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Density of Mid-Gap States for Undoped a-$Si_{1-x}Ge_x$:H and a-Si:H Determined by Steady-State Heterojunction-Monitored Capacitance Method

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A simple technique has been described for determining the density of mid-gap states of highly resistive amorphous semiconductors, using amorphous/crystalline heterojunction structures. The technique has been tested and applied on undoped hydrogenated amorphous silicon films and silicon-germanium alloy films, covering the optical gap range of 1.30 to 1.76 eV. Those densities obtained from this technique have been found to be densities of singly-occupied dangling bonds.

KEYWORDS: density of mid-gap states, singly-occupied dangling bonds, undoped a-Si:H, undoped a-$Si_{1-x}Ge_x$:H, steady-state heterojunction-monitored capacitance

§1. Introduction

The electronic properties of hydrogenated amorphous silicon (a-Si:H) films are critically linked with the density 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 the states is essential. Measurement of the density and an understanding of the nature of the gap states are therefore very important. The problem has received considerable attention, and many techniques have been developed to determine the density. These include both optical and electrical methods.[1-4]

Prior to this letter, an effective density of donor-like states (N_I) for undoped a-Si:H had been obtained from the capacitance-voltage ($C-V$) measurement of undoped (i.e., n-type) a-Si:H/p-type crystalline silicon (p c-Si) heterojunctions under high frequency (100 kHz).[5] This method will be called a steady-state heterojunction-monitored capacitance (HMC) method in this letter. The steady-state HMC method has been tested and applied on undoped hydrogenated amorphous silicon-germanium alloy (a-$Si_{1-x}Ge_x$:H) films which are important as the low band-gap component in tandem-type amorphous silicon solar cells.

§2. Theory of Steady-State Heterojunction-Monitored Capacitance Method

The depletion region formed by an undoped a-$Si_{1-x}Ge_x$:H (or a-Si:H)/p c-Si heterojunction is considered. When a reverse voltage 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 gap states. Origin of the space charge in amorphous semiconductors is schematically discussed. In the neutral region, all the gap states below the Fermi level (E_F) are occupied by electrons, while in the depletion region the states above E_{OB2} are vacant of electrons, where E_{OB2} is determined by thermal-emission rates for electrons and holes and given by

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

Here ν_p and ν_n are the attempt-to-escape frequencies for holes and electrons, respectively. Therefore, the gap states as indicated by the black area in Fig. 1(a) behave as 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 where V_B is the built-in potential. The depletion widths (W_1 and W_2) are given by

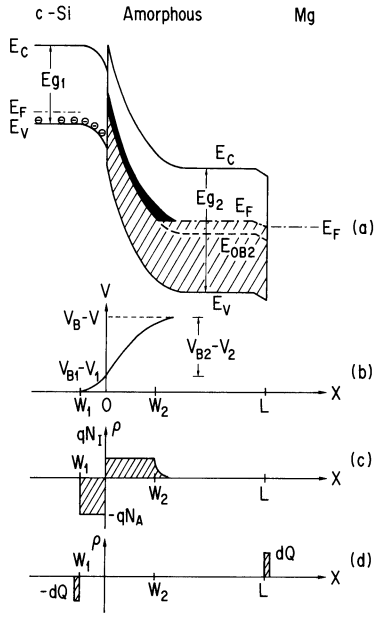

Fig. 1. Schematic sketches of the heterojunction: (a) energy-band diagram; (b) potential variation; (c) space-charge density for a reverse bias voltage; (d) charge in response to a small 1 MHz AC voltage to measure capacitance. The gap states as indicated by the black area are positively-charged states and the states as indicated by the hatched area of (a) are occupied by electrons. Dashed-dotted lines represent the Fermi level. ⊖ represents a negatively-charged acceptor.

$$qN_A W_1 \simeq qN_I W_2, \tag{2}$$

with

$$W_1 = (2\varepsilon_{s1}(V_{B1} - V_1)/qN_A)^{1/2} \tag{3}$$

and

$$W_2 \simeq (2\varepsilon_{s2}(V_{B2} - V_2)/qN_I)^{1/2}. \tag{4}$$

Here N_A is the density of the acceptors in p c-Si and ε_s the semiconductor permittivity. In Fig. 1, E_g is the energy gap of the semiconductor and L the thickness of the amorphous film. The subscripts 1 and 2 refer to p c-Si and a-$Si_{1-x}Ge_x$:H (or a-Si:H), respectively, and the subscripts C and V refer to the conduction band and the valence band, respectively.

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 1 $\Omega\cdot$cm so that the dielectric relaxation time ($\varepsilon_{s1}\rho_1$) becomes about 10^{-12} s, indicating that free holes (majority carriers of p c-Si) can respond to the 1 MHz AC voltage. The capacitance (C_1) in c-Si is given by

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

On the other hand, the minimum value of resistivity (ρ_2) of undoped a-$Si_{1-x}Ge_x$:H used is 10^7 $\Omega\cdot$cm. Then the dielectric relaxation time ($\varepsilon_{s2}\rho_2$) becomes about 10^{-5} s, suggesting that free electrons (majority carriers of those films) cannot respond to AC voltage higher than 100 kHz. 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) in the amorphous film should be given by

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

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

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

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;

$$(V_{B1} - V_1)/(V_{B2} - V_2) \simeq N_I\varepsilon_{s2}/N_A\varepsilon_{s1}. \tag{8}$$

The final equation is obtained as

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

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

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.

§3. Sample Preparation

Undoped a-$Si_{1-x}Ge_x$:H films with the optical gap (E_0) of 1.30 and 1.32 eV and undoped a-Si:H films have been deposited using a diode-type glow discharge reactor from $GeH_4/SiH_4/H_2$ gas mixture and pure SiH_4 gas, respectively. Undoped a-$Si_{1-x}Ge_x$:H films (1.55 eV $\leq E_0 \leq$ 1.70 eV) have been prepared using a triode-type glow discharge reactor from GeH_4/SiH_4 gas mixture. Good quality films can be obtained from these techniques.[6]

The heterojunctions have been fabricated by depositing the amorphous films onto p c-Si substrates ($N_A = 1\times10^{16}$ 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.[7] All the heterojunctions have exhibited good rectifying properties.

§4. Results and Discussion

Figure 2 shows the temperature dependence of $C_{HM} - V$ characteristics for the a-$Si_{1-x}Ge_x$:H ($E_0 = 1.70$ eV)/p c-Si heterojunction at 1 MHz. The value of $1/2\pi\varepsilon_{s2}\rho_2$ corresponding to 304 K remains lower than 1 MHz. The capacitance at $V < -2$ V has been found to be independent of the measuring temperature. This indicates that N_I determined at $V < -2$ V is reliable.

The frequency dependence of $C_{HM} - V$ characteristics for the a-Si:H ($E_0 = 1.76$ eV)/p c-Si heterojunction at 298 K is shown in Fig. 3. The frequency of 1 kHz remains higher than $1/2\pi\varepsilon_{s2}\rho_2$ since $\rho_2 \sim 10^9$ $\Omega\cdot$cm. The capacitance at $V < -2$ V has been found to be independent of the frequency, indicating that N_I determined at $V < -2$ V is trustworthy. Therefore, N_I which is obtained

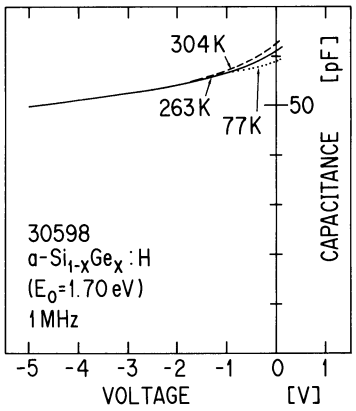

Fig. 2. Set of three $C_{HM} - V$ curves at 1 MHz corresponding to different measuring temperatures for the a-$Si_{1-x}Ge_x$:H ($E_0 = 1.70$ eV) /p c-Si ($N_A = 1.0\times10^{16}$ cm^{-3}) heterojunction.

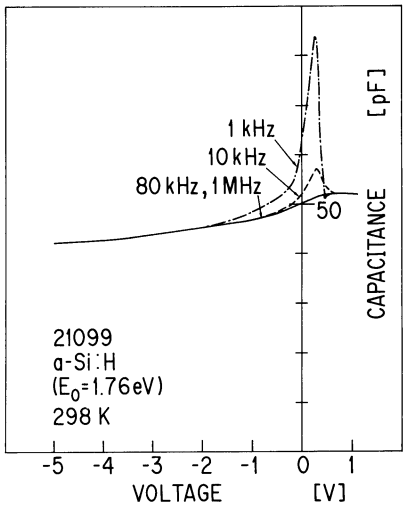

Fig. 3. Set of four $C_{HM} - V$ curves at 298 K corresponding to different measuring frequencies for the a-Si:H ($E_0 = 1.76$ eV)/p c-Si ($N_A = 1.0\times10^{16}$ cm^{-3}) heterojunction.

at high reverse bias is reliable when C_{HM} is measured at frequency higher than $1/2\pi\varepsilon_{s2}\rho_2$.

Figure 4 shows the W_1^2-V characteristics obtained using eq. (9) from $C_{HM}-V$ characteristics of the a-Si_{1-x} Ge_x:H ($E_0=1.63$ 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 §2 is applicable to the present system. As is clear from eq. (10), values of $N_I=1.0\times10^{16}$ cm^{-3} and $V_B=0.26$ V have been obtained from Fig. 4. It has been experimentally found that the W_1^2-V relations for all the heterojunctions obey eq. (10).

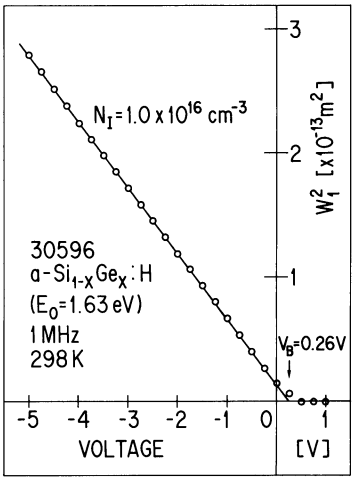

Fig. 4. Width of the depletion region in p c-Si ($N_A=1.0\times10^{16}$ cm^{-3}) as a function of voltage for a-$Si_{1-x}Ge_x$:H ($E_0=1.63$ eV).

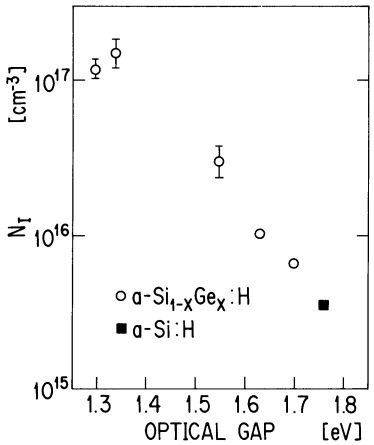

Fig. 5. Effective density of donor-like states as a function of optical gap.

The dependence of N_I on E_0 is shown in Fig. 5. N_I is proportional to the integrated sub-bandgap absorption determined by constant photocurrent measurements (CPM). This optical-gap dependence of N_I coincides with that of the integrated sub-bandgap absorption reported by Aljishi *et al.*[8] The spin densities obtained from ESR are 1.3×10^{17} and 3.6×10^{15} cm^{-3} for undoped a-Si_{1-x} Ge_x:H ($E_0=1.30$ eV) and undoped a-Si:H, respectively, and they are close to N_I. Therefore, these results indicate that N_I represents the density of singly-occupied dangling bonds.

§5. Summary

The densities of mid-gap states of undoped a-Si_{1-x} Ge_x: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.

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