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Midgap-state profiles in undoped amorphous-silicon-based alloys

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ABSTRACT

Midgap-state densities and profiles in undoped hydrogenated amorphous silicon (a-Si : H), silicon–germanium alloy (a-$Si_{1-x}Ge_x$: H) and silicon–carbon alloy (a-$Si_{1-x}C_x$: H) films were obtained from a heterojunction-monitored capacitance method. These midgap states were found to correspond to singly-occupied dangling bonds. The density of midgap states increases slowly with the Ge content in the film, while it increases rapidly with the C content. The peak of the midgap-state profile appears clearly in a-Si : H and a-$Si_{1-x}Ge_x$: H, but it does not appear clearly in a-$Si_{1-x}C_x$: H.

§ 1. INTRODUCTION

Many techniques, summarized by Le Comber and Spear (1986), have been developed to determine the density-of-states distribution, $g(E)$, in hydrogenated amorphous silicon (a-Si : H), silicon–germanium alloy (a-$Si_{1-x}Ge_x$: H) and silicon–carbon alloy (a-$Si_{1-x}C_x$: H) films, because the electric properties of these films are critically linked with $g(E)$. All these techniques have some limitations in their application. It is especially difficult to determine $g(E)$ in highly resistive (undoped) amorphous semiconductors, and undoped films usually limit the performance of amorphous devices, such as solar cells and thin-film transistors. We have developed a technique for determining $g(E)$ below the Fermi level (E_F) in highly resistive amorphous semiconductors from the high-frequency capacitance of amorphous/crystalline silicon (c-Si) heterojunction structures, referred to as the heterojunction-monitored capacitance (HMC) method (Matsuura 1988 a, b).

In this Letter, we have applied the HMC method to undoped a-Si : H, a-$Si_{1-x}Ge_x$: H and a-$Si_{1-x}C_x$: H, and discuss the behaviour of these midgap states when Ge atoms (or C atoms) are incorporated into a-Si : H.

§ 2. EXPERIMENT

Undoped a-Si : H films and undoped a-$Si_{1-x}C_x$: H films were deposited using a diode-type glow-discharge reactor from pure SiH_4 gas and H_2–SiH_4–CH_4 gas mixture respectively. Undoped a-$Si_{1-x}Ge_x$: H films with an optical gap (E_0) of 1·30 eV were deposited using a diode-type glow-discharge reactor from H_2–GeH_4–SiH_4 gas

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mixture, and undoped a-$Si_{1-x}Ge_x$:H ($1{\cdot}55\,eV \leqslant E_0 \leqslant 1{\cdot}70\,eV$) films were prepared using a triode-type glow-discharge reactor from GeH_4–SiH_4 gas mixture. The thicknesses were between 0·5 and 1·2 μm.

The heterojunctions were fabricated by depositing the amorphous films on to p-type c-Si substrates with an acceptor density (N_A) of $10^{16}\,cm^{-3}$, heated to 250°C, and then evaporating magnesium (Mg) on an area ($0{\cdot}785\,mm^2$) of those films at room temperature. Mg forms an Ohmic contact with those amorphous films (Matsuura and Okushi 1987). All the heterojunctions exhibited good rectifying properties. The samples for measurements of optical gap, conductivity, photothermal deflection spectroscopy (PDS) and electron spin resonance (ESR) were fabricated by depositing the amorphous films on to fused silica substrates heated to 250°C.

The capacitance was measured using a Sanwa MI-415 capacitance meter (2 MHz). The HMC was measured as a function of temperature in the range between 213 and 413 K.

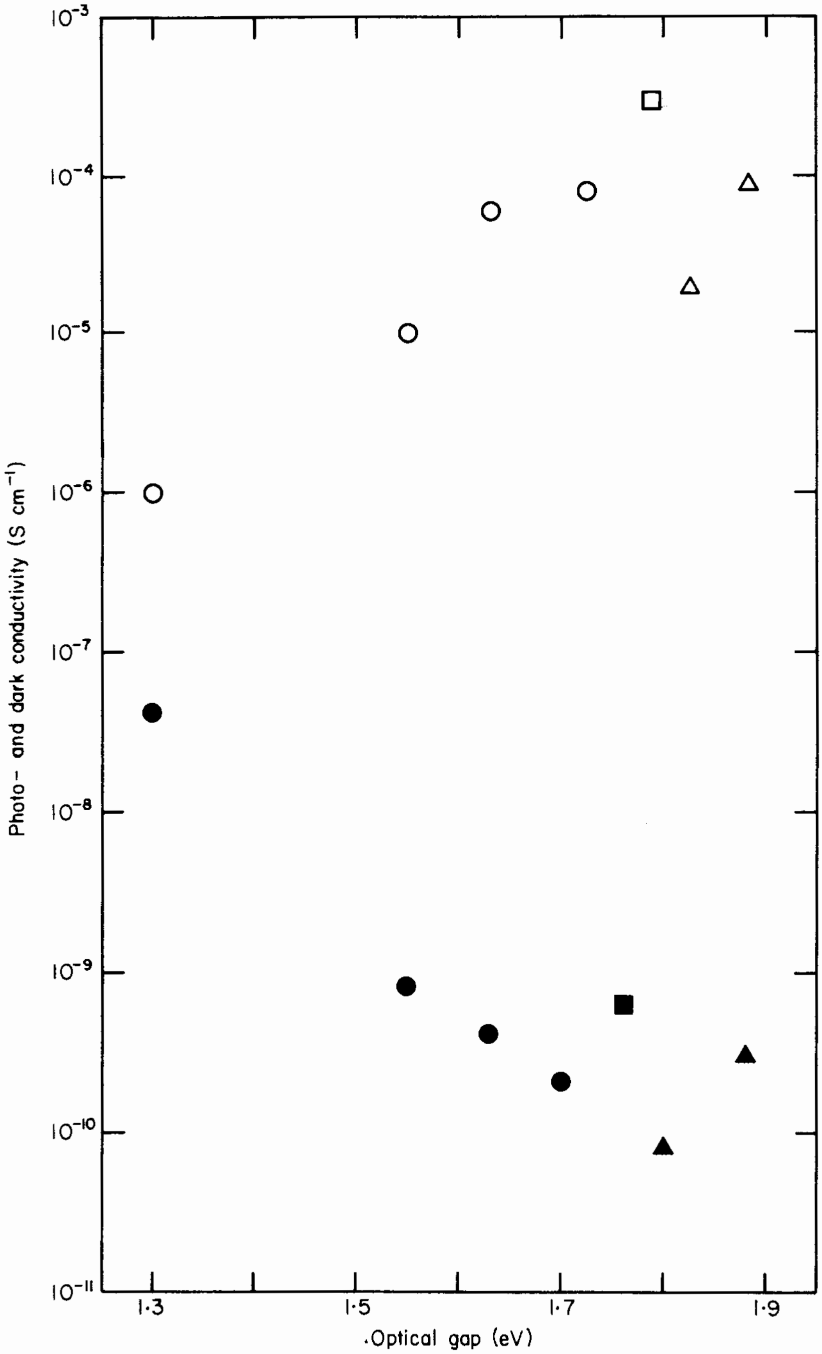
§3. Results and discussion

Figure 1 shows the dark conductivity and photoconductivity of films used in this study, indicating that the quality of the films was good. The Ge contents (x) determined from electron probe microanalysis (EPMA) in a-$Si_{1-x}Ge_x$:H were 0·80, 0·48, 0·44 and 0·27 for $E_0 = 1{\cdot}30$, 1·55, 1·63 and 1·70 eV respectively. The C contents (x) determined from Auger electron spectroscopy (AES) in a-$Si_{1-x}C_x$:H were 0·11 and 0·15 for $E_0 = 1{\cdot}80$ and 1·88 eV respectively. The Urbach energies obtained from PDS were 73, 58, 52, 62, 50, 84 and 67 meV for $E_0 = 1{\cdot}30$, 1·55, 1·63, 1·70, 1·76, 1·80 and 1·88 eV respectively.

Figure 2 shows the relation between the optical gap and the density of midgap states (N_I) obtained from the steady-state HMC method (Matsuura, Okuno, Okushi and Tanaka 1984, Matsuura 1988 c), and the relationship between N_I and the bulk spin densities (N_s) from ESR is inserted. The density of midgap states increases slowly with the Ge content, while it increases rapidly with C content. This optical-gap dependence of the midgap state density coincides with the result obtained from constant photocurrent measurements (Aljishi, Chu, Smith, Shen, Conde, Slobodin, Kolodzey and Wagner 1987). As is clear from the inserted figure, the value of N_I is close to the corresponding bulk ESR spin density where surface state contributions were estimated by results from a series of films over a range of thicknesses, indicating that N_I represents the density of singly-occupied dangling bonds (D^0).

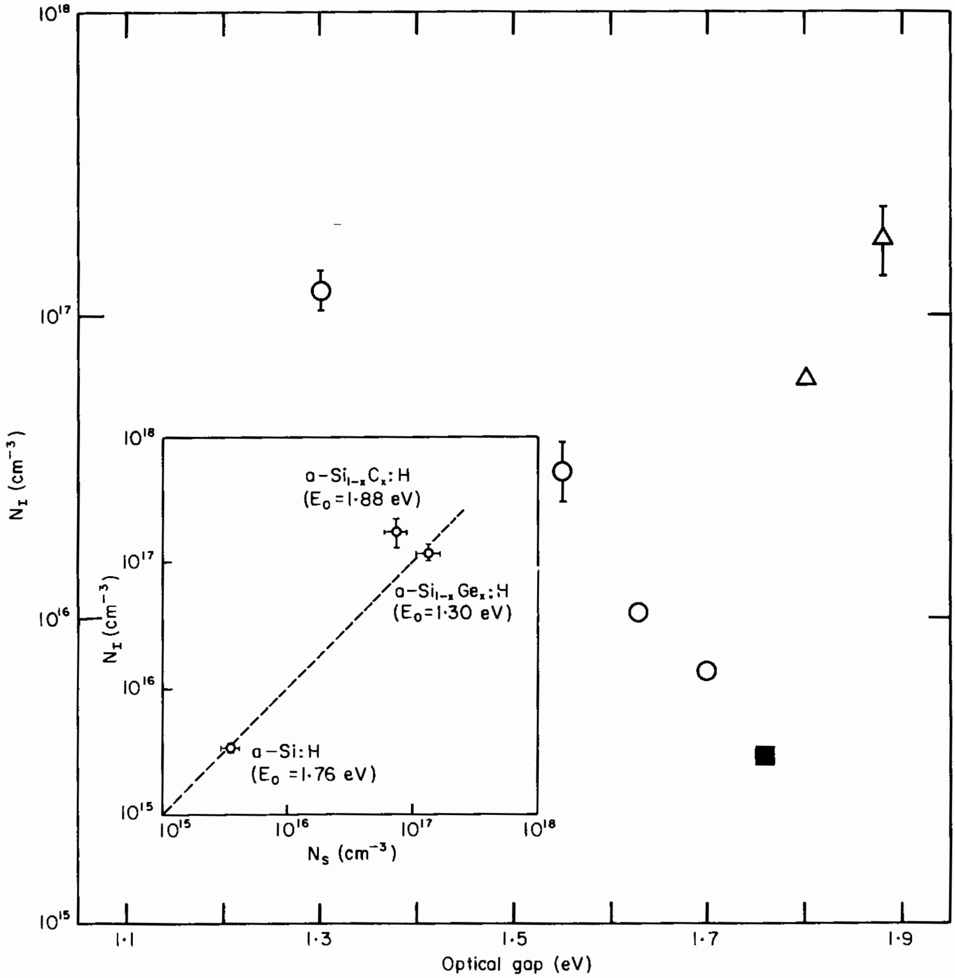
The g values obtained from ESR were 2·018, 2·006 and 2·005 for a-$Si_{1-x}Ge_x$:H ($E_0 = 1{\cdot}30\,eV$), a-Si:H ($E_0 = 1{\cdot}76\,eV$) and a-$Si_{1-x}C_x$:H ($E_0 = 1{\cdot}88\,eV$) respectively. Shimizu, Kumeda and Kiriyama (1981) reported that the g values for dangling bonds of Ge, Si and C are 2·019, 2·0055 and 2·003 respectively. Morimoto, Miura, Kumeda and Shimizu (1981) reported that the ratio of Ge dangling bonds to Ge atoms is higher by a factor of four to fifteen than the ratio of Si dangling bonds to Si atoms. From these experimental results, N_I in a-$Si_{1-x}Ge_x$:H with at least $E_0 \leqslant 1{\cdot}63\,eV$ represents the D^0 density of Ge. In a-$Si_{1-x}C_x$:H ($E_0 \leqslant 1{\cdot}88\,eV$) and a-Si:H, N_I represents the D^0 density of Si. N_I for the C content of 0·15 was $1{\cdot}7 \times 10^{17}\,cm^{-3}$ although N_I for the Ge content of 0·27 was $6{\cdot}5 \times 10^{15}\,cm^{-3}$, indicating that the ratio of Si dangling bonds to Si atoms in a-$Si_{1-x}C_x$:H may be much higher than that in a-$Si_{1-x}Ge_x$:H. This indication seems reasonable in the light of bonding energies (Ge–H < Si–H < C–H) or preferential attachment of H to Ge, Si and C.

Fig. 1



Dark conductivity (σ_d) (●, a-$Si_{1-x}Ge_x$:H; ■, a-Si:H; and ▲, a-$Si_{1-x}C_x$:H) and photoconductivity ($\Delta\sigma_{ph}$) (○, a-$Si_{1-x}Ge_x$:H; □, a-Si:H; and △, a-$Si_{1-x}C_x$:H) under AM1 ($100\,mW\,cm^{-2}$) of undoped films with various optical gaps.

Fig. 2

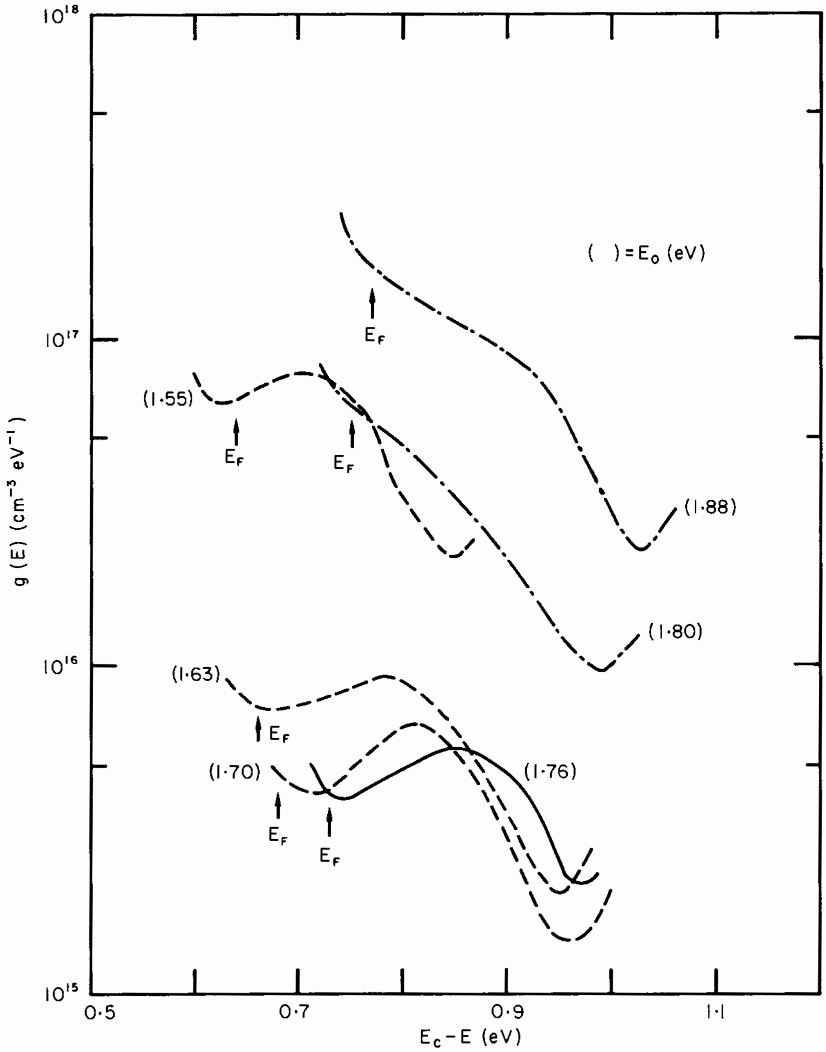


Densities (N_I) of midgap states of undoped films with various optical gaps (○, a-Si$_{1-x}$Ge$_x$:H; ■, a-Si:H; and △, a-Si$_{1-x}$C$_x$:H). The relation between N_I and bulk spin density (N_s) obtained from ESR is inserted.

Figure 3 shows six density-of-states profiles $g(E)$ corresponding to E_0, which are estimated from the transient HMC method (Matsuura 1988a, b). Here the attempt-to-escape frequencies (ν_n) for electrons which were experimentally obtained were 4×10^{12}, 1×10^{12}, 8×10^{11}, 4×10^{11}, 4×10^{11} and 8×10^{11} s^{-1} for $E_0 = 1{\cdot}55$, 1·63, 1·70, 1·76, 1·80 and 1·88 eV respectively, and they were used to estimate $g(E)$. As the Ge content increases in the film, the energy location of the peak in $g(E)$ is shifted slowly toward the conduction band. In a-Si$_{1-x}$C$_x$:H, however, the peak of $g(E)$ does not appear clearly.

As indicated in fig. 3, the energy location of D^0 in a-Si:H is 0·85 eV below the conduction band edge, which belongs to group B classified by Le Comber and Spear (1986). Our result for the energy location of D^0 in a-Si$_{1-x}$Ge$_x$:H coincides with the result obtained by Tsutsumi, Sakata, Abe, Nitta, Okamoto and Hamakawa (1987) who could not, however, determine D^0 densities.

Fig. 3



Density-of-state distributions in undoped films with various optical gaps, (---), a-$Si_{1-x}Ge_x$: H; (——), a-Si : H; and (—·—), a-$Si_{1-x}C_x$: H.

§4. Conclusion

The heterojunction-monitored capacitance methods have been applied to determine densities and profiles of midgap states in undoped a-$Si_{1-x}Ge_x$: H, a-Si : H and a-$Si_{1-x}C_x$: H. The midgap states are correlated with D^0; the density in a-$Si_{1-x}Ge_x$: H ($E_0 \leqslant 1{\cdot}63$ eV) may represent the D^0 density of Ge, and in a-$Si_{1-x}C_x$: H ($E_0 \leqslant 1{\cdot}88$ eV) and a-Si : H it represents the D^0 density of Si.

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