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Contactless thermally stimulated lifetime measurements in detector-grade cadmium zinc telluride

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Contactless thermally stimulated lifetime measurements were performed on detector-grade $Cd_{1-x}Zn_xTe$ ($x \sim 0.1$) crystals using a pulsed laser microwave cavity perturbation method. The carrier lifetime decreased from approximately 30 μs at 110 K to 4 μs at 160 K, and then remained relatively constant from 160 to 300 K. The sudden drop in carrier lifetime within a particular temperature range is consistent with the thermal activation of a charge trap with a detrapping time longer than the carrier lifetime. The maximum trap activation temperature and the minimum detrapping time are estimated from the lifetime versus temperature curve to be approximately 160 K and 10^{-6} s, respectively. © *2000 American Institute of Physics.* [S0021-8979(00)03605-7]

I. INTRODUCTION

The compound semiconductor $Cd_{1-x}Zn_xTe$ (CZT) has received considerable attention because it has the potential to satisfy the requirements for high resolution, room temperature gamma radiation spectroscopy applications.[1–3] Table I provides some of the important properties of this material. The band gap is sufficient to inhibit intrinsic thermal generation of charge carriers at room temperature and the combination of high atomic number and high material density results in good detection efficiency for gamma radiation. For efficient charge collection the carrier lifetime (τ) must be long compared to the maximum drift time (t_d) within the detector, which can be expressed in terms of the drift velocity of the charge carriers (v_d) as $t_d = d/v_d$, where d is the detector thickness or maximum drift length. In the linear region, the drift velocity is proportional to the applied electric field (E) through the relationship $v_d = \mu E$, with mobility (μ) as the proportionality constant. Therefore, relatively large electric fields are normally employed in radiation detectors in order to maximize the drift velocity and minimize the drift time within the detector. However, the application of large electric fields also increases the leakage current density through the relationship $J = \sigma E$, where the conductivity (σ) is the proportionality constant. High resistivity material is, therefore, required. Resistivities greater than $10^{10}\,\Omega$ cm are achieved commercially in CZT through the introduction of a relatively large concentration of deep energy levels, which partially ionize and pin the Fermi level near the middle of the energy gap. This technique, known as compensation, is an effective method of increasing the resistivity of semiconductors plagued by shallow defect levels. However, the same deep energy levels that improve the resistivity of CZT can also trap free charge carriers, reducing the carrier lifetime and degrading the detector performance. Thus, a fine

balance between compensation and trapping is required in order to optimize the performance of radiation detectors based on this material.

Compensation and trapping in detector-grade CZT has been investigated using a number of techniques including thermally stimulated conductivity (TSC), thermoelectric emission spectroscopy (TEES), and thermoelectric voltage spectroscopy (TEVS).[4–8] However, although several important electron and hole traps have been identified in CZT, very little is currently understood about the relative contribution of individual traps to the charge carrier lifetimes.

In this manuscript we report on contactless thermally stimulated lifetime (C-TSL) measurements in detector-grade CZT using a pulsed laser microwave cavity perturbation technique. The method has many similarities to TSC and TEES except that carrier lifetime instead of current is measured during the thermal ionization of traps. The semiconductor sample is first cooled to reduce the thermal energy of carriers and the probability that trapped carriers will be thermally ionized. Traps are then filled by creating electrons and holes in the sample using a pulsed laser excitation source. The sample temperature is then increased and carrier lifetimes are repeatedly measured by monitoring the transient decay in the material conductivity upon low level, pulsed laser excitation. When the Fermi level crosses a trap level, the charge state of the trap is changed (e.g., from a neutral to ionized state). The capture cross section for an ionized trap will, in many cases, be orders of magnitude different than the neutral trap, which can contribute significantly to the overall transport process affecting the carrier lifetime.

II. EXPERIMENT

Figure 1 is a schematic diagram illustrating the basic experimental configuration. A tunable solid-state yttrium–iron–garnet (YIG) oscillator provides the microwave energy with a frequency range of 4–8 GHz and a maximum power output of 100 mW. The microwave energy is directed

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TABLE I. Selected room temperature properties of cadmium zinc telluride.

Band gap (eV)	Atomic number (Z)	Density (g/cm^3)	Hole mobility (cm^2/V s)	Electron mobility (cm^2/V s)	Hole lifetime (s)	Electron lifetime (s)
1.6	48/30/52	6	50–100	800–1200	10^{-7}	10^{-6}

through a waveguide and enters through an adjustable aperture into a cylindrical resonant cavity containing the semiconductor sample. The resonant frequency of the cavity is determined by its size and by the dielectric constant of the sample material and was approximately 6 GHz for the experiments reported here. The cylindrical cavity, used in the TE_{011} mode, was machined out of brass and was plated to increase the quality factor.

A comprehensive treatment of transient microwave cavity perturbation measurements has been reported previously and will only briefly be reviewed here.[9–11] The change in the quality factor and/or resonant frequency of the microwave cavity upon photoexcitation of the semiconductor sample is the basis for the technique. The dielectric loss (ϵ'') is proportional to the material conductivity and can be expressed as

$$\epsilon'' = \sigma/\omega\epsilon_0, \tag{1}$$

where σ is the sample conductivity, ω is the angular frequency of the microwave radiation, and ϵ_0 is the permittivity of free space. Under pulsed laser excitation, the semiconductor conductivity momentarily increases from σ_0 to σ due primarily to the generation of free charge carriers. Defining the excess conductivity factor ($\Delta\sigma/\sigma_0$), it can be shown, assuming that for low level excitation the change in the resonant frequency is negligible, that

$$\Delta\sigma/\sigma_0 = \{1/Q_1 - 1/Q_d\}/\{1/Q_d - 1/Q_0\}, \tag{2}$$

where Q_0, Q_d, and Q_1 are the quality factors of the empty, sample loaded under dark and sample loaded under luminant condition of the cavity, respectively.[9] After the excitation is removed, the conductivity of the sample and quality factor of the cavity return to the unexcited values at a rate dependent on the carrier lifetime. Thus, the carrier lifetime can be determined by observing the time dependence of the quality

factor Q_1 under pulsed laser excitation of the sample. However, for transient measurements it is difficult to determine the value of the quality factor by the full width at half maximum of the resonant curve. It has been previously demonstrated that one can determine Q from the normalized reflected microwave power at resonance, k, such that

$$\Delta k(t) = S\Delta\sigma(t)/\sigma_0, \tag{3}$$

where Δk is the normalized change in the reflected microwave power at resonance and S is the measurement sensitivity.[11] Thus, the effective carrier lifetime can be obtained directly by observing the decay of the reflected microwave signal after the removal of the excitation source. The measurement sensitivity is known to depend on a variety of parameters including the quality factor, the sample size, and the cavity coupling factor. We have previously demonstrated that the sensitivity can be optimized such that the absorption of single high-energy photons can be detected in a semiconductor using this method.[12]

The photoillumination in these experiments was provided by a pulsed Nd: yttrium–aluminum–garnet (YAG) laser with a wavelength of 1064 nm and a pulse duration of approximately 4 ns. The laser energy could be continuously adjusted to a maximum of 90 mW. A 1-mm-diam circular aperture was machined into the side of the cavity for the photoillumination. The semiconductor sample was inserted axially into the center of the cavity using a cylindrical BeO rod. BeO is an electrical insulator and, therefore, creates negligible load to the cavity compared to the CZT sample. However, the thermal conductivity of BeO is quite high and the sample could therefore be cooled to approximately 110 K by placing the external end of the rod into a liquid nitrogen reservoir without the need to introduce coolant directly into the cavity. Condensation inside the cavity was avoided by keeping the cavity under mechanical vacuum.

III. RESULTS

Figure 2 is a plot of the normalized reflected microwave power versus time for the pulsed illumination of the CZT sample at three different temperatures. The reflected microwave signal intensity is a measure of the free charge carrier density as a function of time and in general the signal decay can be described mathematically by an infinite series of exponential functions with independent time constants. The decay curves of Fig. 2 were fit with a least squares method to a simple exponential function with time constant (τ) as the single adjustable parameter.

Figure 3 is a plot of carrier lifetime versus temperature from 110 K to 300 K. The CZT sample was first placed in the microwave cavity and cooled to 110 K. The sample was then illuminated with 1064 nm laser light in order to fill the traps. We have also used the 532 nm first harmonic for the excitation, but have observed no significant change in the results. Recently it has been reported that the optimum wavelength for photoexcitation of CZT is 750–780 nm.[4] Therefore, we suspect that only partial trap filling is occurring in our investigation. After the initial photoexcitation, the sample temperature was increased and the carrier lifetime
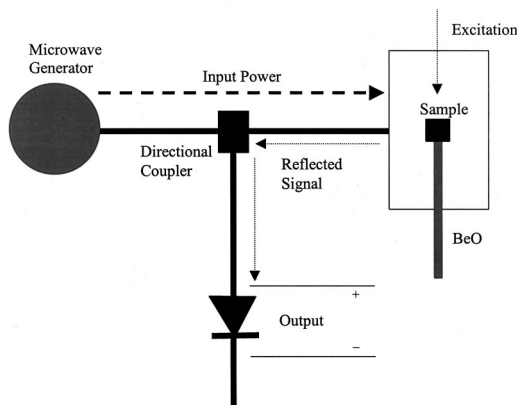

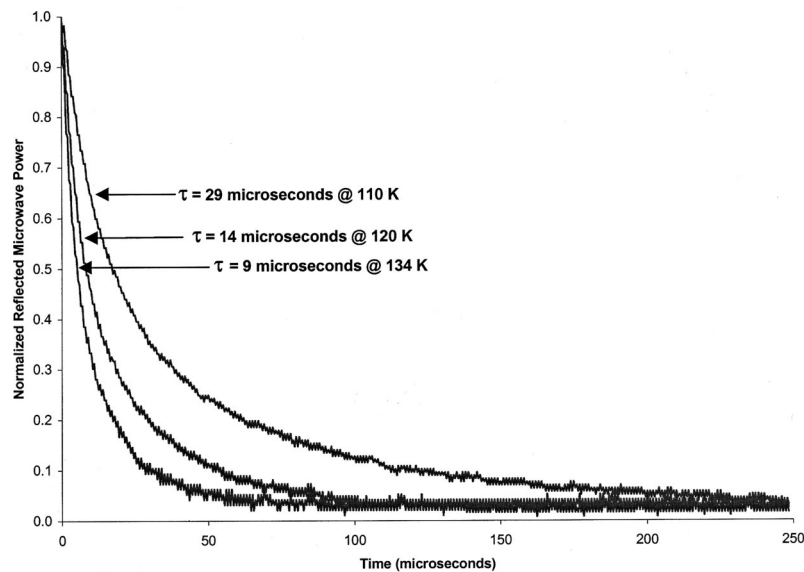FIG. 1. Schematic diagram of the microwave apparatus.

FIG. 2. Normalized reflected microwave signal intensity vs time at three different sample temperatures.

was measured at discrete temperatures by monitoring the duration of the reflected microwave signal upon pulsed laser excitation. As illustrated in Fig. 3, the carrier lifetime decreased rapidly with increasing temperature from approximately 30 μs at 110 K to 4 μs at 160 K and then remained relatively constant from 160 K to 300 K.

IV. DISCUSSION

The carrier lifetimes reported here represent an effective lifetime (τ_{eff}) and in general consist of a surface component (τ_s) and a bulk component (τ_b) through the relationship

$$1/\tau_{eff} = 1/\tau_g + 1/\tau_b . \tag{4}$$

The surface component of the effective carrier lifetime includes important information on the diffusion coefficient (D) which is related to the carrier mobility (μ) and sample temperature (T) through the relationship $D = \mu kT/q$, where k is the Boltzmann constant and q is the unit charge. It is possible to separate the bulk and surface components of the lifetime by varying the sample thickness or excitation wavelength and this would be an interesting follow-up to this preliminary investigation. However, here we are primarily interested in reporting on the temperature dependence of the *effective* carrier lifetime but we do note that the room temperature effective lifetime value determined from our microwave method is consistent with the bulk electron lifetime value reported in Table I determined from conventional time-of-flight methods. This is indirect evidence that surface effects may be negligible at the laser wavelength used in these experiments.

The sudden drop in carrier lifetime in CZT within a particular temperature range is consistent with the thermal ionization of an electron or hole. The trap ionization temperature and the lower limit of the detrapping time can be estimated from the lifetime versus temperature curve. From
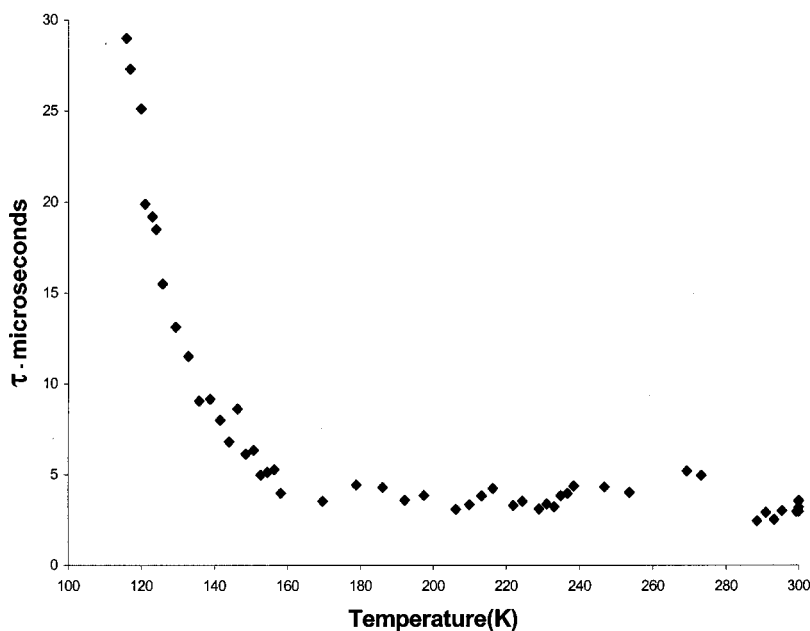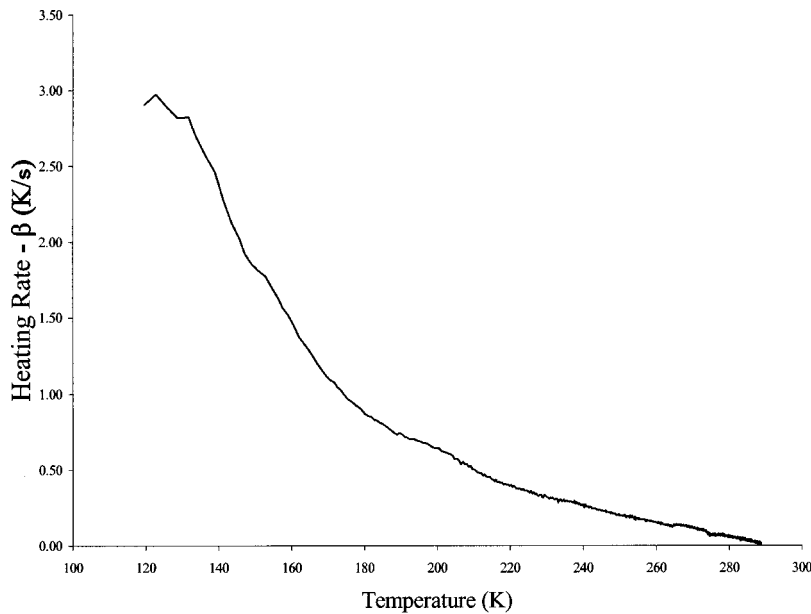

FIG. 3. Carrier lifetime vs temperature from 110–300 K.

FIG. 4. Heating rate β vs sample temperature.

the data in Fig. 3, we estimate that the maximum trap activation temperature is 160 K. However, it will be necessary to extend the C-TSL measurements to lower temperatures in order to improve this estimate, and we are currently modifying the experimental apparatus for lower temperature operation.

It is possible to qualitatively estimate the thermal ionization energy, E_t, from the C-TSL curve using the following equation commonly used for thermally stimulated current measurements:

$$E_t = kT_s \ln\{(cm^* \sigma_t T_s^4)/(E_t\beta)\}, \tag{5}$$

where

$$c = \{4(6\pi^3)^{1/2}k^3\}/h^3, \tag{6}$$

and T_s is the temperature at which the transition in the C-TSL curve occurs, β is the heating rate, σ_t is the trap cross section, m^* is the effective mass, and h is Planck's constant.

Figure 4 is a plot of the heating rate (β) versus temperature for these experiments. The sample was heated simply by removing the liquid nitrogen from the external end of the BeO rod. Initially the heating rate is high due to the large temperature gradient along the sample rod. However, after a few seconds the heating rate drops significantly and is approximately 1.5 K/s near the C-TSL transition temperature of 160 K. Using the effective mass for electrons in CdTe and a trap cross section of 10^{-15} cm^2 gives an ionization energy of 340 meV $\pm$ 50 meV. Due to the logarithmic nature of Eq. (5), the primary uncertainty in our calculation of the trap ionization energy comes from the uncertainty in the ionization temperature T_s. Therefore, the value reported here for E_t can be interpreted as a qualitative estimate of the upper limit of the trap ionization energy.

The carrier lifetime decreased from approximately 30 to 4 μs due to the thermal activation of the charge trap near 160 K. If the detrapping rate were fast compared to these carrier lifetime values, the trap would not be expected to significantly reduce the measured carrier lifetime. We therefore place the minimum detrapping time in the 10^{-6} s range.

The C-TSL measurements reported here depend on the total carrier concentration and it is, therefore, difficult to separate the contributions of electron and hole traps using this method. It is possible to distinguish between electron and hole traps using other techniques such as TEES or TEVS and a recent investigation reports the presence of a partially ionized dominant deep donor level in CZT that compensates a smaller concentration of acceptor levels that may be shallow or deep.[4] However, although our initial C-TSL measurements are consistent with this model, further lifetime measurements over a wider temperature range and on additional samples will be necessary in order to correlate our results to the trapping scheme in CZT.

Recent TSC and TEVS measurements of nine samples from the same supplier of CdZnTe crystals showed three electron traps common to all of the samples and deep electron and hole traps in most of the samples. The energies of the measured electron traps were 77 ± 15, 184 ± 20, and 354 ± 22 meV. These levels are consistent with the results of the C-TSL technique. Figure 5 shows the TSC spectra from three representative samples. Peaks due to the three electron traps can be seen and a strong correlation between the radiation detector performance and the peak intensity was observed and this is reported in detail elsewhere.[13]

A potential advantage of the C-TSL technique is that the lifetime measurements are obtained from a localized region within the sample defined by the laser spot diameter, penetration depth, and carrier diffusion. Therefore, it may be possible to probe specific regions of a sample in order to determine the degree of variation in the carrier lifetimes within a material. We have probed several regions of the CZT sample, but did not observe a significant variation in the carrier lifetimes. However, we suspect that the relatively large interaction volume probed in these initial experiments
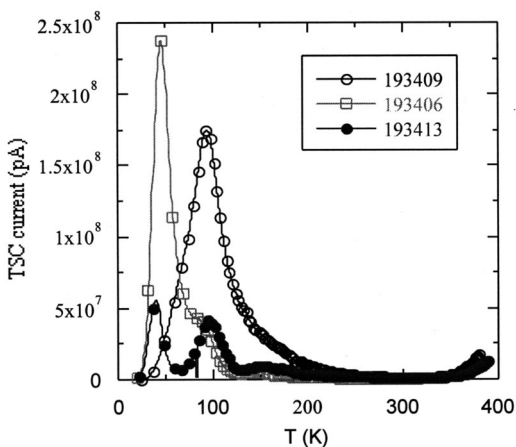
FIG. 5. TSC spectra of three representative samples showing three peaks due to three electron traps.

does not provide sufficient spatial resolution to detect these variances.

V. CONCLUSIONS

Contactless thermally stimulated lifetime measurements have been performed on detector-grade cadmium zinc telluride. This characterization method provides important information on the relative contribution of individual trap levels to the carrier lifetime. Our results provide evidence for the existence of an important lifetime-limiting trap in CZT. The

maximum ionization energy of this trap is estimated to be 340 meV, and the minimum detrapping time is approximately 10^{-6} s. Future investigations will include additional C-TSL measurements at lower temperatures and a correlation between C-TSL curves and detector spectroscopic performance.

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