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# Deep electron traps in hydrogenated amorphous silicon

Richard S. Crandall
*RCA Laboratories, Princeton, New Jersey 08540*

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Deep-level-transient-spectroscopy measurements on both Schottky barrier and *p*-*i*-*n* *a*-Si:H solar cell structures reveal deep electron traps. The unique feature of these traps, whose activation energy varies between 0.5 and 1.5 eV, depending on the sample, is that electron capture is thermally activated. This activation energy is close to the trap energy. These traps are also associated with metastable changes in solar cells.

Light-induced metastable changes in the transport properties of *a*-Si:H have been the subject of intense interest[1,2] since their discovery by Staebler and Wronski.[1] Prolonged illumination affects both the dark and photoconductivity[1] as well as the luminescence.[3,4] In the majority of cases the dark current decreases by orders of magnitude[2] as does the photoconductivity. The luminescence changes, however, are more complex.[3,4] The principle *a*-Si:H luminescence peak decreases and a new band at longer wavelengths appears.[3] It is postulated that the same defect or defects are responsible for both the conductivity and luminescence changes.[3] There is concern that these changes can result in solar cell degradation under prolonged illumination. Some solar cells exhibit degradation whereas others do not or show only small amounts.[5] At present there is no detailed model for solar cell degradation or of the Staebler-Wronski (SW) effect. However, a connection between solar cell degradation[5] and a deep electron trap observed by deep-level-transient spectroscopy (DLTS) can be made. It may be that this trap is also responsible for the SW effect.

In this Communication we present a systematic DLTS study of Schottky barrier and *p*-*i*-*n* *a*-Si:H solar cells to determine the properties of the defect associated with metastable changes produced by illumination. The dominant feature of the defect is its large barrier for electron capture and release. This results in low production and decay rates at room temperature, a common property of the metastable changes in *a*-Si:H. It is shown that one form of the defect can be produced by the introduction of air into *a*-Si:H.

Both *p*-*i*-*n* and Pt Schottky barrier solar cell structures were produced by glow discharge decomposition of silane on heated substrates.[6] Boron and phosphorous were used to, respectively, dope the *p* and *n* layers. For the Schottky barrier structure the *a*-Si:H was *n* type without intentional doping. Because the emission times from the deep levels involved were several seconds, a digital computer was used in conjunction with a PAR Vector Voltmeter to obtain the DLTS signal. Both forward bias current pulses and light pulses from a Krypton laser were used to fill the deep traps.

Figure 1 shows a capacitance transient DLTS signal for a Schottky barrier cell using a time window of 1 s and a measuring frequency of 1 kHz. The negative fractional capacitance, *C*, change, $dC/C$, signifying electron traps was observed following a forward bias pulse. The positive $dC/C$ signifying an excess of hole over electron traps was observed following a light pulse of 674-nm radiation which is absorbed nearly uniformly within the Schottky barrier. The DLTS signal below 400 K indicates a distribution of hole and electron traps that increases toward the band edges. These results are similar to those previously reported for *a*-Si:H.[7,8] Because the DLTS signals are observed in far reverse bias they are due to states in the bulk.

The dominant electron DLTS peak at 440 K was observed using either current or light pulses to fill the electron trap. This is in contrast to the low-temperature regime where hole traps are more numerous than electron traps. It is not apparent from the figure, but the DLTS peak is distorted from the usual shape[9] by the fact that the electron capture is thermally activated.

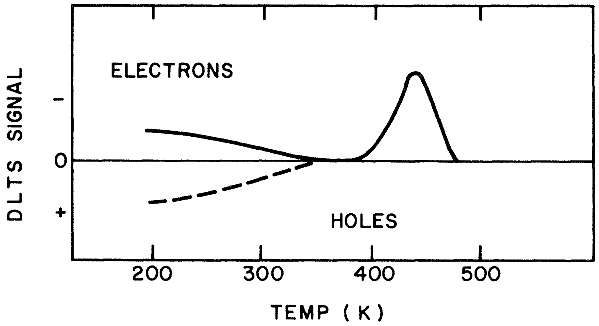

FIG. 1. DLTS signal (fractional capacitance change) caused by either current —— or light – – – pulses plotted as a function of temperature for an *n*-type Schottky barrier cell.

The majority of the devices used for DLTS measurements were *p-i-n* structures. For these structures the interpretation of the capacitance changes is more involved than for Schottky barriers. The depletion widths in both the *n* and *p* layers move in response to the charge change in the *i* layer. For these structures the charge density in the *i* layer is a small fraction of the charge density in the *n* or *p* layers.[10] Moreover, in the cells discussed here, the *n* layer is so thin that it is fully depleted. In this case only the depletion width of the *p* layer moves in response to changes of the charge in the *i* layer. Therefore, the capacitance change can be written as[10]

$$dC/C = -\Delta N_i/N_a \,, \qquad (1)$$

where $N_a$ is the acceptor density in the *p* layer and $\Delta N_i$ the change in impurity density in the *i* layer. A positive charge in the *i* layer results in a decrease in the capacitance. Equation (1) is valid when $\Delta N_i L >> W_p \Delta N_p$, where $L$ is the *i* layer thickness, $W_p$ the depletion width in the *p* layer and $\Delta N_p$ the change in the density of charged defects in the *p* layer. If the defects are produced nearly uniformly then this condition is met because $L/W_p > 100$.

The majority of the structures showed a DLTS signal similar to that in Fig. 1 with an electron trap peak between 440 and 550 K. The activation energy varied between 0.5 and 1.5 eV, depending on sample. Usually a single trap was observed. The density of traps also varied with sample in the range of $2 \times 10^{+14}$ to $8 \times 10^{+16}$ cm$^{-3}$. In some instances a DLTS signal indicating a hole trap was observed above 550 K. However, the DLTS signal increased up to the highest measuring temperature, 580 K. Because of the limited temperature range over which measurements could be made, accurate values for the trap energy were not obtained.

An important feature of these traps is that the capture of either an electron or hole is thermally activated. By itself, this is not surprising since thermally activated capture is often observed in semiconductors.[11] However, here the activation energy is large. It is nearly the same as the trap energy. Evidence of thermally activated capture is presented in Fig. 2 where both the emission rate and capture rate are shown for a *p-i-n* solar cell. In Fig. 2 the logarithm of the capture rate is plotted versus the inverse of the temperature. The line through the data is for an activation energy of 1 eV.

There is an equally high energy for electron emission from the trap. This can be seen in Fig. 2 where the logarithm of the electron emission rate is plotted versus the reciprocal of the absolute temperature. The line through the data gives an activation energy of 0.93 eV, surprisingly close to the activation energy for electron capture.

This similarity in the activation energy for capture and emission was found for the majority of the traps. It can be seen most easily by measuring the steady-state density of filled traps produced by a long excitation pulse. In the steady-state traps are emptied at the same rate that they are filled. The steady-state density of filled traps was found to be independent of temperature, depending only on the excitation intensity. This can only be true if the excitation and emission rates have the same temperature dependence. Actually this type of measurement is easier than measuring the emission or decay rates directly.

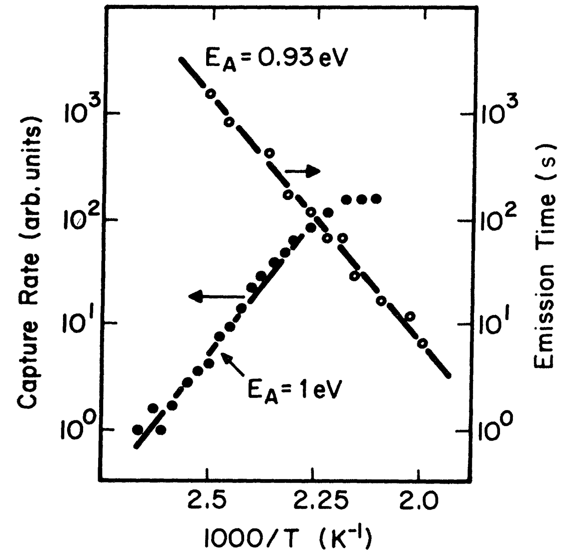

FIG. 2. Logarithm of the emission and capture rates for a high-temperature electron trap DLTS signal similar to that shown in Fig. 1 plotted vs inverse temperature. The sample was a *p-i-n* structure containing $2 \times 10^{21}$ oxygen atoms/cm$^3$ and $1.5 \times 10^{21}$ nitrogen atoms/cm$^3$.

The similarity of the activation energies for emission and decay implies that the electronic energy of the filled and empty states is nearly the same. The most reasonable configuration is that the electronic levels are close to the energy of the conducting state but that they are separated by a large potential barrier. The magnitude of the prefactors for the emission rate were found to vary considerably with trap energy. Since the prefactor for emission from gap states is usually independent of energy[8] this implies that these traps are not simple gap states. The large variation of prefactors of these deep traps reflects the changing nature of the potential barrier with trap energy.

In one case the trap could be associated with impurities. The introduction of air during solar cell growth resulted in an increase in the density of metastable defects. The increase in electron traps with increasing oxygen content is shown in Fig. 3 where the trap density, as determined from the maximum capacitance change, is plotted versus the oxygen concen-

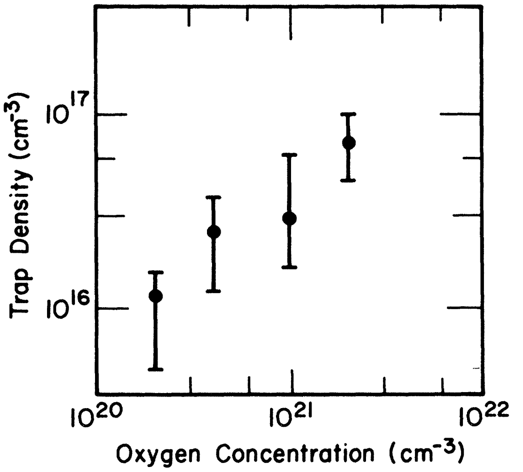

FIG. 3. Electron trap density plotted as a function of oxygen concentration in the *i* layer of a *p*-*i*-*n* solar cell.

tration in the *i* layer of the cell. The oxygen concentration was determined by secondary-ion mass spectroscopy (SIMS). The nitrogen concentration was 60% of the oxygen concentration. Even though the defect density increases with the oxygen concentration, there are order of magnitude fewer defects than oxygen atoms. This implies that either only certain oxygen or nitrogen configurations produce electron traps or the traps are associated with an impurity introduced along with the air. For this trap, the depth and activation energy are about 1 eV as shown in Fig. 2.

It has been shown that a dangling bond is produced upon prolonged illumination of *a*-Si:H.[3,4] It is not clear that this would lead to an electron trap with the above properties. Spin resonance measurements of *a*-Si:H have detected a metastable state associated with oxygen that could be formed by x rays.[12] It was found that a bridging oxygen traps a hole and forms a dangling bond. Since this trap contains a hole it does not seem to be the main one observed by DLTS.

A model for an electron trap associated with oxygen has been suggested by Lucovsky.[13] It consists of four oxygen atoms surrounding a silicon. Because of the large electronegativity of oxygen, an electron will be tightly bound to the interior silicon. Similarly there is a barrier for capture because the electron has to surmount the oxygen barrier when making a transition from an exterior silicon to the interior silicon. Because of the low probability of finding four oxygens bonded to a silicon, the trap density would be low, as found above. Similar considerations indicate that a nitrogen-silicon complex could form an electron trap.

Because silicon is weakly electronegative, there may be a large number of impurities that can form this type of defect in *a*-Si:H. However, there must be four impurities bonded to a silicon, or the electron would find a low-energy escape path along a Si–Si bond. Defects with negative correlation energies have also been postulated to have large-energy barriers for electron capture and release.[14,15] This type of defect might be responsible for DLTS peaks that were present in samples that had not been contaminated with air.

The fact that either light or voltage pulses resulted in the same electron containing defect shows that the purpose of the light is to furnish electrons that can be trapped and not to break bonds as has been postulated for the Staebler-Wronski effect and other light induced metastable changes.

In this Communication we have shown how capacitance transient DLTS measurements made at high temperature can be used to obtain important information about a unique class of deep traps in *a*-Si:H. These traps have the striking property that the electron capture and release rate are thermally activated with nearly the same energy.

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