Comparison of electrical and luminescence data for the *A* center in CdTe

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We have investigated the electrical and optical properties of the deep levels responsible for the 1.4–1.5 eV luminescence band usually observed in II–VI compounds. We compared the energy levels found by cathodoluminescence and junction spectroscopy methods for semi-insulating (CdTe:Cl and $Cd_{0.8}Zn_{0.2}Te$) and semiconducting samples (undoped CdTe). The techniques utilized were deep level transient spectroscopy (DLTS) on semiconducting samples and photoinduced current transient spectroscopy and photo-DLTS on high resistivity materials. These last two techniques are complementary and allow the determination of the trap character (donor/acceptor). Three acceptor levels are seen in the electrical transient data at $E_v+0.12$, 0.14, and 0.16 eV with hole capture cross sections of 2×10^{-16}, 1×10^{-16}, and 4×10^{-17} cm^2, respectively. The lowest level is seen only in Cl doped material corroborating the literature optical and electron spin resonance identification of a level at $E_v+0.12$ eV as being a $V_{Cd}+Cl_{Te}$ donor–acceptor pair center. All three levels may be present in the 1.4 eV luminescence band. © *1996 American Institute of Physics.* [S0003-6951(96)04949-2]

Cadmium–telluride is a wide band gap II–VI compound that has promising applications as an x- and γ-ray detector, thanks to its high average atomic number and to its good mobility-lifetime product, for both electrons and holes. In order to obtain the high resistivity ($\rho > 10^8$ Ωcm) required for such applications, CdTe crystals are usually grown in Te-rich conditions and doped during growth with group III (Ga,In) or group VII (Cl,Br) donors. Due to the Te-rich growth conditions, the dominant intrinsic defect are Cd vacancies (V_{Cd}) and related complexes.[1,2] One of the most interesting complexes is the so called *A* center, a single acceptor formed by a cadmium vacancy and a donor.[3] It has been proposed that it plays a major role in the compensation process, namely in the neutralization of the native acceptor defects (V_{Cd}) which provide most of the free carriers.[1,4,5] Some doubts have been recently cast on models that describe *A* center as the sole center responsible for the high resistivity of compensated materials: as its energy level in the band gap is located at approximately $E_v+0.15$ eV, it is too shallow to account for the pinning of the Fermi level near midgap, which is observed in semi-insulating (SI) materials.[6] In order to understand its actual role in the determination of the electrical and optical properties of the material, we have studied the carrier capture and emission processes of the deep levels located at approximately $E_v+0.15$ eV, obtaining information on the origin of the detected traps.

Luminescence investigations recently carried out on CdTe;Cl provided evidence, for the existence of *A* center in CdTe:Cl and suggested its relation to the band located at $\sim$1.4 eV.[7] Junction spectroscopy methods, such as thermally stimulated current (TSC) and photoinduced current transient spectroscopy (PICTS), have also revealed single deep energy levels scattered around $E_V+0.15$ eV.[8–11] We have resolved, in our samples, three different levels located at this energy. The structure of the luminescence band, whether it is due to a single peak or it has multiple components, is still under discussion, as are its nature and origin. In fact, the 1.4 eV band has been reported in the literature to be present in most II–VI compounds, independently of doping and growth method.[6,7,12–16] This implies that there might be other native defects/complexes, extended defects or residual impurities which either emit in the spectral range 1.3–1.5 eV or form complexes with the available V_{Cd}. Therefore, the 1.4 eV band might not be necessarily related to an actual *A* center.[6,8,13,14,17]

We have studied the various components of the 1.4 eV band in order to understand which ones could be reliably attributed to the *A* center. The techniques we have utilized are cathodoluminescence (CL) and junction spectroscopy, such as deep level transient spectroscopy (DLTS),[18] PICTS,[19] and photo-DLTS (P-DLTS).[20] These methods provide an electrical characterization of the defect but do not straightforwardly identify the structure of the defects responsible. Nonetheless, a comparison of the results obtained from various materials sheds light on the defect origin. Moreover, the comparison of the results obtained with the different and complementary spectroscopies used allowed us to determine the character of each deep trap (either donor or acceptor). We have investigated both semiconducting and semi-insulating II–VI compounds, all *p* type: CdTe undoped ($\rho = 30\,\Omega$ cm), CdTe:Cl ($\rho > 10^8\,\Omega$ cm), and $Cd_{0.8}Zn_{0.2}Te$ ($\rho = 10^{11}\Omega$ cm). The CdTe:Cl and CdTe undoped samples were grown by the traveling heater method (THM) while the $Cd_{0.8}Zn_{0.2}Te$ ones were grown by the high pressure Bridgman (HPB) method. Some CdTe:Cl samples have been annealed at $T = 600$ °C for $t = 5$ h in an inert Ar atmosphere, to study the evolution with temperature of the defective states. While CdTe:Cl is made semi-insulating by the presence of Cl via a compensation process, $Cd_{0.8}Zn_{0.2}Te$ is intrinsically highly resistive, as Zn occupies the Cd site and decreases the

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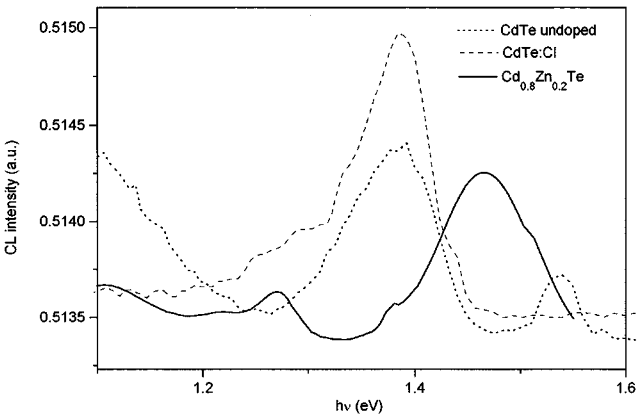

FIG. 1. Cathodoluminescence spectra of CdTe:Cl (dashed line), undoped CdTe (dotted line), and $Cd_{0.8}Zn_{0.2}Te$ (solid line), $T = 80$ K and beam energy 25 keV.

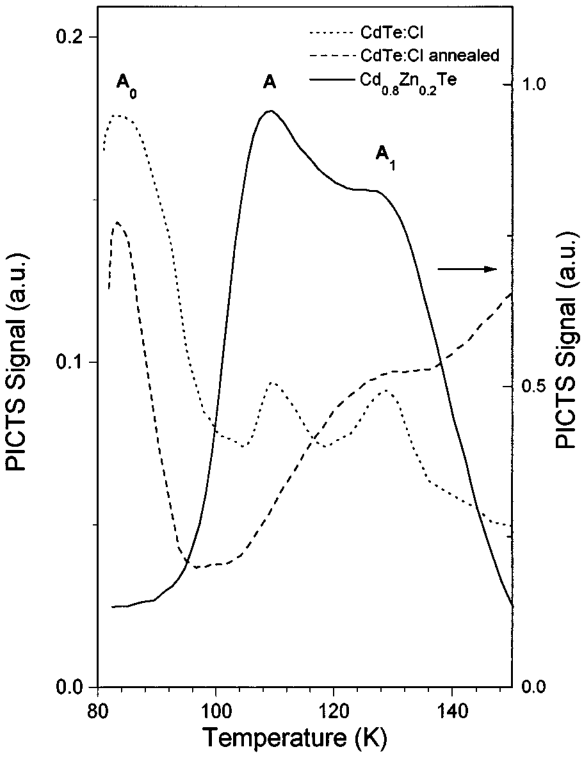

FIG. 2. A comparison of PICTS spectra obtained in identical experimental conditions in three different materials analyzed: CdTe:Cl, CdTe:Cl annealed and $Cd_{0.8}Zn_{0.2}Te$. The pulse width is 1 ms and $e_n = 25$ s^{-1}.

V_{Cd} concentration. While DLTS analyzes capacitance transients and can only be applied to semiconducting materials, PICTS and P-DLTS, which study current transients generated by optical excitation, can be used for the investigation of semi-insulating samples. These last two methods are complementary as PICTS reveals both majority and minority carrier traps without being able to distinguish between them, and P-DLTS reveals only majority carrier traps. Thus, a direct comparison between the PICTS and the P-DLTS results in the same SI sample can provide indication on the donor or acceptor character of the deep levels.

Schottky diodes have been prepared by evaporating Al or In, while the ohmic contacts have been obtained by electroless Au deposition.[26] Junction spectroscopy analyses have been carried out with a SULA Tech. System. The DLTS method has been applied to CdTe undoped samples while PICTS and P-DLTS analyses have been utilized to study CdTe:Cl and $Cd_{0.8}Zn_{0.2}Te$. The excitation wavelength utilized was $\lambda = 880$ nm and the applied bias was $V = 30$ V. The heating rate was 0.2 K/s and the emission rates varied from 5 to 2×10^4 s^{-1}. CL analyses have been performed in an Hitachi S-2500 scanning electron microscope at temperatures between 80 and 300 K, with an accelerating voltage of 25 keV. Emission was measured with a North Coast E0-817 germanium detector.

The results of the CL investigations at $T = 80$ K are reported in Fig. 1 and the 1.4 eV band is clearly visible in all CdTe samples independently of doping.[21] The band in the $Cd_{0.8}Zn_{0.2}Te$ spectrum is shifted to ~1.5 eV, due to the band gap of $Cd_{0.8}Zn_{0.2}Te$ ($E_g \approx 1.65$ eV) being larger than the band gap of CdTe ($E_g \approx 1.54$ eV). The junction spectroscopy data clearly revealed three different peaks in the region corresponding to the 1.3–1.5 eV emission range. A comparison of PICTS spectra, obtained in identical experimental conditions, from the various materials investigated is shown in Fig. 2. The three peaks observed in the region of interest, i.e., the low-temperature region of the spectrum, have been named A_0, A, and A_1. Their apparent activation energies are 0.12, 0.14, and 0.16 eV, with capture cross sections of 2×10^{-16}, 1×10^{-16}, and 4×10^{-17} cm^2, respectively. The errors associated with the activation energies have been calculated from a chi-squared fitting procedure to each data set of the Arrhenius plot (Fig. 3) and are ~6% (± 0.01 eV). The transitions observed in junction spectroscopy experiments can be either identical or complementary to those revealed in CL measurements, and the latter case applies in our samples to the 1.4 eV band and the A center (the band gap of CdTe is $E_g \approx 1.54$ eV). A comparison of a PICTS and P-DLTS spectrum obtained from a CdTe:Cl sample in identical experimental conditions revealed that all three peaks are present in both spectra, thus implying their majority carrier (hole) trap character.

After the annealing treatment peak A seems to disappear. In $Cd_{0.8}Zn_{0.2}Te$ samples only two peaks are present: peaks A and A_1. The peaks are labeled with the same letters in

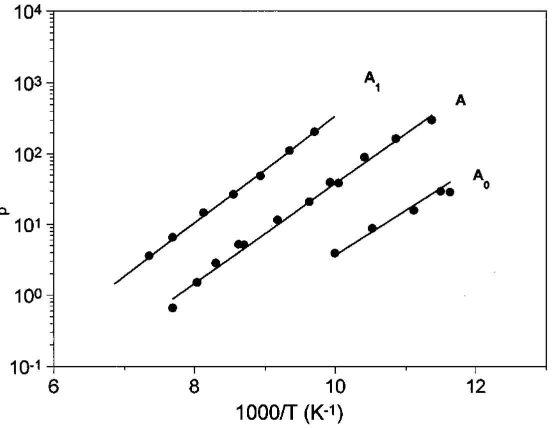

FIG. 3. Arrhenius plots of the deep levels observed in the investigated materials. Experimental data are reported as solid circles, the lines represent the fit to the data sets.

TABLE I. Summary of the levels observed in the various materials investigated.

	CdTe:Cl	CdTe:Cl annealed	CdTe:Cl undoped	CdTe $Cd_{0.8}Zn_{0.2}Te$
A_0	yes	yes		
A	yes		yes	yes
A_1	yes	yes		yes

CdTe as they actually correspond to the same deep levels, as verified by comparing the Arrhenius plot of each level, which is usually considered the ''fingerprint'' of the trap, since it gives both its energy level and apparent capture cross section. The DLTS results have not been included in Fig. 2 together with the other PICTS measurements as they derive from capacitance transients and the determination of the emission rate is different in the current (PICTS, P-DLTS) and capacitance case (DLTS).[18] In order to reliably compare the activation energy and the capture cross section of the levels in undoped CdTe, we have also performed some P-DLTS analyses at low temperature. Both DLTS and P-DLTS revealed the presence of a peak in the 0.12–0.18 eV energy range and, by comparing these results to those relative to CdTe:Cl and $Cd_{0.8}Zn_{0.2}Te$, the peak seen corresponds to level A. The 1.4–1.5 eV bands observed in CL measurements are, in all materials, quite broad and, thus, indicate a complex structure, even though it is hard to resolve their components. The junction spectroscopy measurements (PICTS, P-DLTS, and DLTS) allow us to resolve three possible components of this emission band: peaks A_0, A, and A_1. The peaks that are present in the P-DLTS spectrum correspond to majority carrier traps, i.e., acceptor traps since all materials are p type. In order to achieve a deeper insight on the origin of the revealed traps, we have compared the results obtained from the different materials analyzed. As can be observed in Table I, the shallowest level, A_0, is only present in Cl doped CdTe samples and this suggests its origin is related to the presence of Cl. The Cl association and energy at $E_v + 0.12$ eV corresponds to the (V_{Cd}–Cl_{Te}) complex, the actual chlorine center A.[8] The other two levels, A and A_1, are present in $Cd_{0.8}Zn_{0.2}Te$ which is not intentionally doped. It has been proposed that these levels, recently observed in photoluminescence investigations of undoped CdZnTe, could be related to complexes involving a V_{Cd} and a V_{Te}, respectively.[14] These peaks have been observed to move or to disappear after annealing and cooling treatments,[14] as occurs for level A in CdTe:Cl annealed samples. Other results tend to attribute them to residual impurities, such as Cu or Li, which may combine with native defects to form complexes, with different characteristics than the Cl A center.[3,6,7] Such impurities may also emit in this energy range, as is the case with Cu,[1,6] which is one of the main contaminants of CdTe due to its high diffusion coefficient.

In conclusion, we have investigated the deep energy levels corresponding to the 1.4–1.5 eV luminescence band usually observed in II–VI compounds. Photoluminescence results on CdTe:Cl reported in the literature[7] indicate that the band is composed of three subbands, the shallowest being attributed to a transition involving the chlorine center A (V_{Cd}–Cl_{Te}). Our PICTS and P-DLTS measurements on CdTe:Cl identified three levels, A_0, A, and A_1, with activation energies 0.12, 0.14, and 0.16 eV, respectively, i.e., located in the energy range complementary to 1.4 eV with respect to the 1.54 eV band gap of CdTe. By comparing PICTS and P-DLTS results we were able to determine the acceptor character of all the observed deep levels (hole traps). Levels A and A_1 have also been observed in undoped CdTe and in $Cd_{0.8}Zn_{0.2}Te$ while A_0 results to be peculiar of CdTe:Cl samples. This is in agreement with the attribution of the shallowest of the three bands to the chlorine A center.[7] Moreover, the presence of same A_0 and A_1 levels (i.e., with identical Arrhenius plots) in different Cd-based II–VI compounds, suggests a common origin in the three investigated materials of the defects involved.

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[1] M. Hage-Ali and P. Siffert, Nucl. Instrum. Methods Phys. Res. A **322**, 313 (1992).
[2] P. Höschl, P. Moravec, J. Franc, E. Belas, and R. Grill, Nucl. Instrum. Methods Phys. Res. A **322**, 371 (1992).
[3] J. W. Allen, Semicond. Sci. Technol. **10**, 1049 (1995).
[4] P. Moravec, M. Hage-Ali, L. Chibani, and P. Siffert, Mater. Sci. Eng. B **16**, 223 (1993).
[5] H. Zimmerman, R. Boyn, C. Albers, K. Benz, D. Sinerius, C. Eiche, B. Meyer, and D. Hoffmann, J. Cryst. Growth **128**, 593 (1993).
[6] W. Stadler, D. M. Hoffman, H. C. Alt, T. Muschik, B. K. Meyer, E. Weigel, G. Müller-Vogt, M. Salk, E. Rupp, and K. W. Benz, Phys. Rev. B **51**, 10 619 (1995).
[7] D. M. Hofmann, D. Omling, H. G. Grimmeiss, B. K. Meyer, K. W. Benz, and D. Sinerius, Phys. Rev. B **45**, 6247 (1992).
[8] M. Samimi, B. Biglari, M. Hage-Ali, J. M. Koebel, and P. Siffert, Phys. Status Solidi A **100**, 251 (1987).
[9] C. Eiche, D. Maier, D. Sinerius, J. Weese, K. W. Benz, and J. Honerkamp, J. Appl. Phys. **74**, 6667 (1993).
[10] M. Fiederle, D. Ebling, E. Eiche, D. M. Hofmann, M. Salk, W. Stadler, K. W. Benz, and B. K. Meyer, J. Cryst. Growth **138**, 529 (1994).
[11] A. Castaldini, A. Cavallini, B. Fraboni, L. Polenta, P. Fernandez, and J. Piqueras, Phys. Rev. B (to be published).
[12] C. Norris and K. Zanio, J. Appl. Phys. **53**, 6347 (1982).
[13] K. Suzuki, K. Inagaki, N. Kimura, I. Tsubono, T. Sawada, K. Imai, and S. Seto, Phys. Status Solidi A **147**, 203 (1995).
[14] C. Barnett Davis, D. D. Allred, A. Reyes-Mena, J. Gonzalez-Hernandez, O. Gonzales, B. C. Hess, and W. P. Allred, Phys. Rev. B **47**, 13 363 (1993).
[15] U. Pal, J. Piqueras, P. Fernandez, M. D. Serrano, and E. Dieguez, J. Appl. Phys. **76**, 3720 (1994).
[16] U. Pal, P. Fernandez, J. Piqueras, N. V. Suchinski, and E. Dieguez, J. Appl. Phys. **78**, 1992 (1995).
[17] B. Biglari, M. Samimi, M. Hage-Ali, J. Koebel, and P. Siffert, Nucl. Instrum. Methods Phys. Res. A **283**, 249 (1989).
[18] P. Blood and J. W. Orton, ''*The Electrical Characterization of Semiconductors: Majority Carriers and Electron States* (Academic, London, 1992), Chap. 9, pp. 478–492.
[19] O. Yoshie and M. Kamihara, Jpn. J. Appl. Phys. 1 **22**, 621 (1983).
[20] P. M. Mooney, J. Appl. Phys. **54**, 208 (1983).
[21] U. Pal, P. Fernandez, and J. Piqueras, Mater. Lett. **23**, 227 (1995).

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