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PHOTO-CREATION OF DEFECTS IN PLASMA-DEPOSITED a-Si:H

M.H. Tanielian*, N.B. Goodman** and H. Fritzshe

Department of Physics and James Franck Institute, the University of Chicago, Chicago, IL 60637, U.S.A.

Abstract.—We show that the increase in the density of gap states $N(E)$ resulting from the photocreation of defects in plasma-deposited a-Si:H can be measured by the field effect and by the conductance change due to surface adsorbates. A simple model is presented which explains the doping dependence of the magnitude and the sign of the light-induced conductance changes.

Introduction.—Staebler and Wronski [1] found that exposure of plasma-deposited amorphous silicon-hydrogen alloys (a-Si:H) to band gap light decreases the dark- and photo-conductivity and increases the dark conductivity activation energy $E_a$ and prefactor $G_0$. Jousse et al. [2] deduced from capacitance-voltage measurements that this Staebler-Wronski effect is associated with an increase in the density of gap states $N(E)$ near midgap from $3 \times 10^{16}$ to $1.5 \times 10^{17}$ $eV^{-1}$ cm$^{-3}$. The spin density was found to increase from $9 \times 10^{15}$ cm$^{-3}$ to about $2 \times 10^{16}$ cm$^{-3}$ after an intense but brief light exposure [3]. An increase of the defect-related luminescence peak at $0.8$ eV was observed by Pankove et al. [4]. These changes are all reversible upon annealing above $150^\circ$C.

This paper presents new results on the effect of photocreated defects on the field effect and the conductance change due to surface adsorbates. These are consistent with a simple model which explains the doping dependence of the Staebler-Wronski effect.

Doping Dependence of the Staebler-Wronski Effect.—Fig. 1 shows $G_B/G_A$, the room temperature ratio of the dark conductance after prolonged exposure to light (state B) to the dark conductance after annealing in vacuum (state A) as a function of the activation energy $E_a$ of state A. For most samples $G_B/G_A < 1$ in agreement with the results of Staebler and Wronski [1]. However, we find $G_B/G_A > 1$ when the Fermi level $E_F$ of state A is near and slightly above midgap. The conductance changes disappear in strongly doped films. The preparation conditions of our a-Si:H films have been described earlier [5]. They were anodic films which showed no microstructure under scanning electron microscopic examination.

This general trend can be explained by a simple model which assumes that the photo-created defects produce a band of donor states $N_D = 6.8 \times 10^{16}$ cm$^{-3}$ near midgap and an equal number of acceptor states lying above the donor states by $U = 0.4$ eV, as shown in figure 2. Choosing a simple analytical expression $N(E) = N_0 + N_1 \cosh (E/kT_0)$ for the original density of states, we obtained for different choices of $E_F$ in the annealed state A, the theoretical curve shown in figure 1. In accordance with previous measurements [6], we assumed that the conductivity prefactor follows the Meyer-Neldel relation $G_0 = G_{00} \exp (A E_a)$ with $A = 20$ eV$^{-1}$ for both p- and n-type samples. The agreement of the theoretical curve with our data points in figure 1 is surprisingly good, if one considers that $N(E)$ changes with doping and the plasma conditions. Although various choices of $N(E)$, $N_D$, $U$, and the widths of the photo-created donor and acceptor bands yield similar trends of $G_B/G_A$, some general observations are worth noting: (i) $G_B/G_A > 1$, observed for slightly n-type samples, requires that the center of donor and acceptor states lies above midgap; (ii) the donor states must lie below the acceptors to yield $G_B/G_A < 1$ for both

*Present address: Gould Inc., Rolling Meadows, IL 60008

**Fannie and John Hertz Foundation Fellow; present address: Max-Planck-Institut für Festkörperforschung, Stuttgart, Germany

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Activation Energy $E_a$, (eV)

Fig. 1: Doping Dependence of light-induced conductance change. Comparison of data point with theoretical curve obtained from model of figure 2.

p-type and n-type samples; (iii) lightly doped p-type samples in state A convert to n-type in state B, as indicated by the solid curve in figure 1; (iv) the magnitude of the Staebler-Wronski effect diminishes with increasing $N(E)$.

Field Effect Measurements. - Fig. 3 shows the field effect of an undoped 0.6 µm thick a-Si:H film at (69 ± 2)ºC in the dark and in vacuum after annealing to 175ºC and after successive exposures to a 75W projector lamp separated from the sample by 25 cm. The light was incident on the free surface, opposite to the 150 µm thick quartz substrate and the field electrode. The film was deposited at 430K. In state A we found $E_a = 0.92$ eV and $\sigma_0 = 1.1 \times 10^4$ ohm$^{-1}$ cm$^{-1}$; in state B, $E_a = 0.77$ eV, $\sigma_0 = 7.2 \times 10^2$ ohm$^{-1}$ cm$^{-1}$ and with $G_b/G_A = 7$ at 69ºC. Although the zero field conductance reached its final value within 2.5 hours of light exposure, it took well over 10 hours for the field effect response to saturate. The conductance minimum is observed to shift in qualitative agreement with the decrease in $E_a$ and an upward shift of $E_F$. The second anneal removed the light-induced changes and restored the original state A. The lines through the data in figure 3 are the results of computer fits which yielded the field effect density of states $N_F(E)$ shown in figure 4. Since we do not know the position of $E_F$ in the intermediate exposure states, $N_F(E)$ is plotted against $E - E_F$, the quantity obtained from the data analysis [7]. Fig. 4 shows explicitly an increase in $N_F(E)$ from about $3 \times 10^{16}$ to $10^{17}$ eV$^{-1}$ cm$^{-3}$ near $E_F$.

$N_F(E)$ may be larger than the bulk density of states because of factors discussed elsewhere [6,7]. In addition, we wish to point out the following. The field effect analysis assumes that $\sigma_0$ is constant throughout the space charge region. If, on the other hand, $\sigma_0$ decreases with decreasing separation of $E_F$ from the mobility edges, according to the Meyer-Neldel relation [8], substantially smaller values for $N_F(E)$ are obtained. Using $A = 15$ eV$^{-1}$ and 22 eV$^{-1}$, we find $N_F(E_F) = 10^{16}$ eV$^{-1}$ cm$^{-3}$ and $6 \times 10^{15}$ eV$^{-1}$ cm$^{-3}$, respectively, for the first anneal field effect curve. A similar decrease of $N_F(E)$ is expected for the light-soaked state B. Scaling down all N(E) in figure 4 will not affect the results in figure 3.

Adsorbate-Induced Changes. - An increase of $N(E)$ with light exposure should result in a decrease of the conductance changes caused by adsorbates or insulating overlayers which produce space charge layers. As an example, we show in figure 5 the

Fig. 2: Simple model for $N(E)$ and photo-created donors and acceptors.
decrease of the effect of 20% relative humidity on the conductance of a 1.5 \mu m thick n-type sample as the result of successive light exposures. The light intensity was 0.2 W/cm². In state A we obtained \( E_a = 0.8 \text{ eV} \) and \( \sigma_0 = 3 \times 10^4 (\text{\Omega \ cm})^{-1} \). After different light exposures, the moisture was admitted to a flow of dry \( \text{N}_2 \) at \( t = 0 \). Between runs the sample was heat-dried in vacuum and darkness at 170°C. The observed decrease in sensitivity to moisture corresponds to an increase of \( N(E_F) \) from about \( 8 \times 10^{15} \text{ eV}^{-1} \text{ cm}^{-3} \) to \( 2 \times 10^{17} \text{ eV}^{-1} \text{ cm}^{-3} \) for 44 minute light exposure. This calculation assumed constant \( \sigma_0 \) in the space charge region. In a separate experiment we found that the same final conductance values are reached when the sequence of exposure to light and moisture is reversed.
Summary and Conclusions.- We have shown explicitly a completely reversible increase in $N(E)$ of plasma-deposited a-Si:H from about $4 \times 10^{16}$ to $1-2 \times 10^{17}$ eV$^{-1}$ cm$^{-3}$ near the gap center upon exposure to light. The total number of photo-created states ($\sim 10^{17}$ cm$^{-3}$) observed by the field effect is larger than the additional spins found by Dersch et al. [3]. However, our numbers will be reduced if $g_0$ changes in the space charge region according to the Meyer-Neldel expression.

The doping dependence of the Staebler-Wronski effect suggests that donor and acceptor states are produced at roughly equal concentrations. The chemical potential of the photo-created states lies somewhat ($\sim 0.15$ eV) above the gap center. This causes an increase of $G$ with light exposure for lightly n-type samples and a conversion of lightly p-type samples to n-type. Assuming an appropriate $N(E)$ of state A, the doping dependence can be explained with broad and overlapping distributions of donor and acceptor states in basic agreement with the field effect measurements. Light-induced changes in $G$ depend on $N(E)$, surface layers, and the position of $E_F$. Hence, they are not a reliable measure of the number of light-created defects.

The question remains of what is the origin of these light-induced gap states. The ESR results prove that dangling bonds separated by at least 10Å are created. It is likely that light exposure breaks weak Si-Si bonds with a subsequent relaxation of the neighboring network [3]. Hydrogen can transfer to the arising dangling bonds from neighboring Si-H bonds, thereby separating the dangling bonds and creating a metastable state. This model requires extended clusters of Si-H bonds to attain sufficient dangling bond separation. Such clusters have been observed by NMR [9].

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