PHYSICAL REVIEW B VOLUME 46, NUMBER 15 15 OCTOBER 1992-I

Limitations of the thermally stimulated conductivity as a technique for studying the density of states of a-Si:H

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(Received 24 February 1992)

The thermally stimulated conductivity (TSC) in hydrogenated amorphous silicon has been measured for photoexcitations at various temperatures. It has been clearly demonstrated that a low-temperature (LT) peak exists in the TSC independent of photoexcitation temperature T_e when T_e is sufficiently low. This result indicates that recent interpretations of the LT peak in the TSC are probably incorrect, and throws strong doubt upon the validity of the recent analyses of the TSC and, thus, upon the usefulness of the density of states deduced based on such an analysis. It is shown that the structure in the TSC is correlated with that in the temperature dependence of the steady-state photoconductivity and, therefore, the TSC is probably controlled by recombination.

The thermally stimulated conductivity (TSC) in hydrogenated amorphous silicon (a-Si:H) has been studied by many researchers with a view to obtaining the energy distribution of the density of states (DOS) in the band gap.[1-6] The major attraction of this method lies in the ease with which the experiment can be performed. To measure the TSC, the sample is first cooled to a given low temperature T_e and then photoexcited for a time t_e. After a delay period t_d, the sample is heated in the dark at a constant rate b while the TSC is measured. A typical TSC curve for a-Si:H contains two peaks; the low-temperature (LT) peak is located below about 150 K, and the high-temperature (HT) peak above about 300 K, depending on the experimental conditions as well as on the sample.

The information extracted from the TSC depends critically on the interpretation of the TSC; if the TSC is misinterpreted, false information will inevitably be obtained. Fritzsche and Ibaraki[1] have presented an analysis of the TSC, based on the multiple-trapping model.[7,8] By assuming that retrapping is negligible and that there exists quasiequilibrium between thermal emission and recombination, they obtain for the TSC

$$\sigma_{\mathrm{TSC}} \sim e\mu\tau g(E_m) f_0(E_m) , \qquad (1)$$

where e is the electronic charge, $\mu\tau$ is the free-electron mobility-lifetime product, $g(E)$ is the density of gap states, $f_0(E)$ is the occupation function at the start of the heating, and E_m is the maximum-TSC-emission energy,[3] which moves towards midgap with time (and thus with temperature). As a result, the LT peak is interpreted as being due to a corresponding peak in the initial energy distribution of the product $\mu\tau g(E) f_0(E)$, which arises from a rising $\mu\tau g(E)$ and an exponentially decreasing $f_0(E)$ established during the photoexcitation and subsequent delay period. There are also a number of other analyses,[5,9] but the underlying ideas used are essentially the same as that of Fritzsche and Ibaraki.[1]

According to Fritzsche and Ibaraki,[1] and others, the position of the peak in the product $\mu\tau g(E) f_0(E)$ coincides with the quasi-Fermi-level established during the photoexcitation or with the demarcation energy[1,7,8] attained at the end of the delay period, whichever is the lower. Experimentally, one can always make the demarcation energy the lower by using a sufficiently high light intensity for the photoexcitation, an indication of which being that the TSC measured is independent of the photoexcitation intensity. The demarcation energy is given by[1,7,8]

$$E_d = E_c - kT_e \ln(\nu_0 t_d) , \qquad (2)$$

where E_c is the conduction-band mobility edge, k is the Boltzmann constant, T_e is the photoexcitation temperature, ν_0 is the attempt-to-escape frequency, and t_d the delay time. Equation (2) implies that the demarcation energy is lower for a higher photoexcitation temperature if t_d is fixed. Therefore, a direct consequence of the Fritzsche-Ibaraki interpretation is that there exists a limiting TSC curve which is determined by the product $\mu\tau g(E)$, and that the LT peak in the TSC depends strongly on T_e if the other experimental parameters are kept the same; the peak will move to a higher temperature if T_e is increased, and the magnitude of the peak TSC will decrease correspondingly. These arguments are illustrated in Fig. 1, where the TSC curves for three photoexcitation temperatures, T_1, T_2, and T_3, are sketched, and $T_1 < T_2 < T_3$. The limiting TSC curve is shown by the dark solid line σ_L.

It appears that the principle of the analysis of Fritzsche and Ibaraki has been widely accepted. The DOS has been calculated from the TSC on the basis of such an analysis.[3,5,6] It should also be noted that efforts have been focused on how to improve the TSC technique.[3,5,6] In this Brief Report, the validity of the recent interpretations of the TSC is strongly challenged. We show that the TSC is probably controlled by recombination, rather than by thermal emission of trapped electrons. Therefore, the relationship between the TSC and the DOS is much more complicated than suggested in the recent analyses of the TSC.[1,5,9]

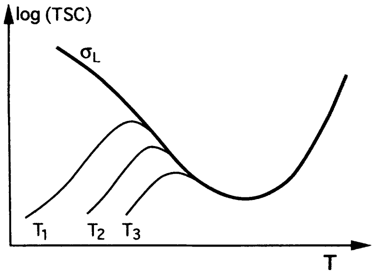

FIG. 1. Illustration showing the TSC predicted by the Fritzsche-Ibaraki interpretation. The dark solid line σ_L is the limiting TSC. T_1, T_2, and T_3 denote the photoexcitation temperatures for the corresponding TSC's (light solid lines), and $T_1 < T_2 < T_3$.

The samples studied in this work were standard undoped glow-discharge *a*-Si:H films on silica substrates prepared at the University of Dundee. The deposition temperature was 300 °C. The characteristics of similar samples can be found in the literature.[10] The film thickness was about 2 μm. Coplanar Al electrodes 7-mm long were evaporated on the top of the film. Ohmic contacts were used. A He-Ne laser was used to generate photoconductivity in the sample. The photon energy was 1.96 eV. The unattenuated light intensity was $F_0 = 3.7$ mW/cm^2, which is equivalent to a carrier generation rate of about 6×10^{19} cm^{-3} s^{-1} if the reflectivity is assumed to be 0.5 and the quantum efficiency is unity. The TSC was obtained with the procedure described at the beginning of this paper, with $t_e = 5$ min, $t_d = 10$ min, and $b = 3$ K/min. The photoexcitation intensity was $F = 10^{-1}F_0$. It was checked that, at this intensity, the TSC was independent of photoexcitation intensity. The effect of intense light soaking[11] on the TSC was also investigated. The annealed state (*A* state) was attained by annealing the sample at 200 °C for 30 min and then cooling it slowly to room temperature, whereas the light-soaked state (*B* state) was achieved by exposing the sample at room temperature to intense white light (about 300 mW/cm^2) for 30 min. All measurements, including the annealing and light soaking, were carried out with the sample in the measurement chamber under a vacuum less than 2×10^{-5} Torr maintained by a diffusion pump with a liquid-N$_2$ cold trap. Two samples were studied; one ($S1$) has an electrode spacing of 0.2 mm, and the other ($S2$) 0.56 mm. The applied electric fields were typically 10^3 V/cm. Similar results were obtained for both the samples. The results reported here are for sample $S2$.

Figure 2 shows the TSC curves measured in the *A* state for illuminations at various temperatures. The photoexcitation temperatures (T_e) are listed in the figure. It is clear from Fig. 2 that a T_e-independent peak appears for T_e below 100 K. The peak is at 118±2 K. This result is obviously contrary to the prediction of the Fritzsche-Ibaraki interpretation illustrated in Fig. 1, and indicates that a LT peak is inherent in the TSC in *a*-Si:H. We note in passing that Misra, Kumar, and Agwaral[2] observed a LT peak at about 110 K in the TSC in their *a*-Si:H samples in the *A* state with the photoexcitation carried out at 30 K and a heating rate of about 4 K/min, in close agreement with our results. The leveling off of the TSC at the lowest temperatures is due to the leakage current of the measurement system, which is about 3×10^{-14} A. For T_e above 100 K, the LT peak moves with T_e and the variation of the peak value follows the TSC measured for illuminations below 100 K. When T_e is close to or above about 160 K, where the minimum in the TSC appears, the LT peak disappears, and the TSC increases monotonically with temperature. A HT peak is expected to appear if the TSC had been measured to sufficiently high temperatures because, when the temperature is sufficiently high, thermal equilibrium will be reestablished and the TSC must drop to zero. Apparently, the results for $T_e > 100$ K are seemingly in agreement with the Fritzsche-Ibaraki interpretation.

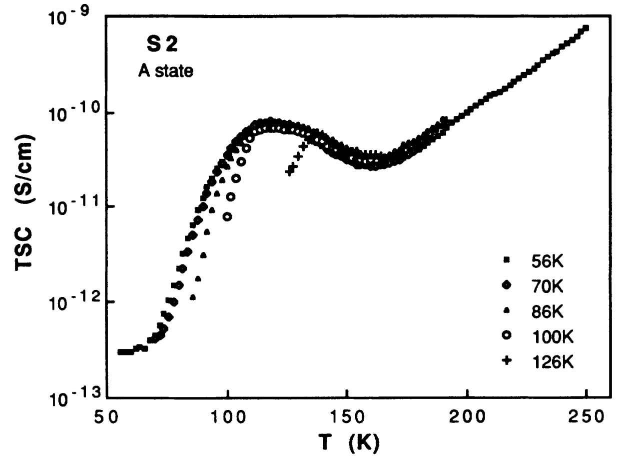

FIG. 2. TSC's in the annealed state (*A*) for the photoexcitation temperatures indicated.

Figure 3 shows the TSC curves measured in the *B* state for illuminations at the temperatures indicated. One can see that the results are qualitatively similar to those in the *A* state. However, the LT peak and the minimum are both shifted to a lower temperature. The peak is now at 104±2 K. As a result, the LT peak is already strongly dependent on T_e for $T_e = 100$ K. It also appears that the

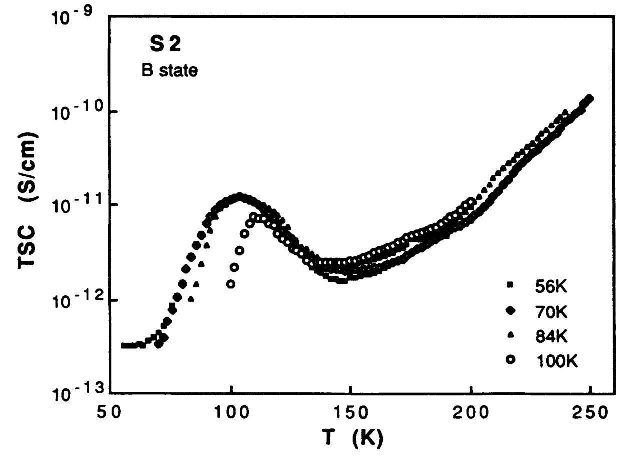

FIG. 3. TSC's in the light-soaked state (*B*) for the photoexcitation temperatures indicated.

LT peak in the *B* state is more pronounced than that in the *A* state. In order to compare further the TSC's in the *A* and *B* states, we plot in Fig. 4 the TSC below 200 K as a function of $1/T$ for $T_e=70$ K in both the *A* and *B* states. It is clear that the TSC is reduced considerably by light soaking in the temperature region above the peak temperature in the *B* state. Particular attention, however, should be paid to the low-temperature region where the TSC changes rapidly with temperature. One can see that, while the TSC in the high-temperature region is significantly reduced by light soaking, the TSC at the lowest temperatures remains essentially unchanged. This is true for all photoexcitation temperatures for which the position of the LT peak is independent of T_e in both the *A* and *B* states.

Figures 2–4 show that there are three regimes in the TSC: the regime of increasing TSC below the peak temperature, the regime of decreasing TSC between the peak and the minimum, and the second regime of increasing TSC above the temperature of the minimum. For convenience of discussion, we label the three regimes as regimes 1, 2, and 3, as shown for the TSC in the *A* state in Fig. 4.

In a recent study of the steady-state photoconductivity of *a*-Si:H, we find that light soaking also only changes the high-temperature photoconductivity.[12] Typical results are shown in Fig. 5, where the photoconductivity for a light intensity $F=1.3\times10^{-2}F_0$ is plotted against $1/T$ in both the *A* and *B* states. It is interesting to see that the effect that light soaking has on the magnitude of the steady-state photoconductivity is quite similar to that which it has on the magnitude of the TSC; while the high-temperature photoconductivity is decreased by about an order of magnitude after light soaking, the low-temperature photoconductivity remains unchanged. There are also three regimes in the temperature dependence of the photoconductivity. For clarity, we only label these regimes for the photoconductivity in the *A* state in Fig. 5. It is important to note that both the transition temperature between regimes I and II and that between the regimes II and III are shifted to a lower temperature by light soaking. By inspection of Figs. 4 and 5, one can see immediately that there is a strong correlation between the structure in the TSC and that in the steady-state photoconductivity; regimes I, II, and III in the photoconductivity correspond, respectively, to regimes 1, 2, and 3 in the TSC. The transition between regimes I and II and that between regimes II and III in the photoconductivity correspond, respectively, to the LT peak and the minimum in the TSC. Obviously, such a correlation indicates that the TSC is probably controlled by recombination of electrons, as in the steady-state photoconductivity. However, the DOS may also play an important role, at least in regime 2, since the TSC decreases with temperature in this regime, whereas in the corresponding regime II in the temperature dependence of the photoconductivity, only a shoulder is observed.

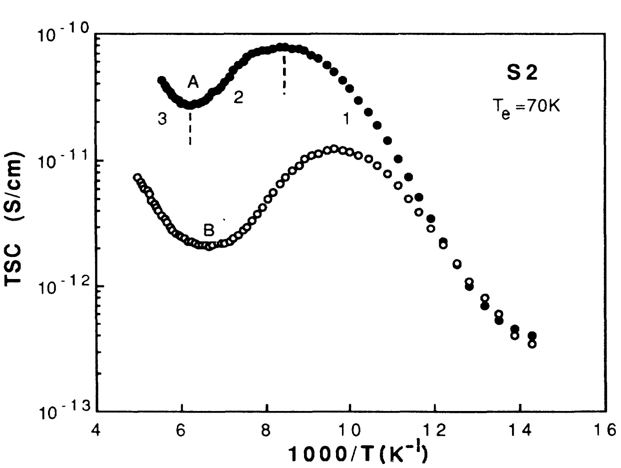

FIG. 4. TSC plotted as a function of $1/T$ for photoexcitation at 70 K. *A*, annealed state; *B*, light-soaked state.

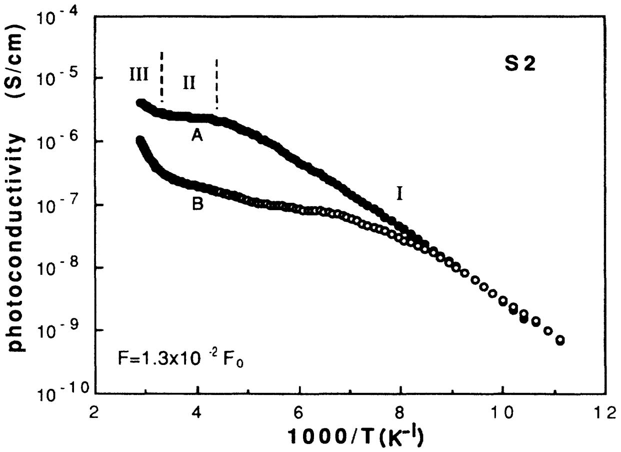

FIG. 5. Temperature dependence of the steady-state photoconductivity at a light intensity $F=1.3\times10^{-2}F_0$, where the unattenuated light intensity was $F_0=3.7$ mW/cm^2, which is equivalent to a carrier generation rate of about 6×10^{19} cm^{-3}s^{-1} *A*, annealed state; *B*; light-soaked state.

The temperature dependence of the photoconductivity shown in Fig. 5 is rather typical for *a*-Si:H. Frequently, thermal quenching of the photoconductivity, instead of a shoulder, is observed in the regime II. There has been considerable investigation of the temperature dependence of the photoconductivity; however, the nature of the recombination processes responsible in the different regimes is still highly controversial.[13] Conventionally, the leveling off or quenching of the photoconductivity in regime II is thought to be caused by a surge in thermal release of trapped holes, which enhances the recombination.[13] However, Fritzsche *et al.*[14] recently argued that the thermal quenching is due to a change from electron-dominated to a hole-dominated conduction. According to the present study, the same argument should also apply to the TSC. Apparently, if a change of sign of the majority carriers indeed happens in the TSC, an additional analysis will be required. In any case, the correlation between the TSC and the steady-state photoconductivity indicates that the TSC is limited by recombination, rather than by thermal emission of trapped electrons as commonly thought. In other words, retrapping is important in the TSC, and the quasiequilibrium between thermal emission and recombination suggested in the recent analyses of the TSC (Refs. 1, 5, and 9) does not exist. Therefore, it seems to us that the information obtained from the TSC based on the prevailing analyses[1,5,9] may be of little use.

The TSC is rather easy to measure experimentally; however, the physics is very complicated, not only because the TSC involves both electrons and holes, but also because thermal emission, trapping, and recombination enter this issue at the same time and usually cannot be dealt with separately. It is clear from this study that our present understanding of the TSC is very limited and is in many respects incorrect. Since the processes involved in the TSC are of fundamental importance, the TSC deserves further investigation. Until a reasonably good knowledge of the underlying processes in the TSC is acquired, the TSC method is not suitable for obtaining the DOS of *a*-Si:H.

In summary, by measuring the TSC for photoexcitations at various temperatures, we have shown that a LT peak exists in the TSC in *a*-Si:H independent of photoexcitation temperature T_e when T_e is sufficiently low. This result cannot be explained in terms of the current interpretation of the origin of the LT peak in the TSC. We have also demonstrated that the structures in the TSC and in the temperature dependence of the photoconductivity are closely correlated and, therefore, the TSC is controlled by recombination, and not by thermal emission of trapped electrons. It is therefore concluded that the TSC in its present state is not an appropriate technique for obtaining the density of states of *a*-Si:H.

The authors would like to thank Professor P. G. Le Comber of the University of Dundee for providing the samples studied in this work. J.-H. Zhou would like to thank Trinity College, Cambridge for financial support.

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