THE DENSITY-OF-STATE DISTRIBUTION IN UNDOPED a-Si:H AND a-SiGe:H DETERMINED BY HETEROJUNCTIONS WITH c-Si

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ABSTRACT

A novel technique has been proposed for determining the density-of-state (DOS) distribution in the mobility gap of highly resistive amorphous semiconductors, using amorphous/crystalline heterojunction structures. This technique has been tested and applied on undoped a-Si:H and a-SiGe:H films, covering the optical gap (E_o) range of 1.30 to 1.76 eV. For undoped a-Si:H with E_o=1.76 eV, the peak of the midgap DOS distribution has been located at 0.85 eV below the conduction band edge, E_c, with a value of 5.6×10^{15} $cm^{-3}eV^{-1}$. For undoped a-SiGe:H (E_o=1.55 eV), the same has been obtained 0.71 eV below E_c, with a magnitude of 7.9×10^{16} $cm^{-3}eV^{-1}$. Those midgap states have been found to be correlated with singly-occupied dangling bonds.

INTRODUCTION

The electronic properties of hydrogenated amorphous silicon (a-Si:H) films are critically linked with the density and distribution of localized states in the mobility gap of a-Si:H. In order to enhance the performance of a-Si:H based devices, a low density-of-state (DOS) distribution, g(E), in the mobility gap, is essential. Measurement of g(E) and an understanding of the nature of the gap states are, therefore, very important. Many techniques have been developed to determine g(E). These include both optical and electrical methods (1,2), while they have some limitations in their application.

In the present work, we have focused on determining g(E) below the Fermi level (E_F) in undoped a-Si:H films and also in undoped hydrogenated amorphous silicon-germanium alloy (a-SiGe:H) films. These films play an important role in enhancing the performance of amorphous solar cells. A few groups have sought to infer the energy location of the dangling bonds in a-SiGe:H (3-6).

Prior to this, the density of midgap states for undoped a-Si:H was obtained from the capacitance-voltage (C-V) characteristics of undoped (i.e., n-type) a-Si:H/p-type crystalline silicon (p c-Si) heterojunction structures under 100 kHz (7). This method will be called a steady-state heterojunction-monitored capacitance (HMC) method in the following sections.

The steady-state HMC method has been applied to undoped a-SiGe:H with the optical gap (E_o) between 1.30 and 1.70 eV. Moreover, it has been demonstrated that the g(E) below E_F in amorphous films (1.30 eV $\leq E_o \leq$ 1.76 eV) can be determined from the experimental results of transient HMC measurements.

THEORY OF HETEROJUNCTION-MONITORED CAPACITANCE METHOD

Steady-state regime

The depletion region formed by an undoped a-Si:H (or a-SiGe:H)/p c-Si heterojunction is considered. When a reverse bias voltage (V_R) is applied, it produces space-charge layers both in amorphous and crystalline semiconductors. Under the assumption that this p c-Si has only shallow acceptors, the space charge in the p c-Si is formed by negatively-charged acceptors. However, the amorphous component possesses midgap states. Origin of the space charge in amorphous semiconductors is schematically discussed, using Fig. 1 where E_g is the band gap of the semiconductor, W the width of the depletion region, L the thickness of the amorphous film, N_A the acceptor density in the p c-Si, and V_B

the built-in potential. The subscripts 1 and 2 refer to p c-Si and undoped films, respectively, and the subscripts C and V refer to the conduction band and the valence band, respectively. In the neutral region, all the gap states below E_F are occupied by electrons, while in the depletion region the states below E_{OB2} are occupied by electrons, where E_{OB2} is determined from the condition that the thermal-emission rate for electrons is equal to that for holes, and given by (8)

$$E_{OB2} = E_C - E_{g2}/2 + (kT/2)\ln(\nu_p/\nu_n) \quad . \tag{1}$$

Here ν_n and ν_p are the attempt-to-escape frequencies for electrons and holes, respectively. Therefore, the gap states as indicated by the black area in Fig. 1(a) behave like positively-charged states, here, referred to as donor-like states and the density of the donor-like states is constant between spatial position 0 and W_2. This together with the density of donors (if they exist) gives the effective density of donor-like states (N_I), as shown in Fig. 1(c). Figure 1(b) shows the potential variation with distance. The depletion widths (W_1 and W_2) are given by

$$qN_AW_1 \simeq qN_IW_2 \quad , \tag{2}$$

with

$$W_1 = (2\varepsilon_{s1}(V_{B1} - V_{R1})/qN_A)^{1/2} \quad , \tag{3}$$

and

$$W_2 \simeq (2\varepsilon_{s2}(V_{B2} - V_{R2})/qN_I)^{1/2} \quad . \tag{4}$$

Here ε_s is the semiconductor permittivity.

The capacitance has been measured using a small AC voltage at 1 MHz. The resistivity (ρ_1) of p c-Si used in this study is about 1 Ωcm so that the dielectric relaxation time ($\varepsilon_{s1}\rho_1$) becomes 10^{-12} s. The capacitance (C_1) at 1 MHz in the p c-Si is given by

$$C_1 = \varepsilon_{s1}/W_1 \quad . \tag{5}$$

On the other hand, the minimum value of resistivity (ρ_2) of undoped a-SiGe:H used is 10^{7} Ω cm. Then, the dielectric relaxation time becomes 10^{-5} s. Thus, the undoped film may be considered as a dielectric material in its behavior in the case of the 1-MHz AC voltage, indicating that the capacitance (C_2) at 1 MHz in the undoped films should be given by

$$C_2 = \varepsilon_{s2}/L \quad . \tag{6}$$

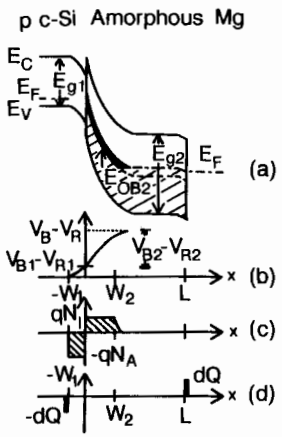

Fig. 1.

Schematic sketches of the heterojunction: (a) energy-band diagram; (b) potential variation; (c) space-charge density for V_R; (d) charge in response to a small 1-MHz AC voltage to measure capacitance. The gap states as indicated by the black area are positively-charged states, and the states as indicated by the hatched area are occupied by electrons.

The measured HMC (C_{HM}) at 1 MHz is from a series of C_1 and C_2, and is expresses as

$$1/C_{HM} = 1/C_1 + 1/C_2 \quad , \tag{7}$$

because spatially the free charged carriers can respond to the 1-MHz AC voltage at W_1 and L, as shown in Fig. 1(d). From Eqs. (2)-(4), the following relation is obtained;

$$(V_{B1} - V_{R1})/(V_{B2} - V_{R2}) \simeq N_I \varepsilon_{s2}/N_A \varepsilon_{s1} \quad . \tag{8}$$

The final equation is obtained as

$$W_1^2 = \varepsilon_{s1}^2 (1/C_{HM} - 1/C_2)^2 \tag{9}$$

$$\simeq 2\varepsilon_{s1}\varepsilon_{s2}N_I(V_B - V_R)/qN_A(N_A\varepsilon_{s1} + N_I\varepsilon_{s2}) \tag{10}$$

from Eqs. (3), (5), (7), and (8). As is clear from Eq. (10), the values of N_I and V_B can be graphically determined from the slope and the intercept on the abscissa, respectively.

Transient regime

In order to estimate g(E), the transient HMC is considered after V_R is applied to the sample over the zero-bias condition ($-t_f \leq t < 0$), as shown in Fig. 2. At t=+0, V_R is applied across the whole of the amorphous and crystalline components. Electrons trapped at shallower states at $t < 0$ get thermally emitted into the conduction band. After V_R has been on for the dielectric relaxation time ($\varepsilon_{s2}\rho_2$) of the amorphous film, the space charge in the vicinity of the heterojunction will redistribute itself in response to the applied potential, as shown in Fig. 2(b). The data of $C_{HM}(t)$ after the dielectric relaxation time can be analyzed from Eq. (10) and N_I at a time of t can expresses as

$$N_I(t) = \varepsilon_{s1}V_c(t)N_A/\varepsilon_{s2}(V_B - V_R - V_c(t)) \tag{11}$$

with

$$V_c(t) = qN_A W_1^2(t)/2\varepsilon_{s1} \tag{12}$$

and

$$W_1(t) = \varepsilon_{s1}(1/C_{HM}(t) - 1/C_2) \tag{13}$$

where $W_1(t)$ is the depletion width at time t and $V_c(t)$ is the voltage across the depletion region of the p c-Si at t. In order to make the above analysis feasible, the absolute value of V_R has to be necessarily much higher than V_B, so that the relation ($N_I(t)W_2(t) \gg N_I(\infty)W_2(0)$) is valid and the average value

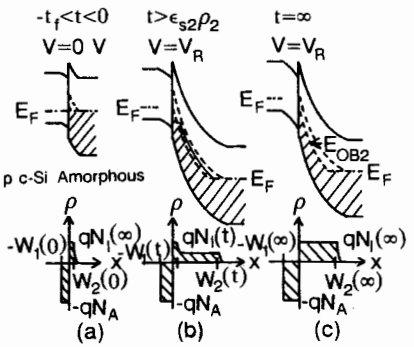

Fig. 2.

Schematic sketches (energy-band diagram and space-charge density) of the heterojunction at three times. The gap states as indicated by the hatched area are occupied by electrons, so that they are neutral. In the depletion region, therefore, the empty gap states between E_F and E_{OB2} behave as positively-charged states.

of N_I over the depletion region at t is close to $N_I(t)$. This condition also suggests that interface states do not affect the measurement of HMC.

The function H(t) is defined as

$$H(t) \equiv -t(d\Delta N_I(t)/dt) \tag{14}$$

with

$$\Delta N_I \equiv N_I(t) - N_I(\infty) \quad , \tag{15}$$

and the measured H(t) is obtained from $C_{HM}(t)$ using Eqs. (11)-(14). The values of V_B and C_2 have been obtained from steady-state HMC measurements.

On the other hand, H(t) is theoretically derived as

$$H(t) = \int_{E_V}^{E_C} (f(E)-F_\infty(E))g(E)t(e_n(E)+e_p(E))\exp(-(e_n(E)+e_p(E))t)dE \tag{16}$$

with

$$f(E) = 1/(1+\exp((E-E_F)/kT)) \quad , \tag{17}$$

$$F_\infty(E) = e_p(E)/(e_n(E)+e_p(E)) \quad , \tag{18}$$

$$e_n(E) = \nu_n \exp((E-E_C)/kT) \quad , \tag{19}$$

and

$$e_p(E) = \nu_p \exp((E_V-E)/kT) \quad . \tag{20}$$

The way of determining g(E) from which H(t) of Eq. (16) can be obtained to fit the measured H(t), has been described in the section of results and discussion.

Under the condition that $e_p(E) \ll e_n(E)$ and $f(E) \simeq 1$ (i.e., for the gap states between E_F and E_{OB2}), the relations

$$g(E(t)) = H(t)/kT \tag{21}$$

and

$$E_C - E(t) = kT \ln(\nu_n t) \tag{22}$$

are obtained, which are similar to the relations obtained from the isothermal capacitance transient spectroscopy (ICTS) analysis (2).

EXPERIMENT

Undoped a-Si:H films (E_O=1.76 eV) were deposited using a diode-type glow discharge reactor from pure SiH_4, and undoped a-SiGe:H films (E_O=1.55, 1.63, 1.70 eV) were prepared using a triode-type glow discharge reactor from GeH_4/SiH_4 gas mixture. Undoped a-SiGe:H films (E_O=1.30 eV) were deposited using a diode-type glow discharge reactor from $H_2/GeH_4/SiH_4$ gas mixture. Good quality films can be obtained from these techniques (9).

The heterojunctions were fabricated by depositing the amorphous films (thickness between 0.5 and 1 μm) onto p c-Si substrates (N_A=1x10^{16} cm^{-3}) heated to 250 °C and then evaporating magnesium (Mg) on an area (0.785 mm^2) of those films at room temperature. Mg forms an ohmic contact with those amorphous films (10). All the heterojunctions have exhibited good rectifying properties.

The C-V characteristics of those heterojunctions were measured at 1 MHz at room temperature. Detailed calculation of W_1 was performed by the minicomputer. The transient capacitance, $C_{HM}(t)$, was measured at 2 MHz under isothermal conditions in the time range of 10^{-4}-10^{3} s, being converted to digital signals and memorized in the minicomputer. Detailed calculation of H(t) was performed by the minicomputer.

RESULTS AND DISCUSSION

Steady-state HMC measurements

Figure 3 shows the W_1^2–V curve obtained using Eq. (9) from C_{HM}–V characteristics of the a-SiGe:H (E_0=1.70 eV)/p c-Si heterojunction. The value of C_2 which has been used to calculate W_1 in Eq. (9) is the saturated capacitance with the forward bias. The data reveal a good linear relationship, indicating that the model mentioned in the previous section is applicable to the present system. As is clear from Eq. (10), values of N_I=6.3x10^{15} cm^{-3} and V_B=0.18 eV have been obtained from Fig. 3.

It has been experimentally found that the W_1^2–V_R relations for all the heterojunctions obey Eq. (10). N_I has been found to be independent of the thickness of the amorphous film. The dependence of N_I on E_0 is shown in Fig. 4. These results remain unaffected at measuring frequencies higher than $1/2\pi\varepsilon_{s2}\rho_2$, where ρ_2 depends on measuring temperature.

The bulk spin densities obtained from electron spin resonance (ESR) measurements are 1.3x10^{17} and 3.6x10^{15} cm^{-3} for undoped a-SiGe:H (E_0=1.30 eV) and undoped a-Si:H (E_0=1.76 eV), respectively, and they are close to N_I. Therefore, these results indicate that N_I represents the density of singly-occupied dangling bonds (D^0). This optical-gap dependence of N_I coincides with that of the integrated sub-bandgap absorption determined by constant photocurrent measurements (8, 11).

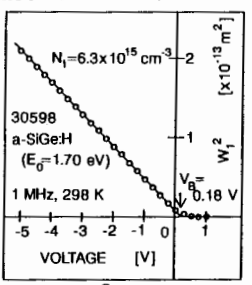

Fig. 3. W_1^2–V relation

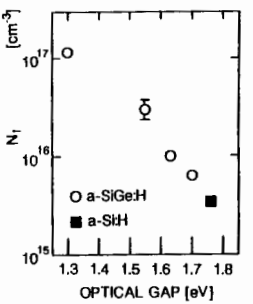

Fig. 4. Dependence of N_I on E_0

Transient HMC measurements

Transient capacitance, $C_{HM}(t)$, has been measured at various temperatures. Only signals of H(t) longer than the dielectric relaxation time are valid. The signals of H(t) get saturated at a filling time, t_f, (under the zero-bias condition) longer than 1 s, and they have been found to be independent of V_R for $V_R \leq$ -3 V. Therefore, $C_{HM}(t)$ has been measured at t_f=50 s and V_R=-4 V.

The measured H(t) for the a-SiGe:H (E_0=1.70 eV)/p c-Si heterojunction at 353 K is shown in Fig. 5. From the temperature dependence of the time (t_p) at

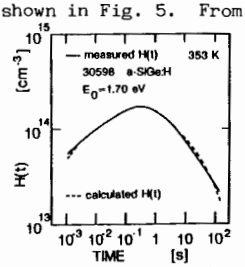

Fig. 5. Comparison between the measured and calculated H(t).

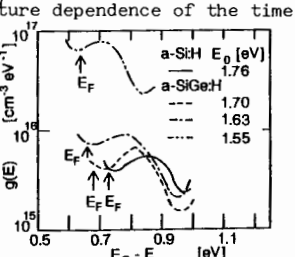

Fig. 6. DOS distribution.

which the signal of H(t) becomes maximum, a value of ν_n=8x10^{11} s^{-1} has been obtained using Eq. (22). The H(t) which has been calculated from Eq. (16) is shown in Fig. 5. Here the g(E) for E_0=1.70 eV as shown in Fig. 6 has been used and ν_p has been assumed to be 1x10^{8} s^{-1} (8). The calculated H(t) have been found to fit the measured H(t) very well at each temperature.

All the g(E) obtained from the fitting procedure are shown in Fig. 6. The values of ν_p obtained from the temperature dependence of t_p are 4x10^{12}, 1x10^{12}, and 4x10^{11} s^{-1} for E_0=1.55, 1.63, and 1.76 eV, respectively, and these values have been used to determine g(E). These g(E) are correlated with D^0, as is clear from the results of steady-state HMC measurements.

Tsutsumi et al. (6) first determined the energy location of D^0 in a-SiGe:H, while Mackenzie et al. (3), Skumanich et al. (4) and Aljishi et al. (5) discussed it in relation with their own experimental results. Our data coincide quantitatively with the data reported by Tsutsumi et al., although all the groups have reported the similar optical-gap dependence of the energy location of D^0. Using the transient HMC method, however, we have determine the magnitude as well as the location of D^0 for the first time.

SUMMARY

The densities of midgap states of undoped a-SiGe:H and undoped a-Si:H have been determined using amorphous/crystalline heterojunction structures. These densities have been found to be independent of the measuring frequency as well as the measuring temperature when the measuring frequency is higher than $1/2\pi\varepsilon_{s2}\rho_2$. They have been found to be densities of singly-occupied dangling bonds in those materials. The DOS distributions for these films have been determined by transient HMC measurements which have been proposed.

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