was 0 V with width of 1 ms. The measurement bias was 1 V. The rate window was 30/s.

shows that In doping could improve quality of GaTe diodes. Both forward and reverse currents of GaTe grown at Fisk University are smaller than those of GaTe grown at EIC Laboratories. The result is possibly due to the fact that larger numbers of deep defects in GaTe sample grown at Fisk University were absent in GaTe grown at EIC Laboratories (please see peak C in DLTS spectra in Fig. 3.). The formation of a high-quality low-leakage Schottky diode is desirable for radiation detector applications. The samples of GaTe grown at EIC Laboratories, GaTe at Fisk University, and GaTe:In at EIC Laboratories were all p-type semiconductor materials and the carrier (hole) concentrations N_A measured by C-V were 2.0×10^{16}, 2.0×10^{16}, and $1.0\times10^{17}/\mathrm{cm}^3$; the built-in potential were -0.9, -1.1, and -1.0 V at room temperature by taking dielectric constant $\varepsilon=7.3$.[2]

Initial DLTS spectra of GaTe and GaTe: In crystals are shown in Fig. 3. The filling pulse was 0 V with width of 1 ms, the measurement bias was 1 V, and the rate window was 30/s. The DLTS spectrum was generated from the difference in capacitance at two points during the emission transient as a function of temperature.[15] The emission rate was extracted from a fit of the capacitance transient at each temperature as follows:

$$C(t) = C_0 + \Delta C \exp(-t\ \ e_p), \tag{1}$$

where C_0 is the capacitance prior to the filling pulse, ΔC represents the difference between the capacitance at the beginning and at the end of the filling pulse, and e_p is the hole emission rate. Three well-defined peaks, labeled as A, B, and C were observed in undoped GaTe grown at Fisk University. Two peaks, A and B, were observed in undoped GaTe grown at EIC laboratory, and peak A was found in GaTe:In sample. In the previous DLTS study in Ref. 4, only one peak was reported, located between 340 and 360 K. The rate window was $320\ \mathrm{s}^{-1}$, which shifts the peak to higher temperature. Therefore, it is reasonable to believe that the defect associated with peak C is the same type defect reported in Ref. 4. The defects associated with peaks A and B had never been reported. Peak A has the strongest signal in the initial measurements in each sample. For undoped GaTe samples from the different sources, peak A appears at slight different positions with different intensities, while the peak intensities and positions of peak B are almost the same in each sample. It is also noteworthy that peak B is thermally stable; their peak positions and intensities are almost the same regardless of their thermal history. Peaks A and C, however, are thermal history dependent. Peak C gets stronger and stronger if the sample is kept at higher temperature (360 K, for example) for longer time. The result seems consistent with that reported in Ref. 4 that the concentration of the defect increases with increasing annealing temperature. The intensity of peak A becomes weaker (for both EIC and Fisk samples); their peaks shift to lower temperature (for EIC sample) if GaTe samples were under thermal treatments. Peaks B and C of GaTe: In are extremely weak compared to the peaks in undoped GaTe; the peaks have been suppressed with indium doping. It is reasonable to suggest that peaks B and C are V_{Ga}-related defects since the doped indium atoms can occupy V_{Ga} sites, and therefore decrease the total number of V_{Ga}.

When the holes are emitted to the maximum of the valence band, the dependence of hole emission rate e_p on the temperature is given as follows:

$$e_p = (\sigma_p v_p N_v)\exp(-E_t/kT), \tag{2}$$

where σ_p is the hole capture cross section, v_p is the hole average thermal velocity, N_v is the density of states of the valence band, E_t is the thermal activation energy, k is the Boltzmann constant, and T is the peak temperature. If one assumes that v_p varies as $T^{1/2}$ and N_v as $T^{3/2}$, the activation energy and capture cross section of the trap levels can be determined from the slope and intercept of Arrhenius plot of $\ln(T^2/e_p)$ versus $1/kT$. Furthermore, the concentration of a trap can be estimated from the peak height of the DLTS rate window spectrum as[15]

$$N_t = 2\ \ N_A(\Delta C/C_0). \tag{3}$$

Figure 4 shows an Arrhenius plot for traps in GaTe and GaTe:In. The trap energies capture cross sections, and assignments are listed in Table I.

Since GaAs, GaN, and CdTe semiconductors are well studied, the defect assignments in GaAs:In,[16] GaN:In,[17] and CdTe (Ref. 18) can shed light on our defect assignments. The defect associated with peak B is thermally stable gallium vacancy V_{Ga} related and sample source independent; it is reasonable to identify the defect as $\mathrm{Te}_{\mathrm{Ga}}$, tellurium-on-gallium vacancy. Peak A of GaTe samples is thermal history dependent; we speculate that the peak is associated with a defect complex consisting of V_{Ga} and gallium interstitial Ga_i, the concentration of V_{Ga} is larger than that of Ga_i. When the sample was thermal treated, some of V_{Ga} and Ga_i were annihilated, while some of V_{Ga} defects remained due to a higher concentration of V_{Ga} relative to the concentration of Ga_i. For GaTe:In samples, the In_i concentration is expected to be

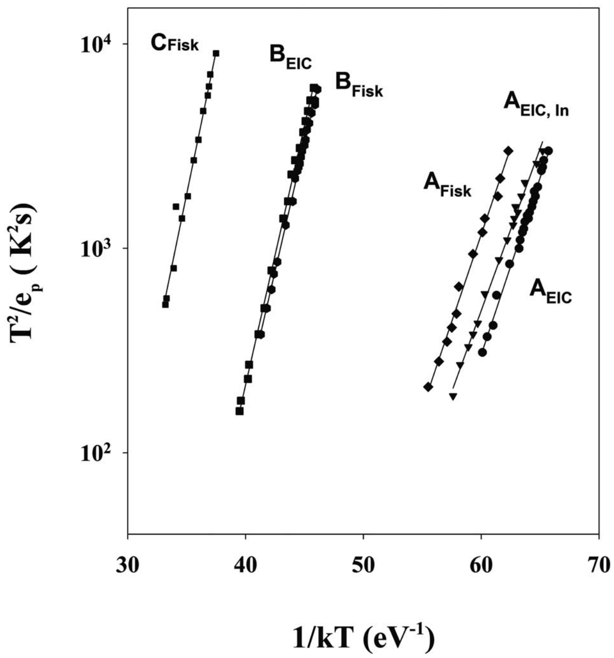

FIG. 4. Arrhenius plot for traps in undoped GaTe grown at EIC Laboratories and Fisk University, and GaTe:In grown at EIC Laboratories. The trap energies capture cross sections, assignments, and concentration are listed in Table I.

larger than that of Ga_i. The defect complex associated with peak A might be composed of V_{Ga} and indium interstitial In_i, In_{Ga} could be formed when the sample underwent higher temperature thermal treatment. The defect energy associated with peak C is at 0.67 eV above the valence band, 0.15 eV shallower than that reported at Ref. 4. Since the defect is V_{Ga} related, the intensity of the defect increases when the sample was kept at higher temperature. The defect is tentatively assigned to be the doubly-ionized gallium vacancy (V_{Ga}^{*}).

The activation energies of acceptor defects of GaTe can be calculated using the model based on the effective-mass theory.[19,20] The model predicted that if the activation energy of the single acceptor level is set to be E, the first and second activation energies of the double acceptor levels will be $1.7E$ and $4.0E$; the first, second, and third activation energies of the triple acceptor levels will be $2.5E$, $5.5E$, and $9.0E$. The acceptor level at 0.14 eV obtained from PL measurements, the levels at 0.59 and 0.67 eV from DLTS measurements might be the acceptor levels of E, $4.0E$, and $5.5E$; however, further investigation using double correlated DLTS (DDLTS) methods are necessary to clarify the charge states of the acceptor levels.

In summary, we have grown GaTe and GaTe:In crystals and fabricated and characterized GaTe and GaTe:In Schottky diodes. We have identified acceptor levels among the crystals by conducting measurements of low-temperature PL and DLTS. Our investigation will be helpful to develop GaTe-based optoelectronic device applications.

TABLE I. The acceptor types, energies, capture cross sections, and concentrations determined by DLTS for the GaTe and GaTe:In crystals.

Peak	Acceptor type	Activation energy (eV)	Capture cross section (cm^2)	Density (cm^{-3})
A_{EIC}	V_{Ga}-Ga_i	0.40	2.7×10^{-14}	1.4×10^{15}
$A_{EIC,In}$	V_{Ga}-In_i	0.38	3.9×10^{-15}	5.6×10^{15}
A_{Fisk}	V_{Ga}-Ga_i	0.39	3.7×10^{-15}	2.0×10^{15}
B_{EIC}		0.59	2.2×10^{-14}	6.0×10^{14}
B_{Fisk}	Te_{Ga}	0.58	2.2×10^{-14}	6.4×10^{14}
C_{Fisk}	V_{Ga}^{*}	0.67	2.7×10^{-15}	4.4×10^{14}

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