Thermal Admittance Spectroscopy Study: Preliminary Observations of a Meyer-Neldel Relationship in CdTe Devices

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ABSTRACT

The present work is an extension of our previous study of the traps in CdTe PV devices characterized by thermal admittance spectroscopy. Preliminary observations of a Meyer-Neldel Relationship (MNR) in the thermal emission of carriers from the traps are presented. In addition two devices processed identically to two devices with trap signatures at different points on the MNR line were characterized by photoluminescence spectroscopy (PL). An initial correlation between the MNR and the stability of devices during accelerated indoor stress testing is also shown.

INTRODUCTION

Since 1991, our work on CdTe PV has led to advances in the areas of: (a) device structure, (b) manufacturing process, and (c) hardware designs suitable for large-scale manufacturing [1]. These advances have been demonstrated on a continuous, in-line process suitable for large volume manufacturing of CdS/CdTe PV devices. This technology has produced devices with an NREL verified efficiency of 12.44 % on unmodified Pilkington TEC 15 substrates [1].

Previously, a correlation between the $CdCl_2$ treatment of CdS/CdTe/CdTe:Cu PV devices and the change in conversion efficiency with light and heat stress indoors (stability) has been shown [2]. A. S. Gilmore et al. have shown that the $CdCl_2$ treatment affects the concentration and distribution of trapping states in CdTe devices [3].

A study was undertaken to find the thermal emission characteristics of the defects acting as traps in various devices as measured by Thermal Admittance Spectroscopy (TAS) [4]. After the initial study further TAS characterization of more CdTe devices was undertaken. Devices fabricated with the same process conditions were also characterized by photoluminescence spectroscopy (PL) and placed in accelerated indoor stress conditions. The relationship of the TAS results to the PL spectrums and a qualitative correlation to accelerated lightsoak stress will be presented.

EXPERIMENTAL

Device fabrication

The devices described in this paper were fabricated in an all in-line continuous vacuum process using modified close-spaced-sublimation (CSS) or heated pocket deposition (HPD) sources as described elsewhere [1,2]. Most samples received a $CdCl_2$ treatment. This $CdCl_2$ treatment was varied as also described elsewhere [2]. A primary Cu containing back contact was applied to selected CdS/CdTe devices. It consists in general of exposure of the CdTe film to a vapor flux from a sublimable Cu compound in a HPD source in vacuum for 2 minutes followed by an annealing process [1,2].

When a contact was applied the Cu back contact process was held constant. In some instances the Cu back contact was left off for comparison. Throughout this paper cells without the Cu back contact will be referred to as “no Cu” devices. This means that there was no intentional application of Cu to the device, these “no Cu” cells do contain very small amounts of Cu as a residual impurity from the CdTe source material and from the $CdCl_2$ treatment. In all cases a back electrode consisting of a layer of conductive carbon coating followed by a layer of conductive Ni coating was applied by a spray process after removal of the substrates from vacuum.

For each of the varied $CdCl_2$ treatments, two substrates were processed with identical $CdCl_2$ treatment. One of these substrates did not receive the Cu back contact application and the other substrate did receive a Cu back contact. From each substrate 15 small area (0.3 cm^2) devices were defined. The individual cells were characterized by light current / voltage (JV) measurement. The quality of the $CdCl_2$ treatment is defined by the JV performance of the cells fabricated with that treatment. Groups of cells with a Cu contact from each $CdCl_2$ treatment were placed in accelerated indoor stress [2]. Cells that were fabricated with the same $CdCl_2$ treatment as cells in the stress groups were characterized by thermal admittance spectroscopy and photoluminescence spectroscopy. A baseline substrate received no $CdCl_2$ treatment and no Cu back contact. One cell from this no $CdCl_2$ substrate was characterized by thermal admittance spectroscopy.

In one case one cell fabricated with a poor $CdCl_2$ treatment was characterized by thermal admittance spectroscopy before being placed in accelerated stress. Two other cells that were processed identically were placed in accelerated stress without characterization by thermal admittance spectroscopy.

Thermal admittance spectroscopy measurements

Thermal admittance spectroscopy (TAS) is a simple yet powerful method for the characterization of the electronic signatures of trap states associated with defects in semiconductors [5] and thin-film semiconductor PV devices [6]. TAS was applied as detailed elsewhere [4]. A total of 17 devices were characterized by TAS.

Results were used to estimate the trap activation energy E_a, apparent capture cross-section σ and trap density N_t. Some devices had undetectable trap signatures as measured by TAS. This means that there were no minima in the ω(dC/dω) spectrum and no peaks in the normalized conductance spectrum in the studied frequency and temperature range.

PL measurements

Photoluminescence spectroscopy (PL) was performed on two cells by the Colorado School of Mines using a 638 nm HeNe excitation laser at 43 K temperature. The use of this technique for the characterization of defects and impurities in CdTe is well known [7].

Indoor accelerated stress testing or lightsoaking

The details of the indoor accelerated tests used in this work are as given elsewhere [2]. All stress temperatures in this work are at 65° C and open circuit bias. Cells were removed periodically from the lightsoaker and measured for JV performance using a standard JV tester with calibrated ELH quartz lamp illumination.

RESULTS

The activation energy of devices versus the open circuit voltage (Voc) is shown in Figure 1. The Voc of three devices with undetectable trap signatures are presented in Table 1. The E_a and apparent capture cross-section σ signatures for the traps in devices in Figure 1 fit

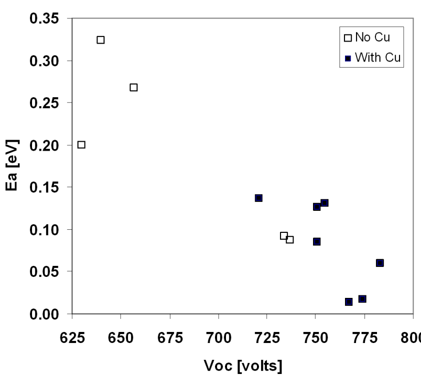

Figure 1: Plot of Trap activation energy vs open circuit voltage for devices with detectable TAS signatures. Lowest Ea = 0.014 eV. Open markers are no intentional Cu cells.

a Meyer-Neldel relation (MNR) that can be plotted as shown in Figure 2. The emission factor ξ_o is proportional to σ. The three devices in Table 1 are not plotted in Figures 1,2,or 3.

Table 1: Open circuit voltages for devices with undetectable trap signatures

device	1	2	3
Voc [volts]	801 w/Cu	774 No Cu	744 No Cu

Figure 3 shows the addition of data from a study of CdTe PV devices by M.A. Lourenco et al. [8]. In this study, the $CdCl_2$ treatment was varied and traps were characterized by DLTS. The open markers for the CSU cells are no Cu cells. Two cells without the $CdCl_2$ treatment are also shown from both the Lourenco data and the CSU data. Figure 4 shows the PL spectrum of two devices processed identically to two other cells from the TAS study. Both devices show an apparent DAP transition at ~ 1.38 eV. The higher intensity peak may be shifted slightly to lower energy. Figure 5 shows the stability performance of sets of devices in the study. The set of devices processed identically to devices with trap signatures that were undetectable by TAS shows the best long term stability performance with average η ~ 9.5% after almost 25000 hours.

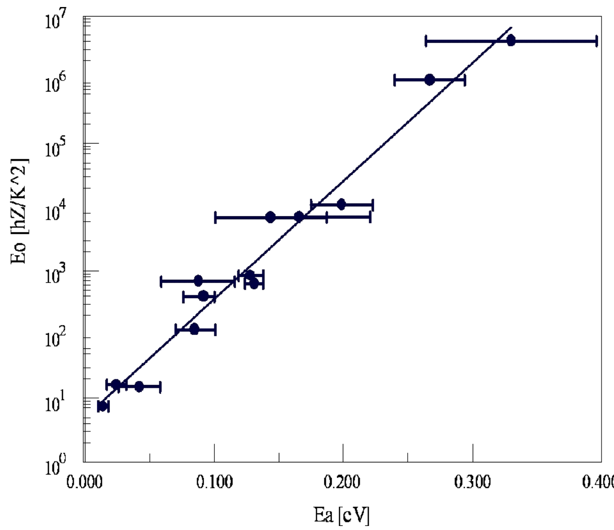

Figure 2: MNR plot for cells fabricated with varied $CdCl_2$ treatment (w/wo Cu back contact). The emission factor Eo is proportional the capture cross section.

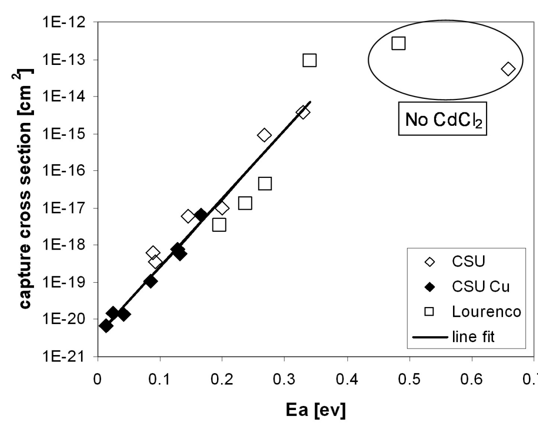

Figure 3: MNR plot adding data from a DLTS study by M.A. Lourenco et al. [8]. The open markers for the CSU cells are no intentional Cu cells. Two devices without $CdCl_2$ treatment are shown. The lowest plotted E_a is 14 meV.

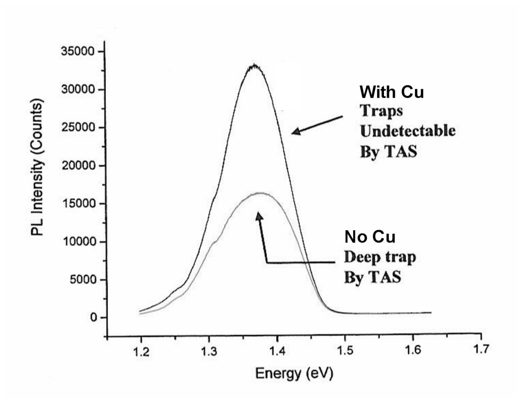

Figure 4: PL spectrum of two devices processed identically to two cells from the TAS study

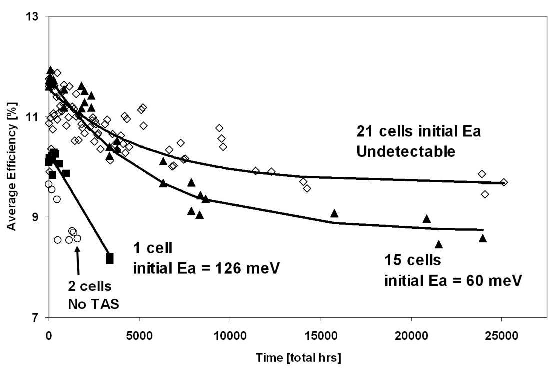

Figure 5: Accelerated indoor stress stability plot. Stress at 65° C and OC bias. All cells have a Cu back contact.

DISCUSSION

Initial JV performance of TAS devices

As shown in Figure 1 there is a trend towards lower trap activation energies as the open circuit voltage increases. Variation in the $CdCl_2$ treatment changes the trap E_a as well as the initial light JV performance of devices prepared without the Cu back contact. The application of the Cu containing back contact in most cases causes a decrease in the trap E_a and an increase in Jsc and Voc for these devices.

Meyer-Neldel relationship

For devices with varied $CdCl_2$ treatment and with and without the Cu back contact, the TAS trap signatures were found to obey a Meyer-Neldel relation (MNR) [9,10,11]. For the MNR in the present work, the exponential pre-factor (proportional to capture cross-section) increases exponentially with E_a. The MNR plot of the TAS signature is shown in Figure 2. An isokinetic temperature T_{iso} = 272 ± 36 K was found from a least squares fit of the MNR plot [11]. For devices with detectable trap signatures only a single trap level was detected and multiple levels were not found in the same device.

More trap signature data from a deep level transient spectroscopy (DLTS) study of CdTe PV devices by M. A. Lourenco et al. [8] is shown in Figure 3. Lourenco characterized ANTEC CdTe material with a variation in the thickness of the $CdCl_2$ film applied during treatment. As can be seen the data fits the MNR line well. The calculated isokinetic temperature is T_{iso} = 274 K for both the Lourenco and CSU data. F. Seymour et al. have also shown four MNR fits to deep states in CdTe devices characterized by transient capacitance measurements and admittance spectroscopy [12] however these MNR fits are not coincident with the MNR data presented here.

The two markers at the upper right in Figure 3 are for cells with no $CdCl_2$ treatment from Lourenco and CSU data. As can be seen, the CSU cell without $CdCl_2$ treatment does not fit on the MNR line. The MNR for the CSU data is related to the $CdCl_2$ treatment and the back contact application.

Devices with the optimum $CdCl_2$ treatment (both with and without the Cu back contact) had trap signatures that were undetectable using TAS. It seems reasonable that since these devices had the best open circuit voltage performance (3 devices in Table 1) that the MNR trend would follow and that the E_a and σ of these devices would be somewhere along the lower end of the MNR plot line fit.

Certain devices were characterized by dark JV measurements with varied temperature. The back contact barrier height Φ_B was calculated for these devices. For these cells, Φ_B ~ 0.44-0.6 eV. This energy range is not represented in the MNR and there is no obvious relationship to a back contact barrier.

Some proposed explanations of the physical basis of MNR's are given by A. Yelon et al. [9 and references therein]. In the present work, high potentials at the grain boundaries must be considered as a possible factor in the observed MNR. Using cathodoluminescence spectroscopy (CL) M. Romero of NREL has shown that donor-acceptor-pair (DAP) transitions become better defined at the grain boundaries than in the bulk grain in our cells and that most likely the potential changes at the grain boundaries in our devices [13]. High potential at the grain boundaries of CdTe devices has been shown by others [14,15]. It is well known that high fields can enhance measured thermal emission rates [5]. M. Lourenco et al. proposed effects related to valance band deformation at the grain boundaries as the mechanism underlying his DLTS results [8].

PL measurements

Two samples that were processed identically to the samples for the PL measurements had the following TAS signatures 1) no traps detectable and 2) one deep trap level at E_a = 324 meV and σ = 1.3×10^{-15} cm^2. The PL spectrum for the two devices is shown in Figure 4. In the PL characterization both samples show an apparent DAP transition at approximately 1.38 eV in the "defect band" [10]. This could be a combination of multiple independent bands [10]. There were no higher energy transitions indicating the presence of shallower energy acceptor states. Even though the TAS measurements have a distinct difference in the trap characteristics the PL measurement of the two PL samples have essentially the same DAP transition energy. For the cells that had undetectable trap signatures by TAS an identically processed cell had the highest PL intensity indicating that a low defect concentration should not be the cause for the TAS result.

Correlation to stability

The stability of devices is shown in Figure 5. Since the open circuit bias condition is the most stressful these efficiency changes with stress should be seen as lower limit values [2]. Devices that were processed identically to the devices in the stress test were characterized by TAS. In general groups of cells processed identically to cells with lower (or undetectable) E_a and σ as measured by TAS were more stable.

Several cells fabricated with poor $CdCl_2$ treatment were stressed. One cell was characterized by TAS (E_a = 0.126 eV) before being placed in accelerated stress. Two other devices processed nominally the same were also placed in stress without TAS characterization and are shown as a separate trace in Figure 5. All of the devices have the same poor stability showing that TAS measurement was not the cause of the efficiency loss. None of these devices lost efficiency due to shunting.

If one accepts that traps with undetectable TAS signatures may have σ and E_a at the low end of the MNR range then the stability performance in Figure 5 is an initial indication that the stability of these devices is related to the MNR defects.

CONCLUSIONS

Preliminary evidence of a Meyer-Neldel relationship (MNR), where the measured trap capture cross-sections σ increases exponentially with the trap activation energy E_a, has been found in CdTe PV devices fabricated with a continuous in-line system. The calculated isokinetic temperature for the MNR is T_{iso}= 272 K. The MNR is related to the $CdCl_2$ treatment process and the application of the Cu containing back contact.

The MNR also fits DLTS data from M. A. Lourenco et al. [8]. Lourenco et al. also varied the $CdCl_2$ treatment on CdTe PV devices.

There is initial evidence of a correlation between the defect signatures in the MNR and the long term stability performance of the devices during indoor accelerated lightsoak stress.

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