Photo-Induced Current Transient Spectroscopy of Semi-insulating Single Crystal Cs₂Hg₆S₇

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The ternary compound Cs₂Hg₆S₇ has shown considerable promise as a wide gap semiconductor for hard radiation detection at room temperature. We report on the measurement of defect levels in Cs₂Hg₆S₇ using photo-induced current transient spectroscopy. We observe a series of defect levels with mean activation energies of 0.053, 0.052, 0.34, 0.35, and 0.46 eV. The defects are attributed to Cs vacancies and Cs and Hg antisite defects. Defect capture cross-sections are in the range 10⁻²⁰–10⁻¹⁵ cm².

Key words: Cs-based semiconductor, wide gap semiconductor, photoconductivity, defects, γ -ray

INTRODUCTION

For efficient gamma-ray radiation detection at room temperature, compound semiconductors with high average atomic numbers, wide band gaps, and high mass densities are much sought after.¹ Currently, there are a number of materials such as CdZnTe, CdTe, HgI₂, PbI₂, and TlBr under investigation for this application.^{2–5} Recently, we have observed that the ternary compound Cs₂Hg₆S₇ with a band gap of 1.63 eV shows considerable promise as a room-temperature x-ray detector.^{6,7} For this compound, the starting polycrystalline materials with higher purity is utilized for growing Cs₂Hg₆S₇ crystals. Crystals with high resistivity of the order of 10⁸ Ω cm were grown. The mobility lifetime ($\mu\tau$) products for electron and hole carriers as determined by photoconductivity measurements are 1.3×10^{-3} and 9.0×10^{-4} cm²/V, respectively. These values are comparable to those of CdZnTe, a leading radiation detector material. We have recently reported on the response of a Cs₂Hg₆S₇ detector to a silver x-ray source and observed a well-resolved spectrum at 22.4 keV at room temperature.⁸

To further improve the performance of the detector, the resistivity and the $\mu\tau$ product need to increase. The efficiency of a semiconductor detector depends on the total charge collection, a property that is proportional to the $\mu\tau$ product of electrons and holes. This product is determined by the electronically active defects that scatter photoexcited carriers.⁹ Furthermore, shallow levels lead to lower resistivity, which in turn leads to higher detector dark current. In contrast, deep level defects can pin the Fermi level in the middle of the band gap leading to higher resistivity and lower dark current. Deep levels, however, can also act as fast recombination centers, leading to decreased carrier lifetime.

We have previously studied the defect formation in Cs₂Hg₆S₇, including shallow and deep levels, by photoluminescence and photoconductivity spectroscopy.^{10,11} From those experiments, we found several levels at 0.08 eV, 0.11 eV, and 0.24 eV. In addition, we have previously calculated, using first-principles density functional theory (DFT), the formation energies of native defects of Cs₂Hg₆S₇ and their concentrations.¹⁰ From these calculations, we concluded that native defects, including the sulfur vacancy V_s , the mercury antisite Hg_{Cs} and the cesium vacancy V_{Cs} , are stable. Among them, V_{Cs} forms a shallow acceptor level. However, one of the

(Received May 13, 2014; accepted August 8, 2014;
published online September 23, 2014)

sulfur vacancy defects, V_S , and the mercury anti-site, Hg_{Cs} , form deep levels. These defects could limit the mobility-lifetime products of the photoexcited carriers of $\text{Cs}_2\text{Hg}_6\text{S}_7$.

In this study, we report on the investigation of defect levels in the semi-insulating semiconductor $\text{Cs}_2\text{Hg}_6\text{S}_7$ by the current transient spectroscopy using light to photoexcite carriers.^{12,13} The photo-induced current transient spectroscopy (PICTS) technique is well-suited for defect detection in semi-insulating materials.¹⁴ The important deep-level defect parameters including trap ionization energy, capture cross-section, and concentration can be obtained. It has been previously used to detect deep-level defects in high-resistivity semiconductors including bulk CdS and CdTe.^{15–17} Although PICTS measurement does not allow one to directly quantify the trap concentration, the spectra can be used to obtain qualitative information on the deep trap concentration.¹⁸ In this study, we report on a series of defect levels in undoped semi-insulating $\text{Cs}_2\text{Hg}_6\text{S}_7$ over the energy range of 0.05–0.46 eV. Identification and subsequent control of these defects should lead to improvements in the semi-insulating semiconductor, leading to both a higher resistivity and a larger $\mu\tau$ product, resulting in high efficiency radiation detectors that operate at room temperature.¹¹

EXPERIMENTAL DETAILS

Growth of $\text{Cs}_2\text{Hg}_6\text{S}_7$ Single Crystals

$\text{Cs}_2\text{Hg}_6\text{S}_7$ polycrystalline materials were first synthesized from high-purity elements using a vapor transport method by reacting appropriate stoichiometric ratios of Cs with $\beta\text{-HgS}$ and S; the detailed procedure has been reported elsewhere.^{6,7} Single crystals were subsequently grown by the Bridgman method using a sealed quartz tube as the crucible. The grown ingots were analyzed by Laue back-scattered reflection to verify their single crystalline nature. Analysis of x-ray diffraction data revealed that the compound is tetragonal with lattice parameters $a = b = 14.505 \text{ \AA}$ and $c = 4.308 \text{ \AA}$. Figure 1 shows the crystal structure of $\text{Cs}_2\text{Hg}_6\text{S}_7$ represented by a ball and stick model. Pink, blue, and yellow balls correspond to Cs, Hg, and S atoms, respectively. The location marked by A indicates the largest interstitial space in the $\text{Cs}_2\text{Hg}_6\text{S}_7$ lattice, which can accommodate an interstitial defect. The $\text{Cs}_2\text{Hg}_6\text{S}_7$ unit cell has one Cs-site, two Hg-sites (tetrahedral site Hg1 and 3-fold planar site Hg2), and three S-sites (2-fold S1, 3-fold S2, and 4-fold S3 coordinated sites).¹⁰ The two mercury atoms have different neighboring atom configurations and therefore their electronic behavior should be different. Similarly, the three sulfur atoms have different neighboring atom configurations and therefore their behavior will also differ.

The dimensions of the $\text{Cs}_2\text{Hg}_6\text{S}_7$ single crystal (HL-2-4-1) used in this study are $\sim 5 \times 4 \times 2 \text{ mm}^3$.

Fig. 1. The crystal structure of $\text{Cs}_2\text{Hg}_6\text{S}_7$ represented by a ball and stick model. Pink, blue and yellow balls correspond to Cs atom, Hg atom, and S atom, respectively. The location marked by A indicates the largest empty space of $\text{Cs}_2\text{Hg}_6\text{S}_7$, which can accommodate an interstitial defect.

Fig. 2. Schematic of PICTS setup. A nitrogen-pulsed laser was used as the excitation source.

Ohmic contacts were made by vacuum depositing 80 nm of semi-transparent gold electrodes on the top and bottom surfaces of the crystals in a parallel plate configuration. The quality of the contacts was assessed from the I–V characteristics. The contacts are ohmic. The crystals are semi-insulating. The measured room temperature resistivity of the crystal cut perpendicular to the growth direction is of the order of $1 \times 10^8 \Omega \text{ cm}$.

Fig. 3. Transient current versus time for different temperatures. For the 20 datasets observed, only 5 are shown. Transient current was measured from 80 K to 310 K. Datasets were collected at 10-K intervals.

Fig. 4. Typical PICTS signals versus temperature for the two-gate method (shifted water fall drawing). Gate 1 was chosen at 100 μ s, 150 μ s, 200 μ s, 250 μ s, and 300 μ s, and gate 2 at 600 μ s, 650 μ s, 700 μ s, 750 μ s, and 800 μ s, respectively.

The PICTS Technique

The PICTS technique is a powerful tool for the determination of the electronic properties of defects in semi-insulating materials. It can identify both the acceptor and donor levels. In PICTS, the device is illuminated with light pulses of definite duration. Above the band gap, light creates electron-hole pairs in a region underneath the semi-transparent metal electrode. When a bias is applied to the device, electrons or holes are transported into the bulk that can be trapped by the defect centers. A positive bias applied to the contact injects only holes into the bulk of the crystal and hence the transient signal is due to the hole current. Similarly, a negative bias applied to the electrode injects electrons and produces a current transient due to detrapping of captured electrons.

The PICTS apparatus consists of a pulsed laser, a high-gain low-noise Keithley 428 current amplifier, a digital oscilloscope, and a liquid nitrogen cryostat. The

Fig. 5. Arrhenius plots for the observed levels, showing the data points and the resulting linear fits. The thermal activation energy and capture cross-section are derived from the slope and intercept of the linear fittings, respectively.

schematic of the system is shown in Fig. 2. The sample is placed in the vacuum cryostat with an optically transparent entrance window. A thermocouple is attached to the sample for monitoring its temperature, and is also connected to a temperature controller. A heater attached to the sample holder enables temperature control from 77 K to 325 K. The excitation light source is a nitrogen-pulsed laser with a wavelength of 337 nm (above band gap excitation). The laser has a pulse width of 3 ns and an output power large enough to saturate the traps in the semiconductor. A DC voltage of +75 V was applied to bias the sample. The crystal was illuminated through the semitransparent Au electrode. Pulsed light excitation results in a transient current signal that is amplified using the current amplifier. The current is then converted into a voltage signal using a 50- Ω resistor and the signal is fed to an oscilloscope. The trigger signal for the oscilloscope is generated by the nitrogen-pulsed laser supply. The measurement of the transient signal is carried out over the temperature range of 80–310 K with a step of 10 K during the heating of the sample with a rate of 2 K/min. The transient curves were sampled at 2000 equally spaced points ($\Delta t = 50 \mu$ s).

To calculate the trap parameters of thermal activation energy and the capture cross-section, the current transient is analyzed using the normalized double-gate PICTS method, whereby two gate times t_m and t_n are selected ($t_n > t_m$) on the transient current curve.¹⁵ Here, the PICTS response signal $S(t)$ is given by:

$$S(t) = I(t_m) - I(t_n) \quad (1)$$

where $I(t)$ is the transient current. The transient current after cessation of the pulse is given as^{19,20}

$$I(t) = Ke_i e^{-e_i t} \quad (2)$$

where e_i is the emission rate (s^{-1}) for trap i with an activation energy E_a . The prefactor K depends on the device parameters and applied bias. The emission rate e_i is given by

Table I. Defect activation energies, carrier capture cross-sections, and tentative defect assignments determined by PICTS for $\text{Cs}_2\text{Hg}_6\text{S}_7$ crystals

Defect	ΔT (K)	E_a (eV)	σ_i (cm^2)	Assignment
A	85–100	0.053 ± 0.020	2.3×10^{-19}	V_{Cs}
B	125–160	0.052 ± 0.011	1.2×10^{-20}	$\text{Cs}_{\text{Hg}1}$
C	200–230	0.34 ± 0.07	4.5×10^{-15}	$\text{Cs}_{\text{Hg}2}$
D	235–260	0.35 ± 0.09	1.0×10^{-15}	Hg_{Cs}
E	285–310	0.46 ± 0.06	5.6×10^{-15}	$V_{\text{S}3}$

Fig. 6. Schematic diagram showing the types of defects in a $\text{Cs}_2\text{Hg}_6\text{S}_7$ crystal.

$$e_i(\text{s}^{-1}) = Ngv_{\text{Th}}\sigma_i e^{-\frac{E_a}{kT}} = HT^2\sigma_i e^{-\frac{E_a}{kT}} \quad (3)$$

where N is the density of states, v is thermal velocity of carriers, g is the trap degeneracy factor,¹⁴ the term σ_i is the capture cross-section of the trap in cm^2 , and T is the temperature. The constant H is given by $H = 2\left(\frac{2\pi m^* k}{h^2}\right)^{1.5} \left(\frac{3k}{m^*}\right)^{0.5}$, where m^* is the effective mass for hole (electron) carriers, k is the Boltzmann constant, and h is Planck's constant. The PICTS signal $S(t)$ has a maximum when

$$\frac{dS}{de_i} \times \frac{de_i}{dT} = 0 \quad (4)$$

Using the condition given by Eq. 4, the relationship between e_i , t_m , and t_n for the maxima of the PICTS peaks is given by:

$$\left(t_n - \frac{1}{e_i}\right) = \left(t_m - \frac{1}{e_i}\right) e^{(t_n - t_m)e_i} \quad (5)$$

Thus, the emission coefficients (e_i) of a defect for different pairs of gate positions t_n and t_m are obtained

using Eq. 5. For a given defect level, a graph of $\log(e_i/T^2)$ versus $1/T$ is plotted. The temperature T corresponds to the temperature that yields a maximum PICTS signal for each pair of gate settings, t_n and t_m . From Eq. 3, it can be seen that the log of the emission rate over T^2 is linear with a slope $-E_a/k$, where E_a is the defect activation energy. The intercept with the $\log(e_i/T^2)$ axis is $\ln(H\sigma_i)$.

RESULTS AND DISCUSSION

Figure 3 shows the observed transient current signal versus time for different temperatures for semi-insulating $\text{Cs}_2\text{Hg}_6\text{S}_7$. Datasets were collected between 80 K and 310 K with a 10-K interval. Of the 20 temperatures in the dataset, only 5 are shown. Five typical PICTS signals versus temperature for the double-gate method of a semi-insulating $\text{Cs}_2\text{Hg}_6\text{S}_7$ crystal is shown in Fig. 4. Sampling gate 1 is chosen at 100 μs , 150 μs , 200 μs , 250 μs , and 300 μs , and gate 2 at 600 μs , 650 μs , 700 μs , 750 μs , and 800 μs , respectively. Five distinct defect levels labeled A, B, C, D, and E are observed.

By plotting the temperature dependence of the thermal emission rate for levels A, B, C, D, and E as $\log(e_i/T^2)$ versus $1/T$ (Fig. 5), the thermal activation energy and the capture cross-section are calculated from the slope and intercept of the linear fitting. In order to determine the capture cross-section σ_i , the prefactor H for the hole carriers is calculated by assuming the effective mass for hole as $0.25m_e$ and a defect degeneracy factor of 2.¹⁰ The calculated H constant is $8.1 \times 10^{20}/(\text{s cm}^2 \text{ K}^2)$ for the hole carriers. The values of activation energy E_a of the traps and the effective capture cross-section σ_i are listed in Table I, together with the temperature range in which the defect is detected. The measured activation energies are 0.053, 0.052, 0.34, 0.35, and 0.46 eV above the valence band maximum, respectively, for peaks A, B, C, D, and E.

Table I lists the five levels and their corresponding energies and capture cross-sections. The parameter σ , in units of cm^2 , is the capture cross-section of the holes. By comparing the trap energies obtained from previous DFT calculations with those obtained in the current PICTS measurements, we tentatively assign the levels to metal vacancies (V_{Cs} , V_{Hg1} , or V_{Hg2}), interstitials (S_i) or antisite defects (Cs_{Hg1}).¹⁰ Referring to Fig. 1, the two mercury atoms as well as the three sulfur atoms each have a different neighboring atom configuration (crystal field), and therefore the assignment of peaks is linked to specific atoms. As shown in Fig. 6, there are five acceptor-like defects and four donor-like defects present in $\text{Cs}_2\text{Hg}_6\text{S}_7$. The measured acceptor levels have ionization energies ranging from 0.053 eV to 0.35 eV. The energy levels for peaks A and B are attributed to acceptor levels V_{Cs} and Cs_{Hg1} . The two deeper levels C and D are attributed to Cs_{Hg2} and Hg_{Cs} . Peak E is attributed to a sulphur vacancy V_{S3} .

For comparison, photoluminescence (PL) and photoconductivity (PC) spectroscopic measurements on semi-insulating $\text{Cs}_2\text{Hg}_6\text{S}_7$ single crystals have been previously reported.¹¹ The PL spectroscopy indicates the presence of acceptor states with ionization energies of 0.057 eV, 0.078 eV, and 0.115 eV above the valence band, whereas the PC spectroscopy indicates the presence of localized acceptor levels located at 0.05 eV, 0.070 eV, 0.12 eV, and 0.24 eV from the valence band edge. The energy levels for peaks A, B, C, D, and E in the present study are in good agreement with both the PL and PC spectroscopic measurements.

CONCLUSIONS

In conclusion, we have measured the electronic defect levels in the ternary compound $\text{Cs}_2\text{Hg}_6\text{S}_7$ using the PICTS technique. From the spectral measurements, a series of acceptor levels with activation energies of 0.053 eV, 0.052 eV, 0.34 eV, 0.35 eV, and 0.46 eV, respectively, are observed in the undoped material. The first four levels are tentatively attributed

to Cs vacancies and Hg and Cs antisites, which have been shown to be stable using DFT calculations. The deep level at 0.46 eV is attributed to a sulphur vacancy, which is a deep donor. The detect studies indicate that, by optimizing the ambient during crystal growth, improvements in material resistivity will result leading to detectors with lower dark current and improved resolution. The results of this study thus provide useful insights for understanding and improving the performance of $\text{Cs}_2\text{Hg}_6\text{S}_7$ radiation detectors through native defect control.

ACKNOWLEDGEMENTS

This work was supported by DTRA under Grant Number HDTRA1-09-1-0044. Extensive use of the microfabrication facilities of the Materials Research Center at Northwestern University supported by the NSF (No. DMR-1121262) is acknowledged. HL was partially supported by the National Science Foundation (Grant DMR-1410169).

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