$$H(t_m) \fallingdotseq [f(E_m) - F_\infty(E_m)]g(E_m) \int_{E_V}^{E_C} D(E,t_m)dE$$

$$\fallingdotseq [f(E_m) - F_\infty(E_m)]g(E_m) \int_{0}^{\infty} D(E,t_m)dE$$

$$= [f(E_m) - F_\infty(E_m)]g(E_m)kT \quad , \qquad (5\text{-}17)$$

where E_m is the energy at which D(E,t) has a maximum value when

$$e_n(E_m)t_m = 1 \quad . \qquad (5\text{-}18)$$

Therefore, the relation between E_m and t_m is derived from Eqs. (5-12) and (5-18):

$$E_C - E_m = kT\ln(\nu_n t_m) \quad . \qquad (5\text{-}19)$$

In a more general form, this equation can be expressed as

$$E_C - E(t) = kT\ln(\nu_n t) \quad . \qquad (5\text{-}20)$$

Under the conditions that $e_n(E)$ is much higher than $e_p(E)$ [i.e., $F_\infty(E)=0$] as well as that f(E) is close to unity for the gap states between E_F and E_{OB}, the relation between H(t) and g(E) is generally obtained from Eq. (5-17) as

$$g(E) = H(t)/kT \quad . \qquad (5\text{-}21)$$

Therefore, the g(E) around the middle of the energies between E_F and E_{OB} can be easily estimated from the measured H(t) using Eqs. (5-20) and (5-21).

5-4. Transient HMC Measurements

Undoped a-Si:H films were deposited by the rf glow-discharge decomposition of pure SiH_4, and undoped a-$Si_{1-x}Ge_x$:H films were prepared by the rf glow-discharge decomposition of

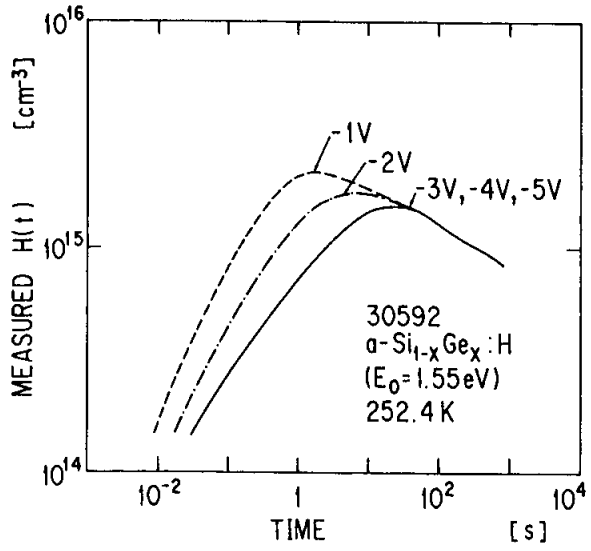

Fig.5.3. Reverse-bias dependence of measured H(t).

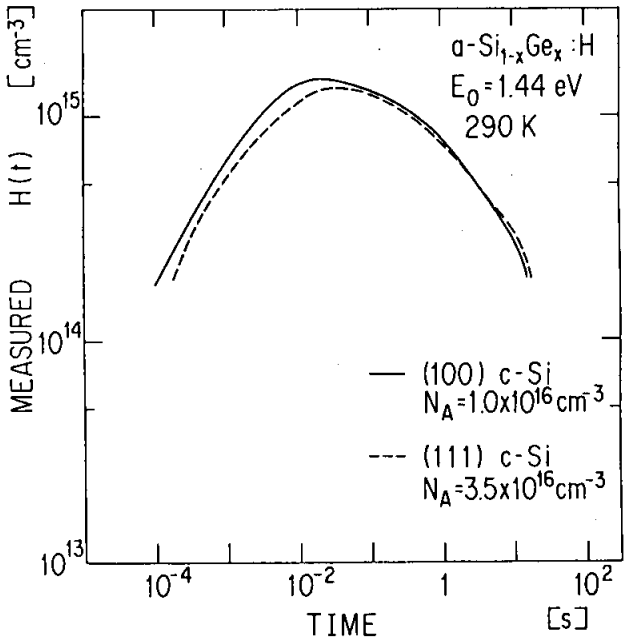

Fig.5.4. Set of two measured H(t) corresponding to (111) and (100) surfaces of p c-Si for undoped a-Si_{1-x} Ge_x:H (E_0=1.44 eV).

$GeH_4/SiH_4/H_2$ gas mixture. Good quality films could be obtained by those techniques. The optical gap (E_0) was determined by the Tauc plots of $(\alpha h\nu)^{1/2}=B_1(h\nu-E_0)$, where α is the optical absorption coefficient, $h\nu$ is the photon energy, and B_1 is a constant. The heterojunctions were fabricated by depositing the amorphous films onto p c-Si substrates (N_A=1.0x10^{16} or 3.5x10^{16} cm^{-3}) heated to 250 ℃ and then evaporating Mg on an area (0.785 mm^2) of those films at room temperature in a vacuum of 7x10^{-7} Torr. Thicknesses of amorphous films were kept between 0.8 and 1.2 μm. Mg formed a good Ohmic contact with those amorphous films. All the heterojunctions exhibited good rectifying properties.

Transient HMC measurements were carried out at 2 MHz for various temperatures. Only signals of H(t) at time longer than the dielectric relaxation time are valid as mentioned in Section 5-3. The signals of H(t) get saturated at a filling time τ_f (under the zero-bias condition) longer than 1 s. In the following measurements, H(t) has been measured at τ_f=50 s under the zero-bias condition.

Figure 5.3 shows the reverse-bias dependence of H(t) for an $a\text{-}Si_{1-x}Ge_x$:H(E_0=1.55 eV)/p c-Si heterojunction. The signals of H(t) for -5 V$\leqq V_R \leqq$-3 V are found to be independent of the reverse bias V_R, while the signals for V_R of -1 V and -2 V depend on V_R, indicating that the relation, that $N_I(t)W_2(t)$ is much larger than $N_I(\infty)W_2(0)$, is invalid for the reverse biases of -1 V and -2 V. As described in Section 5-3, these H(t) include information not only on the bulk but also on the interface. Since the g(E) in the bulk is necessary, H(t) has been measured at V_R=-4 V.

In order to check to what extent the interface states can affect the signal of H(t), the signals of H(t) with different surfaces of c-Si are compared, as shown in Fig. 5.4. The (111) surface of c-Si has the largest number of available bonds per cm^2, and the (100) surface has the smallest. According to the experimental results from Si/SiO_2 systems,[3,4] the interface-state density for the (100) surface is reported to be lower by a factor of 10 compared to that for the (111) surface. In the

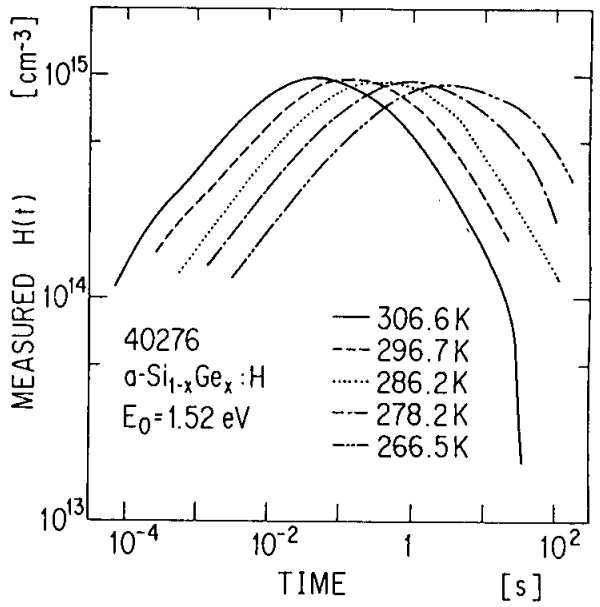

Fig.5.5. Set of five measured H(t) corresponding to five different measuring temperatures for undoped a-$Si_{1-x}Ge_x$:H/p c-Si:H (N_A=1.0x10^{16} cm^{-3}) heterojunction.

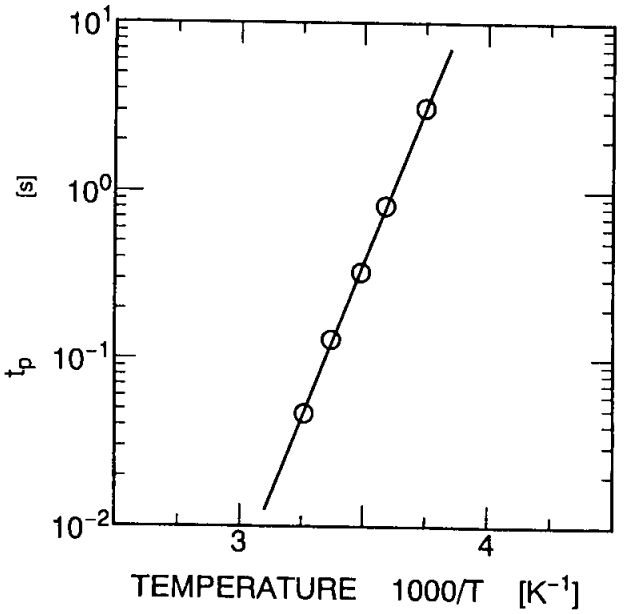

Fig.5.6. Temperature dependence of time (t_p) at which H(t) becomes maximum for undoped a-$Si_{1-x}Ge_x$:H/p c-Si (N_A=1.0x10^{16} cm^{-3}) heterojunction.

present work, however, H(t) has not shown any significant variation with surface orientation, as is clear from Fig. 5.4. Thus, H(t) is considered to be unaffected by the interface states in the present heterojunctions. From the figure, moreover, H(t) is considered to be independent of the resistivity of p c-Si, which is considered to be natural since N_I obtained from the steady-state HMC method is independent of the p c-Si resistivity as discussed in Chapter Ⅲ.

In order to calculate H(t) using Eq. (5-14), only ν_n and ν_p are necessary. Here, an undoped a-$Si_{1-x}Ge_x$:H/p c-Si heterojunction with $N_A=1.0\times10^{16}$ cm^{-3}, as shown in Fig. 5.5, is considered in order to estimate the values of ν_p and ν_n. The electron thermal-emission rate [$e_n(E)$] for a particular gap state at a depth (E_C-E) from the conduction band is given by Eq. (5-12), and the time , which is required for a trapped electron to be thermally re-emitted, is $1/e_n(E)$. Under the assumption that the gap states corresponding to the peak of H(t) is located between E_F and E_{OB}, the $g(E_p)$ is obtained as $H(t_p)/kT$ from Eq. (5-21). Therefore, the value of ν_n can be approximately estimated from the temperature dependence of the time (t_p) at the peak of H(t). Then,

$$t_p = 1/e_n(E_p)$$

$$= (1/\nu_n)\exp[(E_C - E_p)/kT] \quad , \qquad (5\text{-}22)$$

if ν_n is independent of temperature and energy. Figure 5.6 shows the temperature dependence of t_p, and from the intercept on the vertical axis in the figure using Eq. (5-22) the value of ν_n is found to be 2×10^{13} s^{-1}. Next, a maximum value of ν_p/ν_n is estimated as follows. Figure 5.7 shows the calculated H(t) for different ν_p with $g(E)=1\times10^{17}$ $cm^{-3}eV^{-1}$ and $\nu_n=2\times10^{13}$ s^{-1}. The measured H(t) at 1.4 s (T=306.6 K) is about 5×10^{14} cm^{-3} from Fig. 5.5, while in the case of $\nu_p/\nu_n=1$ using $E_{g2}=E_0=1.52$ eV the calculated one is about 10^8 cm^{-3} from Fig. 5.7, suggesting that the value of g(E) corresponding to 1.4 s should attain an unreasonable value of 5×10^{23} $cm^{-3}eV^{-1}$ simply because

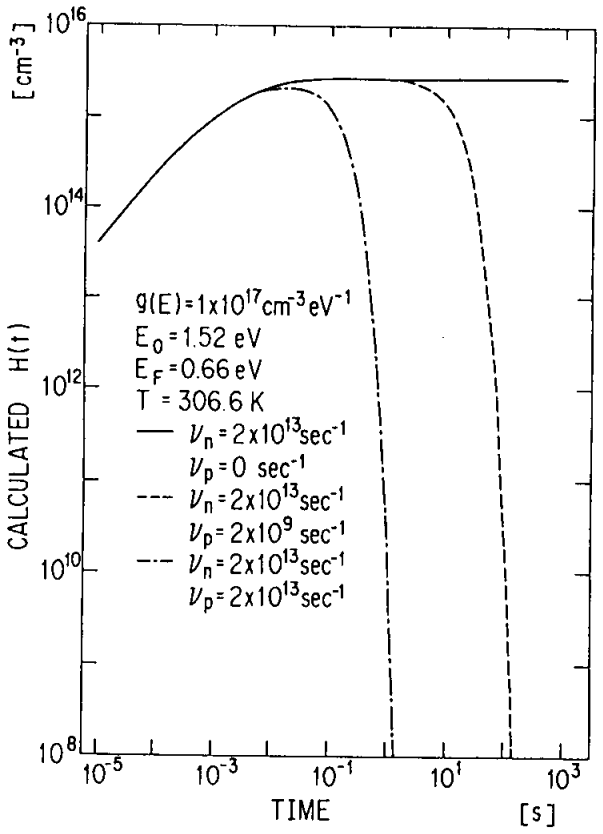

Fig.5.7. Set of three calculated H(t) corresponding to three different attempt-to-escape frequencies for holes with $g(E)=1x10^{17}$ $cm^{-3}eV^{-1}$ and $\nu_n=2x10^{13}$ s^{-1} for $E_{g2}=E_0=1.52$ eV.

$$g(E) : 1x10^{17} = 5x10^{14} : 10^{8} \quad .$$

From the above consideration, the value of ν_n and the maximum value of ν_p are taken as $2x10^{13}$ and $2x10^{9}$ s^{-1}, respectively. The calculated H(t) was approached to the measured H(t) by changing g(E), and then the g(E) shown in Fig. 5.8 made the calculated H(t) fit in with the measured H(t) very well, as shown in Fig. 5.9. Here, it is assumed that the mobility gap coincides with E_0. Figure 5.10 shows the temperature dependence of the calculated H(t) which fits in with the measured H(t) at each temperature.

The g(E) for undoped a-Si:H, estimated from the measured H(t) in Fig. 5.11, is shown in Fig. 5.12 using ν_n=$1x10^{11}$ s^{-1}, ν_p=$1x10^{8}$ s^{-1}, and E_{g2}=E_0=1.70 eV. Density-of-state distributions for other amorphous silicon-based alloys will be discussed in Chapter VI.

The distribution g(E) obtained here is found to be the bulk DOS distribution unaffected by interface states. This appears to be the first systematic effort to electrically estimate the g(E) below the Fermi level for undoped amorphous materials. Therefore, the following part of this section considers the validity of this transient HMC method in more detail. The following pertinent questions could arise, viz.,

(1) Is the assumption that ν_n and ν_p are independent of temperature and energy correct?

(2) Are the values obtained for ν_n and ν_p reasonable?

(3) To what degree does tunneling affect g(E)?

There has been a controversy in opinion regarding the answers to (1) and (2) mainly on the basis of results obtained from DLTS[1,5,6] and ICTS.[2,7] These techniques have mainly been applied to P-doped a-Si:H, but no data exist for undoped a-Si:H and undoped a-$Si_{1-x}Ge_x$:H.

If ν_n has a temperature dependence of the form

$$\nu_n = \nu_{n0} T^2 \exp(-\Delta E_\nu / kT) \quad , \qquad (5\text{-}23)$$

where ν_{n0} and ΔE_ν are constants independent of T, Eq. (5-22)

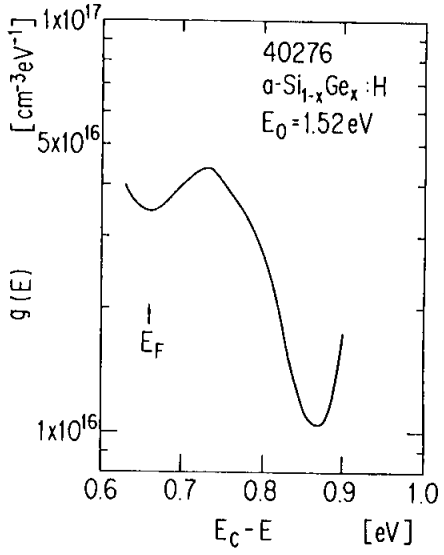

Fig.5.8. Density-of-state distribution for a-$Si_{1-x}Ge_x$:H (E_0=1.52 eV).

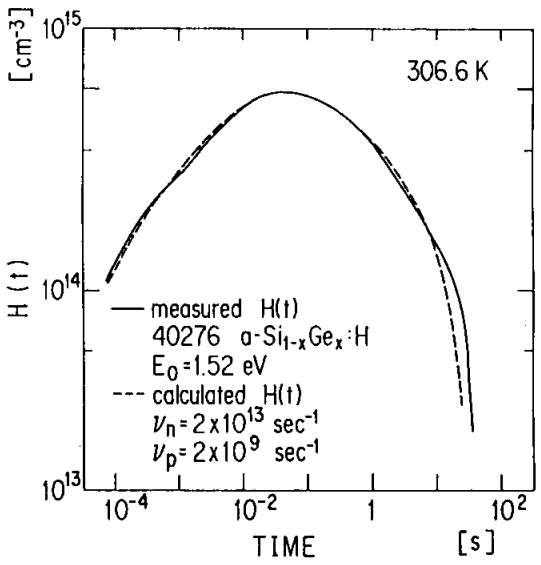

Fig.5.9. Comparison between measured H(t) for a-$Si_{1-x}Ge_x$:H (E_0=1.52 eV) and calculated H(t) with E_{g2}=1.52 eV, ν_n=2x10^{13} s^{-1} and ν_p=2x10^9 s^{-1}.

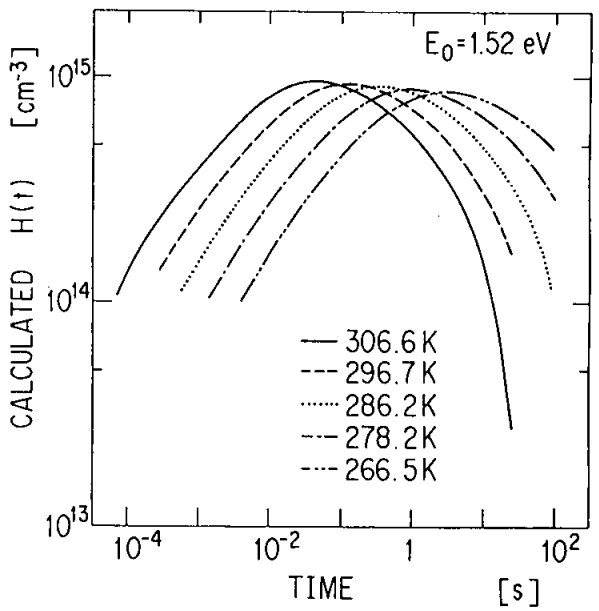

Fig.5.10. Set of five calculated H(t) corresponding to five different temperatures for E_{g2}=1.52 eV with ν_n=2x10^{13} s^{-1} and ν_p=2x10^{9} s^{-1}.

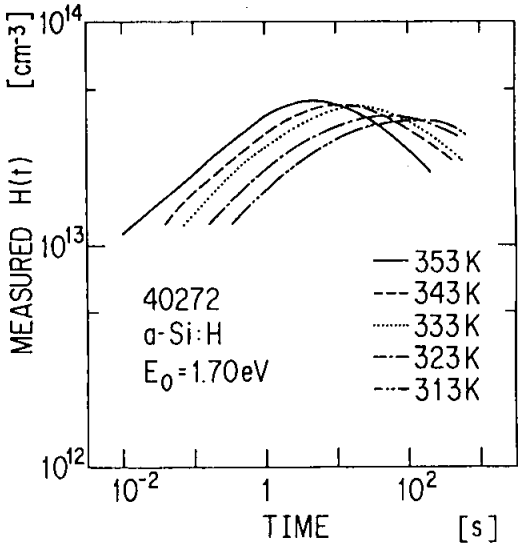

Fig.5.11. Set of five measured H(t) corresponding to five different measuring temperatures for undoped a-Si:H/p c-Si (N_A=1.0x10^{16} cm^{-3}) heterojunction.

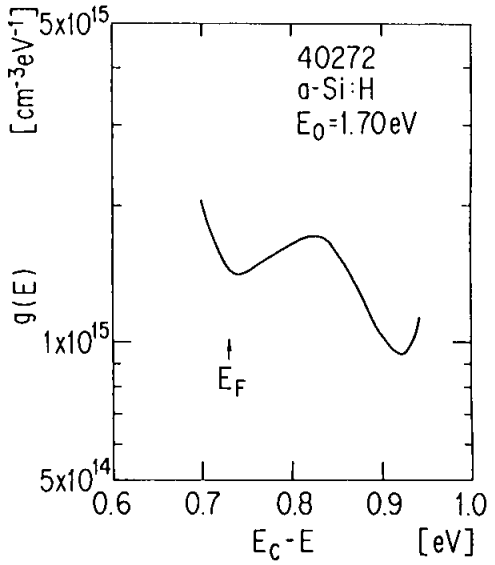

Fig.5.12. Density-of-state distribution for a-Si:H (E_0=1.70 eV) which can fit measured H(t) with calculated H(t) using E_{g2}=1.70 eV, ν_n=1x10^{11} s^{-1}, and ν_p=1x10^8 s^{-1}.

changes into

$$t_p = (1/\nu_{n0}T^2)\exp[(E_C - E_p + \Delta E_\nu)/kT] , \qquad (5\text{-}24)$$

indicating that the energies shown in Figs. 5.8 and 5.12 are overestimated because of the assumption that $\Delta E_\nu = 0$. The situation is the same as that reported by Lang and Cohen.[1] Therefore, it is important to investigate the temperature dependence of ν_n. Furthermore, Lang and Cohen[1] assumed that ν_n was independent of energy locations of gap states which were ascribed to the same origin, while Okushi[2] reported that ν_n has an energy dependence. In the above discussion, the energy-independence of ν_n is adopted. We has tried to investigate the temperature- and energy-dependencies of ν_n by means of the trap filling method like ICTS which investigates the dependence of H(t) on the filling time (τ_f),[2] but difficulty has been encountered owing to the long dielectric relaxation time of amorphous films. However, the energy locations of the peak of DOS for undoped materials are found to be close to those reported by Tsutsumi et al.,[8] and Kocka, Vanecek and Schaver.[9]

Since the values of ν_n are reported to be between 10^9 and 10^{13} s^{-1} for Si dangling bonds,[1-2] the values obtained here are considered to be reasonable. On the other hand, there is no experimental data on the values of ν_p. The value of ν_p estimated from the fitting procedure depends strongly on the mobility gap (E_{g2}) because $e_p(E)$ is a function of $(E_C\text{-}E)\text{-}E_{g2}$. The g(E) estimated with $\nu_n = \nu_p = 1\times10^{11}$ s^{-1} and E_{g2}=1.91 eV is the same as the g(E) shown in Fig. 5.12 with $\nu_n = 1\times10^{11}$ s^{-1}, $\nu_p = 1\times10^{8}$ s^{-1}, and E_{g2}=1.70 eV because E_{OB} is the same in both cases. The value of the mobility gap poses an open question. Vanecek et al.[10] concluded that the mobility gap of a-Si:H was quite close to E_0 ($\sim$1.7 eV). On the other hand, Lang and co-workers[6] used the values between 1.9 and 2.1 eV for the mobility gap of a-Si:H based on the assumption of $\nu_n = \nu_p = 10^{13}$ s^{-1}. Jackson et al.[11] reported it as 1.93 ± 0.2 eV. However, the estimated g(E) does not change at all when the best fit is obtained using the maximum of ν_p/ν_n which is determined by the

value of E_{g2}.

Regarding the third question, it seems like tunneling does not affect the g(E) in the range of the measuring temperatures from the consideration similar to the ICTS analysis of P-doped a-$Si_{1-x}Ge_x$:H.[12] The value of t_p , when the tunneling process affects H(t), is not on the linear relation between t_p and 1/T expected from the range of higher temperature. In the present study, the linear relations between them are obtained in the whole temperature range studied here for all the samples. This transient HMC method will be applied not only to determining the g(E) in other undoped amorphous silicon alloys but also to investigating the changes of g(E) by light-soaking, rapid cooling, and thermal annealing in the following chapter.

5-5. Summary

A novel technique for determining the magnitude as well as energy location of midgap states in highly resistive amorphous materials has been developed from the study of the transient capacitance in the highly resistive amorphous/lowly resistive crystalline semiconductor heterojunctions. This transient HMC method has been tested and applied on undoped a-Si:H and undoped a-$Si_{1-x}Ge_x$:H. The g(E) obtained by the transient HMC method is found to be representative of a homogeneous bulk property of the amorphous material, unaffected by their interface states.