

Trapping Lifetime and Carrier Mobility Measurements in CuInSe₂ Using Surface-Acoustic-Wave Technique

Massood Tabib-Azar, Hans-Joachim Moller, and Neil Shoemaker

Abstract—A novel technique based on the measurement of the frequency spectrum of the acoustoelectric current is used to determine the trapping time associated with dominant traps in *p*-type CuInSe₂. At room temperature, two trap levels with trapping time constant of 2×10^{-4} and 6.7×10^{-5} s are detected. Under white incandescent light, two more traps with trapping time constants of 1.4×10^{-3} and 6×10^{-4} s are detected. The minority (electron) and majority (hole) carrier mobilities in this material are also measured using the acoustoelectric technique and they are 6 ± 3 and 3.1 ± 0.15 cm²/V·s respectively. The hole carrier concentration was estimated to be around 5×10^{15} cm⁻³, and the surface of the sample was depleted.

I. INTRODUCTION

Due to its potential application in high-efficiency, low-cost photovoltaics, CuInSe₂ has received considerable attention in recent years [1]. At the present, however, material issues are still the main problems preventing the full employment of this material in solar cells. Whether the main application of CuInSe₂ will be in the area of solar cells or other devices such as light emitting diodes and nonlinear optical devices, it is not clear yet. However, one of the existing application areas is in solar cells.

Among the important parameters of any solar cell material are the minority carrier recombination lifetime (τ) and the carrier mobility (μ). These two parameters determine the minority carrier diffusion length, L ($= \sqrt{kT\mu\tau/q}$, k is the Boltzmann constant, T is temperature in Kelvin, and q is the elementary charge). The solar cell reverse leakage current (I_0) is indirectly proportional to the square root of the minority carrier lifetime, and minimizing I_0 is one of the primary goals of solar cell design.

In well established single crystal semiconductors, where making ohmic and Schottky contacts to the material are readily known, the Hall measurement and deep-level-transient-spectroscopy (DLTS) are usually used to measure the carrier mobility and lifetime, respectively. In novel and polycrystalline materials, however, it is more desirable to have non-

destructive means of measuring these parameters. Here we present preliminary results of carrier mobility and lifetime measurements using acoustoelectric voltage technique [2]–[6] in a single crystalline *p*-type CuInSe₂. Through an interaction mechanism, an acoustic wave in a semiconductor can exchange momentum with the semiconductor's free carriers. The relative velocity of the carriers and the acoustic wave determines the loss or gain in the wave momentum. The interactions, always described through the Poisson relation, are usually provided by the piezoelectric or potential deformation mechanisms. When the acoustic wave velocity is larger than the carrier velocity, it results in a dc electric current in the material. This electric current is measured to determine the carrier mobilities [2].

Generating acoustic waves in semiconductors is not very convenient. In the present work we have coupled the electric field of surface acoustic waves (SAWs) [2]–[6], generated in a piezoelectric material, to the free carriers of CuInSe₂. The SAW is generated by applying 55-MHz RF to the interdigital transducers at the surface of the LiNbO₃ where the CuInSe₂ is placed (see Fig. 1). In LiNbO₃, the SAW is accompanied by an electric field. This electric field has an evanescent component with a decay constant of ~ 64 μ m (55-MHz SAW) outside the LiNbO₃. The distance between the CuInSe₂ and LiNbO₃ surfaces is 1–10 μ m, so that there is an overlap between the SAW's electric field and the CuInSe₂. The interaction of this electric field with the free carriers of the CuInSe₂ produces a dc current in the semiconductor. The longitudinal component of this acoustoelectric current (I_{ae}) is detected using electrodes at the surface of the LiNbO₃, as shown in Fig. 1(b).

In high-resistivity materials, it is more convenient to measure the longitudinal and transverse acoustoelectric voltages (LAV and TAV). The SAW is usually pulsed, with millisecond durations, and LAV and TAV are detected using a lock-in amplifier. Fig. 2 shows a SAW pulse and the resulting LAV and TAV waveforms across a *p*-type CuInSe₂. TAV and LAV are positive in *n*-type semiconductors and they are negative in *p*-type semiconductors.

When the SAW amplitude is noiseless, and in a material without trap levels, the acoustoelectric current does not fluctuate. When traps are present, the trapping and de-trapping of the charged carriers results in the fluctuation in the I_{ae} . Trap levels with different activation energies, therefore, can be detected by examining the fluctuation spectrum of I_{ae} .

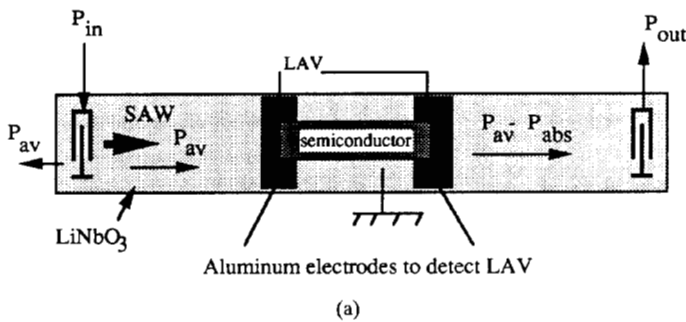
The samples that are used here were *p*-type single-crystalline CuInSe₂ provided by the Solar Energy Research Institute. They

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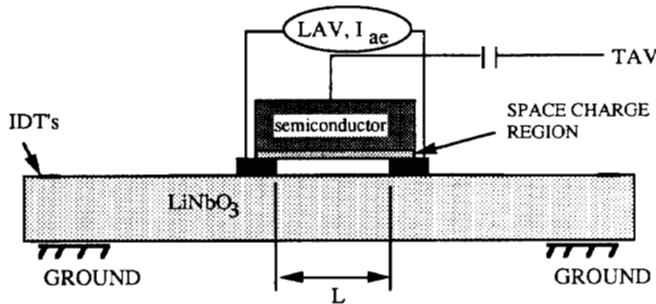
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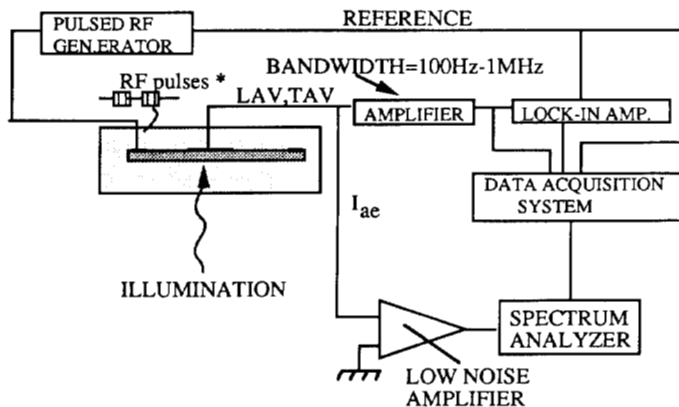
(a)



(b)

$$P_{out} = \eta (P_{av} - P_{abs})/2$$

$$P_{abs} = (1 - e^{-2\alpha L}) P_{av}$$



* continuous when measuring I_{ae}

(c)

Fig. 1. Schematic representation of the experimental set-up used in the SAW measurement. The SAW is generated at the surface of a piezoelectric substrate (LiNbO_3). The semiconductor is simply placed on top of the piezoelectric substrate. The transverse acoustoelectric voltage (TAV), the longitudinal acoustoelectric voltage (LAV), and current (I_{ae}) are measured across and along the semiconductor, respectively. A lock-in amplifier is used to detect the TAV and LAV signals, and the data-acquisition system is used to acquire and to analyze the data.

were not intentionally doped and they are heavily compensated as shown by others [9].

II. CARRIER MOBILITY MEASUREMENTS

The acoustoelectric current (I_{ae}) is related to the carrier mobilities and concentrations as follows [2]:

$$I_{ae} = \frac{P_{abs}}{LV_s} \left(\frac{\mu_n n - \mu_p p}{n + p} \right) \quad (1)$$

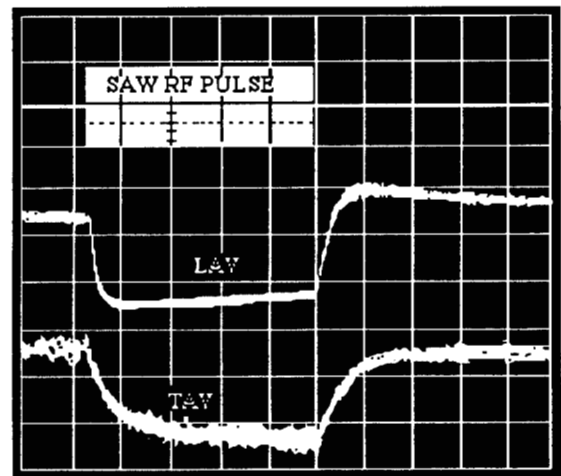


Fig. 2. The RF pulse used to generate the SAW and the resultant longitudinal and transverse acoustoelectric voltage detected across a p -type single-crystalline CuInSe_2 . The horizontal scale is $100 \mu\text{s}/\text{div}$, and the vertical scales are $5 \text{ V}/\text{div}$ for the SAW RF pulse, $0.5 \text{ V}/\text{div}$ for the LAV waveform, and $1 \text{ V}/\text{div}$ for the TAV waveform. LAV and TAV are amplified ($\times 1000$).

where P_{abs} is the SAW power absorbed by the free carriers, L is the length of the interaction (see Fig. 1(b)), V_s is the SAW velocity (3480 m/s in Y -cut, Z propagating LiNbO_3), μ_n and μ_p are the electron and hole mobilities, and n and p are the corresponding densities. In deriving (1), it is assumed that the semiconductor surface states unable to respond to the SAW (SAW frequency is 55 MHz). In extrinsic semiconductors, conductivity of the majority carriers dominates and I_{ae} becomes directly proportional to the majority-carrier mobility. The carrier mobility, then, is calculated from the slope of the $I_{ae} - P_{abs}$ curves. There are different techniques for directly measuring or calculating (from the input SAW power) P_{abs} . I_{ae} is amplified using a current sensitive amplifier and detected using a data acquisition system (see Fig. 1(c)).

The minority-carrier mobility can be determined using two different methods: 1) by using the field-effect and inverting the semiconductor sample as discussed in [2], and 2) by illuminating the p -type semiconductor surface by a light having photon energies larger than the semiconductor band-gap energy. Since electrons usually have larger mobilities than holes, high illumination levels can lead to domination of electron conductivities over hole conductivities at the semiconductor surface (within a diffusion length). The electron mobilities measured using this technique are slightly larger than the field-effect technique because of the different processes responsible for the enhanced surface electron conductivity.

Fig. 3 shows the I_{ae} versus P_{abs} measurement across CuInSe_2 in the dark and under illumination. The measurement is repeated two times and the reproducibility is better than 5% with the $I_{ae} - P_{abs}$ linearity of better than 10%. The hole mobility, calculated from the slope of the $I_{ae} - P_{abs}$ curve that was measured at dark, is $3.1 \pm 0.15 \text{ cm}^2/\text{V}\cdot\text{s}$. The electron mobility, calculated from the slope of $I_{ae} - P_{abs}$ curve that was measured under illumination, is $65 \pm 3 \text{ cm}^2/\text{V}\cdot\text{s}$. The hole concentration is $5 \times 10^{15} \text{ cm}^{-3}$, which is calculated from the resistivity of the sample, measured using a four-point probe, and the hole mobility. The position of the Fermi-level is

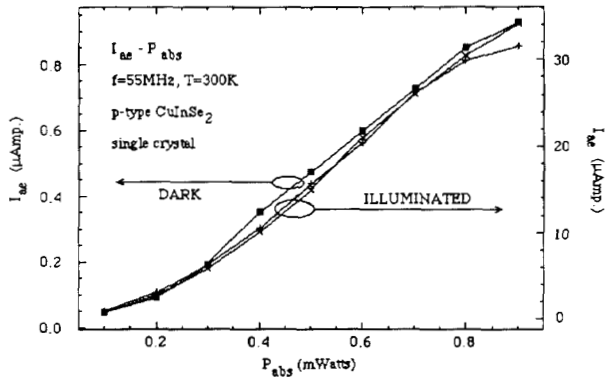


Fig. 3. Acoustoelectric current as a function of the absorbed SAW power in CuInSe_2 .

calculated using the well known relationship in nondegenerate semiconductors:

$$\begin{aligned} E_v - E_f &= kT \ln(p/N_v) \\ &= 0.0259 \ln(5 \times 10^{15}/2.3 \times 10^{19}) \\ &= -0.22 \text{ eV.} \end{aligned} \quad (2)$$

The acoustoelectric interaction depth is on the order of the SAW wavelength ($\approx 64 \mu\text{m}$ when $f_{\text{SAW}} \approx 55 \text{ MHz}$ or the semiconductor Debye length, whichever is shorter). When the semiconductor surface is depleted, the acoustoelectric interaction takes place at the boundary between the surface depletion region and the bulk quasi-neutral region. The effective mobility that is measured, hence, is an average mobility of the near surface carriers. This may explain the relatively low values of the measured mobilities. Bulk hole mobilities of $50\text{--}180 \text{ cm}^2/\text{V}\cdot\text{s}$. and electron mobilities of $100\text{--}1000 \text{ cm}^2/\text{V}\cdot\text{s}$ have been reported by the others [10]. On the other hand, depleted surfaces have higher resistivity and the current in the four-point probe measurement will flow through the least resistant path yielding the resistivity of the region underneath the surface. The carrier density has an exponential dependence on the band bending energy while the surface mobility is usually one or two orders of magnitude smaller than the bulk mobilities, depending on the surface condition. Hence, the Fermi-level energy of 0.22 eV is approximately that of the region underneath the semiconductor surface and not at the surface.

In the previous $I_{ae} - P_{\text{abs}}$ directly using a second interdigital receiving transducer as shown in Fig. 1(a). However, we had to measure the transfer efficiencies (η) for the emitting and receiving transducers separately since they were different. To calculate η 's, it is noted that P_{abs} is proportional to ηP_{in} ; I_{ae} is measured twice, first using transducer #1 and then using transducer #2 as the emitter.

III. GENERATION/RECOMBINATION LIFETIME MEASUREMENTS

It has been reported previously that the rise and fall time constants associated with the TAV waveform are functions of carrier generation and recombination lifetime [3]–[5]. We have exploited this dependence to perform deep-level spectroscopy

in GaAs and $\text{Al}_x\text{Ga}_{1-x}\text{As}/\text{GaAs}$ [3]. In previous work we measured the rise/fall time constants directly in the time domain. Time domain measurements are quite convenient when the time constants are longer than $30 \mu\text{s}$. where one can use an IBM-compatible AT computer with a data acquisition board to acquire data either as a function of illumination, temperature, or any other external stimuli. In high-resistivity GaAs and Si, the time constants usually range between $30\text{--}1000 \mu\text{s}$.

Here, we use the frequency spectrum of the acoustoelectric current, I_{ae} , to detect deep levels. The absorbed SAW power, P_{abs} , can be shown to be directly proportional to the carrier density in the semiconductor. In an extrinsic p -type semiconductor, where hole density dominates, I_{ae} becomes:

$$I_{ae} = \frac{P_{\text{abs}}}{LV_s} \mu_p = - \left[\frac{C}{LV_s} \mu_p \right] p \quad (3)$$

where C contains the effective interaction cross section, elementary charge, SAW velocity, interaction length, and the SAW electric field inside the semiconductor. Therefore, any fluctuations in the hole density would result in fluctuations in I_{ae} .

Following [8], the rms noise current generated by trap levels with well-defined trapping time constants is given by

$$\begin{aligned} \frac{\langle i^2 \rangle}{\Delta f} &= \frac{1}{1 + (f/f_0)^2} \\ &\cdot \left\{ \frac{2I\tau N_t}{p^2 V} \frac{g \exp((E_n - E_f)/kT)}{[1 + g \exp((E_n - E_f)/kT)]^2} \right\} \end{aligned} \quad (4)$$

where $f_0 = 1/\tau = 1/\tau_c + 1/\tau_e$, and τ_e and τ_c are, respectively, the emission and capture time constants; N_t is the density of deep levels; p is the hole density; V is volume; g is the spin degeneracy of the deep level ($1/2$ for donors and 2 for acceptors); E_n is the energy of the deep level, kT is the thermal energy, and I is the dc current passing through the device. In our measurement this dc bias is established by the SAW. It should be noted that the fluctuations in the majority carrier density are responsible for the observed fluctuations in the current and the majority carrier trapping time constant is measured.

We have used a Nicolet 222 Spectrum Analyzer to obtain the spectrum of I_{ae} . The experimental setup is shown in Fig. 1(c). The I_{ae} is amplified using a 1-MHz bandwidth, low-noise amplifier. Using the spectrum analyzer, the spectrum is averaged 128 times and the output is either printed out or directly transmitted to a Keithley 570 Data Acquisition System connected to a PS2/30 IBM computer.

To examine the effect of the deep levels on the I_{ae} spectrum, in the present work we have illuminated the semiconductor by an incandescent white light generating electron-hole pairs at the surface of the semiconductor. Generation of excess electron-hole pairs establishes quasi-Fermi levels resulting in the alteration of the occupancy of the deep levels. When deep levels are distributed inside the energy band gap, N_t and τ are

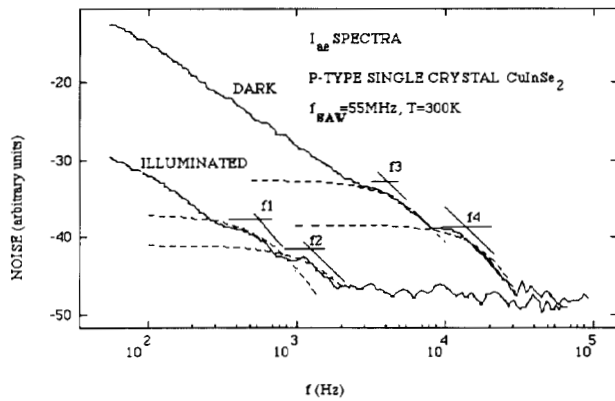


Fig. 4. The noise spectrum of I_{ae} .

functions of E_n inside the band gap. Noting that only those levels that are near the Fermi level are the most active ones, it can be easily seen that τ and N_t also vary depending on the level of the illumination. This is the primary reason for the change in the I_{ae} spectra as a function of the illumination.

Fig. 4 shows the spectra of I_{ae} in the dark and under illumination. Under illumination, there are two distinct levels: one at $f_0 \approx 7 \times 10^2$ Hz and, another at $f_0 \approx 1.7 \times 10^3$ Hz. These are respectively denoted by f_1 and f_2 . In the dark, the I_{ae} spectrum has a larger amplitude with two distinct trap levels at $f_0 \approx 5 \times 10^3$ Hz and 1.5×10^4 Hz. These are denoted by f_3 and f_4 , respectively. The trap time constants (given by $\tau = 1/f_0$) are 1.4×10^{-3} ($= 1/f_1$), 6×10^{-4} ($= 1/f_2$), 2×10^{-4} ($= 1/f_3$), and 6.7×10^{-5} ($= 1/f_4$) s. It is not readily clear why the I_{ae} spectrum should have a small amplitude under illumination. This might be due to the screening of the SAW electric field by the photogenerated excess carriers.

From (4) it is evident that trap levels near the Fermi level energy will be most active in contributing to the fluctuations in the carrier density (the term in the curly bracket has a maximum at $E_n = E_f$ for donors). Hence, E_n in the dark is approximately equal to the Fermi energy, which is 0.22 eV above the valence band according to (2). A better technique to obtain the trap energy E_n , of course, is to vary the temperature and measure the I_{ae} spectrum at different temperatures from which the trap density can also be determined.

IV. DISCUSSION

It is necessary to comment on the difference between the trapping lifetimes, which we have measured previously, and the actual recombination/generation lifetimes that are needed in the solar cells. The difference between the trapping centers and recombination/generation centers lies mainly in their energy inside the band gap. Other parameters such as the ability of a level to capture electrons and holes, which can be described in terms of the corresponding cross sections, are also important [11]. However, most of the levels in the middle of the gap are of the recombination/generation type because

of the fact that they can be equally accessed by holes and electrons in the valence and conduction bands.

The estimated hole concentration of $5 \times 10^{15} \text{ cm}^{-3}$ in our sample, which was calculated from four point probe data and the hole mobility, is high enough to completely screen the SAW electric field. The fact that the SAW signal is relatively large indicates that the surface is most probably depleted. Therefore, the Fermi level at the surface is near the middle of the energy band gap. Noting that the trap levels around the Fermi level are usually the most active levels, it can be concluded that the trap levels detected here have energies around the middle of the energy band gap. It should be noted that in (2) we calculated a Fermi energy of 0.22 eV (from the valence band) based on the four point measurement data and the mobility measurement data. As mentioned in connection with (2), when the semiconductor surface is depleted, the acoustoelectric interaction takes place at the edge of the surface depletion region and the bulk quasi-neutral region. However, any fluctuations in the acoustoelectric current will reflect trapping and de-trapping in the region of overlap between the acoustoelectric field and the semiconductor. In other words, any charge trapping or release event would cause a modulation in the depletion width or it would directly increase or decrease the magnitude of the acoustoelectric current. Strictly speaking, more measurements concerning the activation energies of the trap levels are required to connect the trap lifetime to the recombination/generation lifetimes.

It would be extremely useful to apply the aforementioned technique to study thin-film CuInSe₂. Various substrates such as CdS and glass are used. In the past we have used the SAW technique to study heteroepitaxial layers such as Hg_xCd_{1-x}Te on CdTe [2] with great success, and in principle the CuInSe₂ CdS or CuInSe₂/CdS or CuInSe₂/glass systems are not any different. However, the effect of grain boundaries of polycrystalline CuInSe₂ should be carefully taken into account. In the case of CuInSe₂/glass, the SAW technique will be a particularly important technique since it does not require electrical contacts to the sample. Preliminary results so far indicate that the SAW technique can be applied to study CuInSe₂ on glass. However, the signal level was low due to the low resistivity of the film that was available to us, and the sample temperature was lowered to reduce the carrier density and improve the acoustoelectric signal level. We will report these results in a separate publication.

V. CONCLUSION

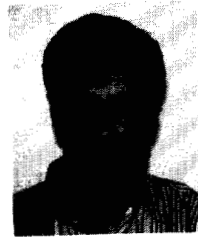
In conclusion, a SAW technique is used to nondestructively determine carrier mobilities and trapping lifetimes in *p*-type, single crystalline CuInSe₂. Hole mobility of 3.1 cm²/V·s and electron mobility of 65 cm²/V·s and four different trap levels with well defined time constants of 1.4×10^{-3} , 6×10^{-4} , 2×10^{-4} , and 6.7×10^{-5} s, are detected. We plan to perform the aforementioned measurements again to study polycrystalline CuInSe₂, which would be very difficult using other conventional techniques.

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In 1987, he joined Case Western Reserve University as an Assistant Professor. His current research interests include ultra high speed devices and electrical and optical properties of novel materials such as multiple quantum wells, superlattices, and high T_c superconductor devices. His teaching interests include development of courses in the area of electronic devices with an emphasis on the problem solving approaches and the use of computer aided instruction tools. He is author and co-author of more than 30 journal publications.

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Hans-Joachim Moller, photograph and biography not available at time of publication.

Neil Shoemaker, photograph and biography not available at time of publication.