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Model for ac conduction in amorphous SiO_2 films

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It is now well established that the intrinsic bonding defects in amorphous SiO_2 are normally charged (C_1^- with negative correlation energy and C_3^+ with positive correlation energy) which are different from those for amorphous chalcogenides. It is proposed here that correlated barrier hopping of single polarons (electronic transfer between neutral and charged defects) based on the intrinsic bonding defects model contribute to ac transport in sputtered amorphous SiO_2 films. An expression for ac conductivity, $\sigma(\omega,T)$, is able to account for all the features observed in the given material. The densities and energy levels of defects are estimated from the present model, and these are supported from the ESR, ir, and drift-mobility studies in amorphous SiO_2.

I. INTRODUCTION

The ac conductivity in the radio frequency (rf) range which depends on frequency ω and temperature T in amorphous chalcogenide semiconductors, $\sigma(\omega,T)=A\omega^s$, where A and s (<1.0) are temperature-dependent parameters, is now well interpreted by the combined mechanism of correlated barrier hopping (CBH) of bipolarons (two electrons hopping between charged defects D^+ and D^-) (Ref. 1) and single polarons (electrons hopping between neutral defects D^0 and D^+ and holes between D^0 and D^-).[2] It is, however, not clear whether the CBH model is applicable to amorphous SiO_2 (a-SiO_2) whose ac property in the rf range[3] is very similar to that for amorphous chalcogenides. There is a great deal of interest in the nature of intrinsic defects in amorphous SiO_2.[4–10] Street and Lucovsky[8] and Lucovsky[9] proposed that dominant intrinsic bonding defects in amorphous SiO_2 are C_3^+ and C_1^-, where C is for oxygen and the subscript gives the coordination and the superscript the charged state. They also pointed out that these charged defects could not have a negative correlation energy (negative U) which has been fairly well established in amorphous chalcogenides.[11–13] Then interconversion between charged centers ($C_3^+ +2e\rightarrow C_1^-$ and $C_1^- +2h\rightarrow C_3^+$) cannot be expected to occur in this material, since the ability of interconversion between charged centers is a necessary condition of a negative U.[8,9] Thus the bipolarons as proposed in amorphous chalcogenides could not exist in a-SiO_2, because the CBH of bipolarons is based on interconversion between D^+ and D^-.[1] If the neutral defect states such as C_1^0 and/or T_3^0 exist in a-SiO_2, where T stands for silicon, ac conduction can be attributed from single polarons. The similar situation has been considered previously for the case of amorphous As (Refs. 14 and 15) and chalcogenides.[2]

It is shown in the present study that single polarons (holes hopping between C_1^0 and C_1^- and electrons between T_3^0 and C_3^+) contribute to ac conduction in sputtered a-SiO_2. The neutral defects, C_1^0 and T_3^0, exist in irradiated vitreous SiO_2 (v-SiO_2) (Ref. 10) and could exist in sputtered a-SiO_2. The energy levels and densities of intrinsic defect states for sputtered a-SiO_2 films are deduced from a comparison of the theory with experimental data.

II. CORRELATED BARRIER HOPPING OF SINGLE POLARONS

The theory of the classical hopping of carriers between localized states over a potential barrier W, as shown in Fig. 1, was developed initially by Pike[16] to explain ac conduction in scandium oxide films. Elliott[1] then extended Pike's theory to ac conduction for amorphous chalcogenides, namely, the CBH of bipolarons. By assuming a Coulombic interaction, the barrier height W over which carriers must hop is given by

$$W=W_M-\frac{4ne^2}{\epsilon R}\ , \qquad (1)$$

where n is the number of carriers that hop (e.g., $n=2$ for bipolarons, $n=1$ for single polarons), W_M is the maximum barrier height (the energy difference between the ground states and the ionized states), ϵ is the effective dielectric constant, and R is the separation of two sites. The pair relaxation time

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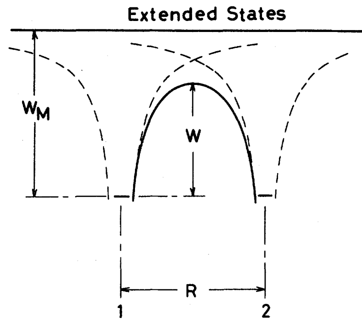

FIG. 1. Model of overlapping Coulomb-type wells for charged centers. The ground-state energy is W_M, the potential barrier separating these states is W, and the potentials are centered a distance R apart.

is assumed to be

$$\tau=\tau_0\exp(W/kT)\ , \tag{2}$$

where τ_0 is the characteristic relaxation time (1×10^{-12} s in the present study).

Following Pike[16] and Elliott,[1] the real part of ac conductivity is written as

$$\sigma_{ac}=\frac{\pi^2 n N_c N\epsilon\omega R_\omega^6}{24}\ , \tag{3}$$

where N_c is the carrier density that hops, N is the density of levels participating, ω is the angular frequency, and R_ω (the distance of pairs for which $\omega\tau=1$)[1] is given from Eq. (1) by

$$R_\omega=\frac{4ne^2}{\epsilon(W_M-W_\omega)} = \frac{4ne^2}{\epsilon\left[W_M-kT\ln\left[\frac{1}{\omega\tau_0}\right]\right]}\ . \tag{4}$$

As stated in Sec. I, bipolarons could not exist in a-SiO_2. We therefore only consider the CBH of single polarons ($n=1$).

Before proceeding with the discussion of single polarons in a-SiO_2, we review the bipolarons and

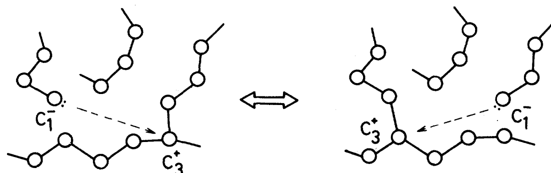

FIG. 2. Schematic diagram of the hopping process for bipolarons in amorphous chalcogenides (e.g., a-Se). Two electrons transfer from a C_1^- to a C_3^+ center.

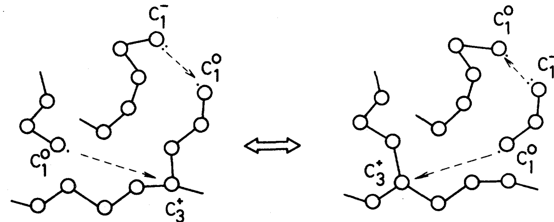

FIG. 3. Schematic diagram of the hopping process for single polarons in amorphous chalcogenides. A hole transfer from a C_1^0 to a C_1^- and an electron transfer from a C_1^0 to a C_3^+.

single polarons in amorphous chalcogenides. Figures 2 and 3 show, as an example, bipolarons[1] and single-polaron[2] processes in a-Se, respectively. Two electrons transfer from a $C_1^-(D^-)$ to a $C_3^+(D^+)$ in the bipolaron process (Fig. 2), and a hole transfer from a $C_1^0(D^0)$ to a $C_1^-(D^-)$ and an electron transfer from a $C_1^0(D^0)$ to a $C_3^+(D^+)$ in the single-polaron process (Fig. 3), which thereby exchange places (interconversion) accompanied with negative U.

Returning to a-SiO_2, Street and Lucovsky[8] and Lucovsky[9] have pointed out that the charged defects in a-SiO_2 could not have a negative U because of strong ionicity of this material. Following their conclusions in a-SiO_2, $C_1^-(1T)$ and $C_3^+(3T)$ can be intrinsic bonding defects, and the interconversion between $C_1^-(1T)$ and $C_3^+(3T)$ cannot occur in contrast with that for amorphous chalcogenides, where $1T$ and $3T$ in parentheses mean bonding one silicon to C_1^- and three silicons to C_3^+, respectively (see Fig. 4). Because the bonding constraints increase with the coordination of the atoms, $C_3^+(3T)$ defects could not have a negative U as expected for low coordinated C_1^- defects. Hence we cannot expect the CBH of bipolarons in a-SiO_2.

Neutral defects (paramagnetic centers) $C_1^0(1T)$ and $T_3^0(3C)$ are produced in irradiated v-SiO_2, giving two different ESR signals[10]: E' center and oxygen hole center (OHC). Lucovsky[10] suggested that the trapping of photogenerated excess electrons and holes at the respective defects $C_3^+(3T)$ and $C_1^-(1T)$, yields the E' and OHC centers. The same centers are also associated with radiation-induced absorption and luminescence.[5] These neutral centers could exist in sputtered a-SiO_2 films without irradition. Schematic diagrams of interconversion between $C_1^0(1T)$ and $C_1^-(1T)$ with negative U (process I) and interconversion between $T_3^0(3C)$ and $C_3^+(3T)$ with positive U (process II) are shown in Fig. 4. The latter (process II) accompany the reconstruction of defects.[9] These pictures are consistent with paramagnetic centers by irradiation proposed by Lucovsky,[10] and are also characteristic features of sin-

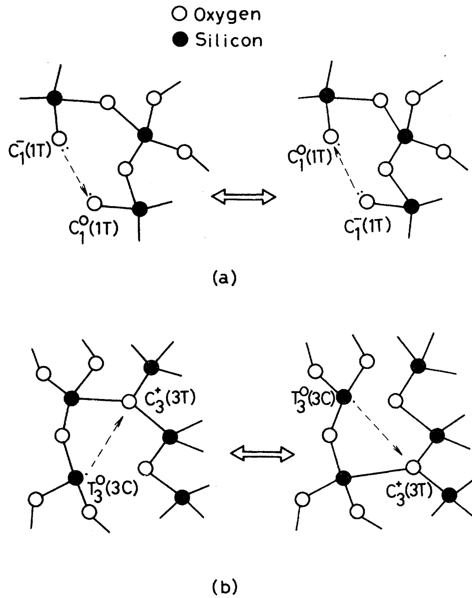

FIG. 4. (a) Schematic diagram of the hopping process for single polarons in a-SiO_2. A hole transfer from a $C_1^0(1T)$ to a $C_1^-(1T)$ with negative U (process I). (b) An electron transfer from a $T_3^0(3C)$ to a $C_3^+(3T)$ accompanied by reconstruction of bonding network with positive U (process II).

gle polarons [holes process in Fig. 4(a) and electrons in Fig. 4(b)].

The resulting states in the gap are shown in Fig. 5. When a $C_1^-(1T)$ captures a hole or when a $C_3^+(3T)$ captures an electron, $C_1^0(1T)$ and $T_3^0(3C)$, respectively, are formed and reexcitation energies of the carriers back to their respective bands are W_1 and W_2, respectively. Thus the maximum barrier height W_M (see Fig. 1) equals W_1 for process I and W_2 for process II. We assume here that W_2 is smaller than W_1, supporting from the fact that the electron trap depth (0.28 eV) is smaller than the hole

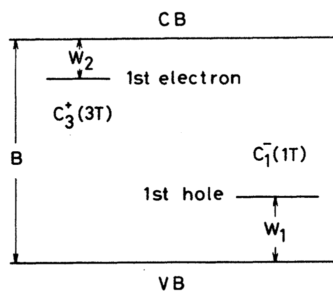

FIG. 5. Thermal energy levels associated with $C_1^-(1T)$ and $C_3^+(3T)$. W_1 is the energy needed to take an electron from the valence band to turn $C_1^0(1T)$ into $C_1^-(1T)$, and W_2 is the energy needed to take an electron from $T_3^0(3C)$ to the conduction band and hence turn $T_3^0(3C)$ into $C_3^+(3T)$ with reconstruction. B is the band gap.

(0.42 eV) in glassy $GeSe_2$ (Ref. 17) whose defect natures are expected to be quite similar to those for a-SiO_2.[8]

The relaxation processes I and II both contribute to ac conductivity σ_{ac} (I) and σ_{ac}(II), respectively. Then the total ac conductivity is written as

$$\sigma_{ac}=\sigma_{ac}(\mathrm{I})+\sigma_{ac}(\mathrm{II}) \ . \tag{5}$$

The quantities N_cN in Eq. (3) are given by

$$\begin{aligned} N_cN &= N(C_1^0)N(C_1^-)=N(C_1^0)\frac{N_T}{2} \quad (\text{process I}) \\ &= N(T_3^0)N(C_3^+)=N(T_3^0)\frac{N_T}{2} \quad (\text{process II}) \ , \end{aligned} \tag{6}$$

where $N(C_1^0)$, $N(C_1^-)$, $N(T_3^0)$, and $N(C_3^+)$ are densities of $C_1^0(1T)$, $C_1^-(1T)$, $T_3^0(3C)$, and $C_3^+(3T)$, respectively, and N_T $[=N(C_1^-)+N(C_3^+)$; $N(C_1^-)=N(C_3^+)]$ the total charged defects. The second term in Eq. (5) (process II) produces a large temperature dependence of σ_{ac} due to a smaller value of W_M $(=W_2)$ than that for process I, because a large temperature dependence of R_ω [see Eq. (4)] comes from small W_M.

III. APPLICATION OF THE MODEL TO EXPERIMENTAL DATA

The experimental data[3] (open circles) in sputtered a-SiO_2 film after annealing at 569 K in 10^{-6} torr for 36 h are shown in Fig. 6. The conductivity σ_{ac} is relatively independent of temperature below about 400 K, but increases rapidly with increasing temperature above 400 K, predicting that two mechanisms contribute to ac conductivity. This behavior is quite similar to that of amorphous chalcogenides,[2] while defects natures for a-SiO_2 are different from those of amorphous chalcogenides. The dashed and dotted curves, I and II, are calculated results using Eqs. (3)–(5). The total conductivity calculated, shown by the solid curves, agrees very well with the experiments except at 10 kHz. The onset of a quadratic dependence of ω on σ_{ac} has been observed around 10 kHz (Ref. 3) which may be related to a contact effect.[18,19]

Values for the energy bound states $W_1=2.5$ eV and $W_2=1.4$ eV as shown in Fig. 5 were carefully chosen to fit the experimental data reported for all temperatures and frequencies, producing $N(C_1^0)N_T$ and $N(T_3^0)N_T$ as 1.4×10^{37} cm^{-6} and 5.8×10^{35} cm^{-6}, respectively. The effective dielectric constant, $\epsilon=3.0$, here was assumed to be about half the high-frequency dielectric constant ϵ_∞.[2] By putting $N_T=3.0\times10^{19}$ cm^{-3} which is deduced from the infrared absorption[6] and from the drift-mobility[7] stud-

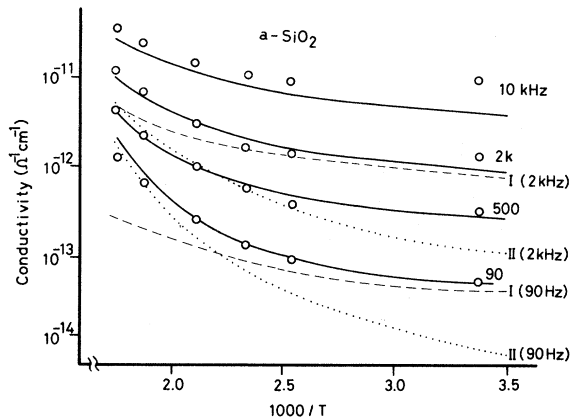

FIG. 6. The temperature dependence of σ_{ac} in sputtered a-SiO_2 film. Experimental data (open circles) were from Meaudre and Meaudre (Ref. 3). The dashed and dotted lines, I and II, are calculated results for processes I and II, respectively. The total ac conductivity calculated is shown by the solid lines.

ies, $N(C_1^0)$ and $N(T_3^0)$ are estimated to be 4.7×10^{17} cm^{-3} and 1.9×10^{16} cm^{-3}, respectively. These probably produce the same kinds of ESR centers as observed in irradiated in v-SiO_2—OHC and E' centers.[10]

An alternative model for ac conduction in this material has been proposed by Meaudre and Meaudre.[3] They have suggested that their data (Fig. 6 in the present study) can be interpreted in terms of the CBH of holelike small polarons. The maximum barrier height W_M they deduced is about 0.4 eV which equals to the activation energy for drift mobility of holes in a-SiO_2.[4,7] Their interpretation, however, seems to have two difficult problems. First, the condition $\omega\tau_{max} \gg 1$ invoked in the CBH model[16] may not hold at higher temperature owing to the small value of W_M (=0.4 eV), where τ_{max} is written as

$$\tau_{max} \simeq \tau_0 \exp(W_M/kT) . \qquad (7)$$

In such a case, there will be a dielectric loss ($\sigma_{ac} \propto \omega^2$) (Refs. 1, 16, and 20) below frequency $\omega_M = 1/\tau_{max}$. The frequency ω_M is estimated to be about 10^7 Hz at 400 K. Such a behavior has not been observed in their data (see Fig. 6).[3] Second, although the existence of the holelike small polarons by irradiation (creation of electrons and holes) has been supported by the drift-mobility study,[4,7] there is no evidence of existence of thermally created small polarons in a-SiO_2. The density of small polarons, N_c, created thermally can be written as[21]

$$N_c = N \exp(-E/kT) , \qquad (8)$$

where E is the creation energy of small polarons and N the density of equivalent carrier sites ($\sim 10^{22}$ cm^{-3}). The value of E in a-SiO_2 may not be as small as that expected for AsTe glass ($\simeq$0.25 eV).[21] Then, at reported temperature range ($\sim$330—570 K), N_c is expected to be very small. Furthermore, as the density N_c is a thermally activated process with energy E, a large termperature dependence of σ_{ac} can be predicted since σ_{ac} is proportional to $N_c N$ [see Eq. (3)]. Actually such data have not been obtained in a-SiO_2.

We thus conclude that small polarons cannot contribute to ac transport in a-SiO_2. Dominant contribution to ac conduction could be attributed to the single polarons in sputtered a-SiO_2 films.

IV. CONCLUSIONS

The ac transport in sputtered a-SiO_2 films has been well interpreted in terms of single polarons based on the neutral and charged defects model. The densities and energy levels of these defects have been estimated from the present model. These are almost consistent with that from the ESR and ir studies. The holelike small polarons supported by the drift-mobility study could not contribute to ac conduction in reported frequency and temperature ranges in a-SiO_2.

[1]S. R. Elliott, Philos. Mag. 36, 1291 (1977); B37, 553 (1978).
[2]K. Shimakawa, J. Phys. (Paris) 42, 4, 927 (1981); Philos. Mag. B46, 123 (1982).
[3]M. Meaudre and R. Meaudre, Philos. Mag. B40, 401 (1979).
[4]N. F. Mott, Adv. Phys. 26, 363 (1977).
[5]G. N. Greaves, Philos. Mag. B37, 447 (1978).
[6]G. Lucovsky, Philos. Mag. B39, 513 (1979).
[7]G. Lucovsky, Philos. Mag. B39, 531 (1979).
[8]R. A. Street and G. Lucovsky, Solid State Commun. 31, 289 (1979).
[9]G. Lucovsky, J. Non-Cryst. Solids 35&36, 825 (1980).
[10]G. Lucovsky, Philos. Mag. B41, 457 (1980).
[11]R. A. Street and N. F. Mott, Phys. Rev. Lett. 35, 1293 (1975).
[12]M. Kastner, D. Adler, and H. Fritzsche, Phys. Rev. Lett. 37, 1504 (1976).
[13]N. F. Mott and E. A. Davis, *Electronic Processes in Non-Crystalline Materials,* 2nd ed. (Clarendon, Oxford,

1979).

[14]S. R. Elliott and E. A. Davis, *Amorphous and Liquid Semiconductors,* edited by W. E. Spear (Center for Industrial Consultancy and Liaison, University of Edinburgh, Edinburgh, 1977), p. 637.

[15]G. N. Greaves, S. R. Elliott, and E. A. Davis, Adv. Phys. 28, 49 (1979).

[16]G. E. Pike, Phys. Rev. B 6, 1572 (1972).

[17]G. I. Kim and J. Shirafuji, Jpn. J. Appl. Phys. 17, 1789 (1978).

[18]A. I. Lakatos and M. Abkowitz, Phys. Rev. B 3, 1791 (1971).

[19]X. LeCleac'h, J. Phys. (Paris) 40, 417 (1979).

[20]K. Shimakawa, S. Nitta, and M. Mori, Phys. Rev. B 16, 4519 (1977); 18, 4348 (1978).

[21]D. Emin, in *Electronic and Structural Properties of Amorphous Semiconductors,* edited by P. G. LeComber and J. Mort (Academic, London, 1973), p. 261.