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Unusual Capacitance Emission Transients in CIGS Caused by Large Defect Entropy Changes

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UNUSUAL CAPACITANCE EMISSION TRANSIENTS IN CIGS CAUSED BY LARGE DEFECT ENTROPY CHANGES

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ABSTRACT

Capacitance transient data from bias-pulse experiments on CdS/CIGS solar cells show an unusual behavior at high temperatures. Above 350K a minority carrier trap, with a *larger* activation energy than a majority carrier trap, emits *faster* than the *lower* activation-energy minority trap. A simple enthalpy model for trap emission cannot explain this counterintuitive behavior, but the more complete Gibbs free energy model that includes entropy can explain it. We show that entropy plays a major role in carrier emission from traps in CIGS.

INTRODUCTION

$CdS/CuIn_{1-x}Ga_xSe_2$ (CIGS) thin-film solar cells have achieved record efficiencies of greater than 19%[1] despite the high concentration of electronic trap levels in CIGS.[2, 3] A variety of experimental techniques[4-6] have measured both minority- and majority-carrier traps in CIGS with widely varying energy levels and concentrations. It is well established that carrier emission from filled traps in CIGS generally does not follow an exponential decay, but rather, a stretched exponential decay,

$$A(t) = A_o e^{-(t/\tau)^{\beta}}, \qquad (1)$$

With τ a characteristic time constant for the decay and β having values between 0.3 and 0.8.[7] In addition, bias-pulse, trap-filling experiments show that there are energy barriers to filling and that saturation of the traps requires bias pulses on the order of 100s of seconds.[7] Data also suggest that bias pulse length and annealing can change the nature of the trap being filled (e.g. from a minority to a majority carrier trap).[8] This latter feature suggests a trap metastability similar to the bipolar D defect found in a-Si:H.[9] Similar to a-Si:H, it is generally found that the emission rates from the traps seen in CIGS follow the ubiquitous Meyer-Neldel rule (MNR).[10-12] Adherence to the MNR implies that a change in entropy plays a significant role in the thermal emission of the traps. Measuring the magnitude of the entropy change involved with the traps will greatly improve our understanding and possibly our control of the traps.

In this paper, we present capacitance emission transient data at elevated temperatures from CIGS/CdS solar cells. The data show ambipolar carrier emission; we observe both a fast-decaying minority carrier and a slower-

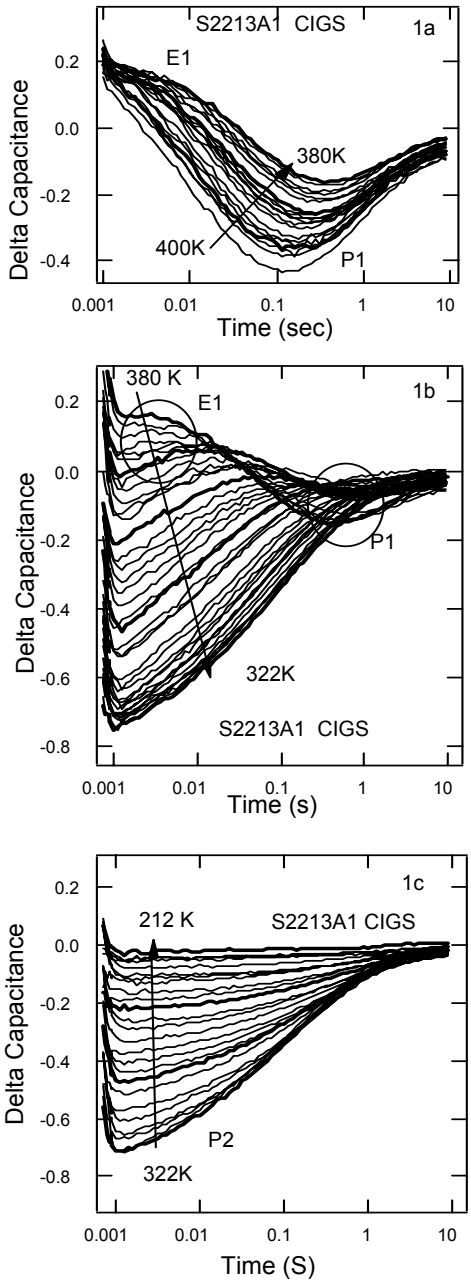

Fig. 1. Capacitance transients as a function of temperature.

decaying majority carrier. The minority carrier has a *shorter* time constant for emission, but a *larger* activation energy than the majority carrier (i.e., the deeper state emits faster than the shallower state). This bizarre behavior is inconsistent with the notion that shallow states always thermally emit faster than deeper states. However, these data are consistent with the Meyer-Neldel rule, which predicts such counterintuitive effects for temperatures above the isokinetic temperature. For temperatures above the isokinetic temperature, the change in free energy is negative upon carrier emission. But below the isokinetic temperature, the change in free energy is positive and the emission transients are normal: the shallower state emits faster than the deeper state. The free-energy sign-reversal effect has been seen in hydrogenated amorphous silicon solar cells, but this is the first time this behavior has been observed in CIGS. Our data demonstrate a large entropy change associated with carrier emission from these defects, which has implications for solar cell parameters, models of transport in CIGS, and the interpretation of defect spectroscopies.

EXPERIMENT

Thin-film ZnO/CdS/CIGS solar cells were grown on molybdenum-coated, soda-lime glass. The CIGS absorber layer was grown using the three-stage process by thermal evaporation. Details of the complete cell growth and solar cell characterization may be found elsewhere.[1] Cells were contacted with pressure probes on In dots and placed in a commercial temperature stage in the dark. The capacitance of the cell was measured by a Stanford Research SR830 lock-in amplifier operating at 11 kHz with a 100 μs time constant. Capacitance transients were monitored by a high-speed data acquisition card with log time-data averaging accomplished by in-house software. The initial capacitance, C_o, was measured while a cell was held at a bias of –0.3 volts. The voltage was then pulsed to either 0 or +0.3 volts, depending on the experiment, for a set amount of time and then returned to –0.3 volts. Data collection was triggered on the return of the bias back to –0.3 volts. The change in capacitance ($C(t) – C_o$) was recorded for up to 1000 s.

DATA

Figure 1 shows capacitance transient curves for sample S2213A1 ($CuIn_{1-x}Ga_xSe_2$, x~0.3) over the temperature range of 400 K – 212 K using a filling pulse time of 1 s at zero bias. Figure 1a shows the transients between 400 K and 380 K, with the arrow in the figure indicating the scan sequence. The data show a fast-emitting minority carrier trap ($\Delta C > 0$)[13] labeled E1, followed by a slower-emitting majority-carrier trap ($\Delta C < 0$) labeled P1. All of the transients return to the original C_o value ($\Delta C = 0$) for times greater than 10 s. Note that the amplitude of the E1 and P1 transients increase and decrease with decreasing temperature, respectively. Figure 1b is a continuation of the transients in Fig. 1a for temperatures between 380 K and 320 K. Here, the transients shift from the minority- and majority-carrier traps at the high temperatures to a single, large-amplitude majority-carrier trap, labeled P2, at the lower temperatures. Figure 1c continues the transient trend with a decrease in amplitude of the majority-carrier trap, P2, until it is not observed below 212 K. In this contribution, we focus on the emission behavior of traps E1 and P1, but note that trap P2 was previously analyzed by our group.[7]

For high temperatures (Fig. 1a), the transient data may be fit with the sum of two stretched exponentials simulating the two-carrier nature (E1, P1) of the transients. Figure 2 shows a good fit to the data, along with the deconvoluted transients for the E1 and the P1 traps. A series of transients at different temperatures were fit in this manner to produce the Arrhenius plots of Fig. 3, giving the activation energies for traps E1=1.4 ± 0.04 eV and P1= 0.3 ± 0.13 eV. The unusual aspect of Fig. 3 is that the trap with the faster emission time, E1, has the higher activation energy. The crossing point of the two extrapolated line-fits to the Arrhenius data of Fig. 3 gives the so-called isokinetic temperature at about T_{iso} = 350 K. This measured value is similar to that measured for B-doped a-Si:H,[15] InGaAsN,[18] and CIGS[19] samples. Below this temperature, P1 is expected to emit faster than E1. As is evident in Figs. 1 a-c, P2's influence on the transient signal interferes with the low-temperature E1 and P1 contributions to the transient. Nevertheless, a wealth of new information can be drawn from our high-temperature data.

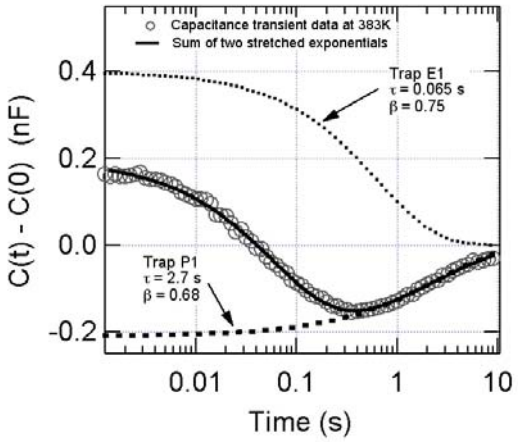

Fig. 2. Fit to transient data with the sum of two stretched exponential functions.

MNR EMISSION RATE INVERSION

Bias-pulse length experiments have led us to believe E1 and P1 are related to each other and are a result of an amphoteric, metastable defect. These results will be presented in a later paper. We cannot view these traps as simple, but rather as a much more complex entity that is strongly coupled to the phonons and the emitted charge. In this case, one must view it as a thermodynamic object (trap)[14] and describe transitions using

$$r = \tau^{-1} = \nu_{oo} e^{-\beta \Delta G} = \nu_{oo} e^{(\Delta S / k_B)} e^{-\beta \Delta H}, \quad (2)$$

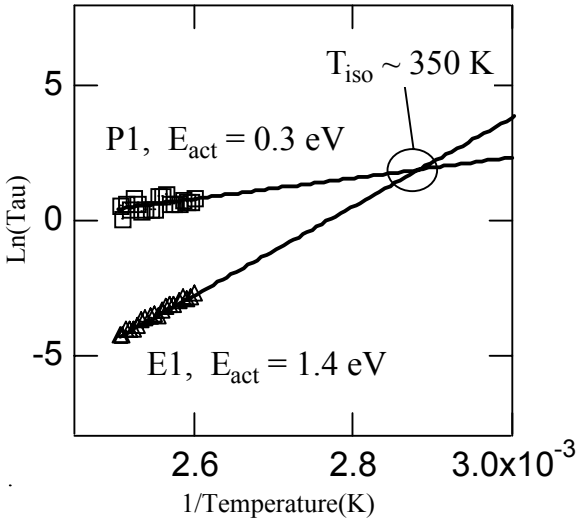

Fig. 3. Arrhenious plot of data for traps E1 and P1.

where $\Delta G = \Delta H - T\Delta S$ is the difference in Gibbs free energy between initial and final states during carrier emission from a trap. ΔH is the change in enthalpy (emission activation energy, E_{act}), and ΔS is the change in entropy with $\beta = 1/k_B T$ and k_B is Boltzmann's constant. $\nu_{oo} = k_B T/h$ is the Eyring constant.[14] Note that the relevant quantity in determining the rate of a transition is the Gibbs free energy and not just the activation energy. Most of the literature on defects in CIGS has *assumed* ΔS to be small enough to ignore. Our data show this is not the case. From Fig. 3, we see that at $T = T_{iso}$ the emission rates are equal for both the minority- and majority-carrier traps. This implies that ΔG is the same for both traps (subscripts 1 and 2) at T_{iso}, which gives[15]

$$T_{iso} = \frac{(\Delta H_1 - \Delta H_2)}{(\Delta S_1 - \Delta S_2)}. \qquad [3]$$

Taking the ratio of reaction rates for two reactions gives

$$\frac{r_1}{r_2} = e^{-\beta\{(\Delta H_1 - \Delta H_2)[1-(T/T_{iso})]\}}, \qquad [4]$$

revealing the origin of emission inversion between the two reactions for temperatures above and below T_{iso}. The transition with the *larger* ΔH (E_{act}) has the *faster* transition rate for $T > T_{iso}$ and the *slower* transition rate for $T < T_{iso}$. Equation [2] allows a calculation of the individual entropy changes associated with each transition reaction by noting that at T_{iso} the reaction rates must be equal for both traps and independent of ΔH. For the simplest case, considering only changes in entropy that scale with changes in enthalpy, such as phonon contributions, $\Delta S = \Delta H/T_{iso}$.[15] It should be noted that other entropy contributions to emission can and do exist[16] that do not scale with changes in enthalpy, but they will not be discussed in this paper. Data from Fig. 3 give the measured entropy changes for E1 and P1 to be

$$\Delta S_{E1} = 48 \pm 8k_B \qquad \Delta S_{P1} = 11 \pm 5k_B.$$

The magnitude of these ΔS values are consistent with those found for electron and hole traps in B-doped a-Si:H solar cells.[15] Current theories on the origin of ΔS associate these values with the number of ways to assemble the required number of phonons to surmount the transition barrier.[17] More information on the phonon spectrum and the coupling potential of the lattice to the particular defects for CIGS are needed to corroborate our experimental ΔS values with the phonon assembly theory. We refer the reader to our recent work in this area.[16]

DISCUSSION

Our high-temperature transient data suggest that two traps, one a minority carrier and one a majority carrier, emit their carriers over the time scale of seconds. These especially long emission times are due to a barrier to emission related to the change in Gibbs free energy during the transition. The change in Gibbs free energy is a function of both the change in enthalpy (the activation energy) and the change in entropy. The large ΔS values

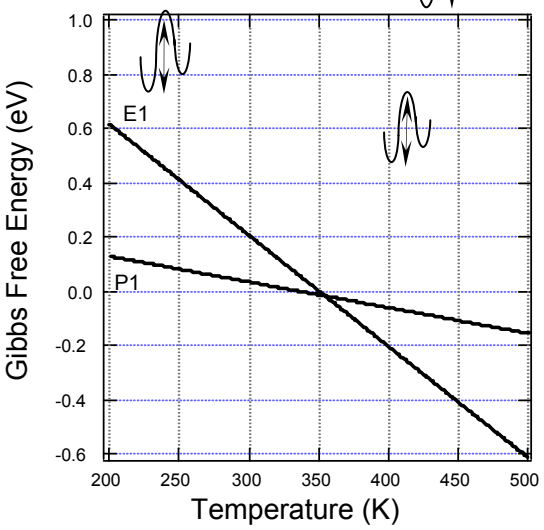

Fig. 4. Gibbs free energy vs. temperature for traps E1 and P1. The arrows on the diagrams illustrate the relative energy barrier for emission.

calculated from our data for traps E1 and P1 confirm that entropy contributions to trap emission may *not* be ignored in models for these defects. Note that the large change in entropy values seen in our data *decrease* the barrier to emission. This characteristic is a result of the change in entropy scaling with the change in enthalpy. The larger enthalpy barrier of E1 requires a larger change in entropy during a transition for a given change in Gibbs free energy ($\Delta G = \Delta H - T\Delta S$). Calculating ΔG above and below T_{iso}

gives the relative energy barriers for E1 and P1 and reveals the physical reason why the reversal of emission time with activation energy above T_{iso} can be observed in materials that follow the MNR. Fig. 4 shows the Gibbs free energy for E1 and P1 vs. temperature, along with conceptual energy barrier diagrams for E1 and P1 above and below T_{iso}. Note that the Gibbs free energy changes sign at T_{iso}, which is the reason for the relative barrier-height change.

SUMMARY

Our capacitance transient data show minority- and majority-carrier trap-emission following a bias pulse for temperatures between 380 and 400 K. The data show an odd behavior in the emissions such that the traps with the *larger* activation energy emit *faster* than the lower activation-energy traps. This counterintuitive event is well described by a model that treats the defect as a thermodynamic object with a Gibbs free energy barrier to emission. The data show large changes in entropy are involved in the emission process, that lower the Gibbs free energy barrier to emission for the higher activation emissions above the isokinetic temperature. We believe the concept of entropy must be included in future theoretical work to better understand defects in CIGS and related materials.

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