# Mechanisms for ac conduction in rf sputtered SiO<sub>2</sub> films

M. Meaudre

Laboratoire de Physique Electronique, Université Claude Bernard-Lyon 1, Villeurbanne, F-69622 Cedex, France

R. Meaudre

Département de Physique des Matériaux,\* Université Claude Bernard-Lyon 1, Villeurbanne, F-69622 Cedex, France (Received 17 May 1983; revised manuscript received 6 December 1983)

The models proposed to explain the ac conduction in our rf sputtered SiO<sub>2</sub> films are compared. The ac conductivity observed in the (77-570)-K range is well explained when considered as the sum of two contributions: the first dominating at low temperatures, arising from bipolaron correlated barrier hopping, and the second dominating at high temperatures, arising from quantum-mechanical tunneling of holelike polarons. It is emphasized that correlated barrier hopping of one or two types of carriers cannot render an account of the entire range of experimental results. It is shown that this ac transport is controlled by  $D^-, D^+, D^0$  defects and that a different choice of defects is unfounded.

## I. INTRODUCTION

Recently, and almost simultaneously, two models<sup>1,2</sup> were proposed to explain the ac conduction that we had obtained in rf sputtered SiO<sub>2</sub> films.<sup>3</sup> Shimakawa and Kondo suggested that correlated barrier hopping (CBH) of single polarons contributed to ac transport and proposed the following processes:<sup>2</sup> hopping of holes between  $C_1^0(1T)$  and  $C_1^-(1T)$  and of electrons between  $T_3^0(3C)$  and  $C_3^+(3T)$ ;  $C_1^0(1T), C_1^-(1T), T_3^0(3C), \text{ and } C_3^+(3T)$  are the defects proposed by Lucovsky for irradiated vitreous SiO<sub>2</sub>.<sup>4-8</sup> We put forward another approach: the examination of different transport mechanisms [dipolar mechanism, quantummechanical tunneling (QMT), classical hopping, continuous time random walk] did not allow, at first, a description of ac transport over the entire temperature range, and the investigation was pursued in correlation with dc conduction,<sup>9</sup> ESR, and uv absorption measurements.<sup>10</sup> It was finally concluded that two mechanisms contributed to the ac conduction:<sup>1</sup> bipolaron CBH between  $D^-$  and  $D^+$  and QMT of single polarons between  $D^0$  and  $D^-$ ;  $D^-$ ,  $D^+$ , and  $D^0$  are the de-

TABLE I. Defect configuration models. •: silicon; O: oxygen; ----: covalent bond; - - -: partial bond with three electrons; =: lone-pair orbital 2p (orbital 2s nonrepresented).



fects proposed by Mott for thermal a-SiO<sub>2</sub> at the SiO<sub>2</sub>-Si interface.<sup>11</sup>

It seems now interesting to compare these two interpretations, and in order to make the discussion easier we recall the experimental facts that Shimakawa and Kondo and we ourselves attempted to explain. The ac conductivity measured in the frequency and temperature ranges  $40-10^5$  Hz and 77-750 K presents two behaviors:<sup>3</sup> for 320 K < T < 570 K the conductivity obeys an equation of the form  $\sigma(\omega) = a(T)\omega^s$ , where s is linearly dependent on the temperature and is close but less than unity, and for 77 K < T < 320 K  $\sigma(\omega)$  is almost temperature independent and obeys an equation of the form  $\sigma(\omega) = A\omega$ . In the previous frequency and temperature ranges, the dielectric constant varies by less than 1%. Shimakawa and Kondo and we our-

TABLE II. Energy levels associated with the defects represented in Table I. — : optical levels; --: thermal levels of  $D^0$ (donor and acceptor); --: thermal level of  $C_1^0$ .



selves have considered different defects to explain the ac transport observed in rf sputtered SiO<sub>2</sub> films and, in order to make the discussion clearer, a recall of defect configurations possible in SiO<sub>2</sub> is given in Table I; the energy levels associated with these defects are given in Table II. One can note that  $D^-$  and  $C_1^-(1T)$  have the same configuration but very different energy levels, and that  $D^0$  acceptor and  $C_1^0(1T)$  have the same configuration and are located at the same level above the valence band.

#### **II. TRANSPORT MECHANISMS**

Shimakawa and Kondo (SK) have envisaged two transport mechanisms operating simultaneously to try to explain the ac conductivity observed in our films. They proposed that total ac conductivity is due to the CBH of two kinds of carriers and they used the following formula of Pike and Elliott<sup>12, 13</sup> to calculate the contributions  $\sigma_1(\omega)$  and  $\sigma_{II}(\omega)$  due to each of them:

$$\sigma(\omega) = \frac{\pi^2 n N_c N \epsilon \omega R_{\omega}^6}{24} \quad , \tag{1}$$

$$R_{\omega} = \frac{4ne^2}{\epsilon [W_M - kT \ln(1/\omega\tau_0)]} , \qquad (2)$$

where  $N_c$  is the carrier density that hops, N the total charged defect density,  $\omega$  the angular frequency,  $\tau_0$  the characteristic relaxation time,  $\epsilon$  the dielectric constant, and  $R_{\omega}$  the distance of pairs for which  $\omega \tau = 1$ . They chose the following data to fit experimental results:

$$n = 1$$
,  $\epsilon = 3$ ,  $\tau_0 = 10^{-12}$  s.

 $N_c N = 7 \times 10^{36}$  cm<sup>-6</sup> and  $W_M = 2.5$  eV for process I.  $N_c N = 2.9 \times 10^{35}$  cm<sup>-6</sup> and  $W_M = 1.4$  eV for the process II. The curves they calculated are reported in Fig. 1 (Fig. 6 of Ref. 2). It seems that the values of  $N_c N = 7 \times 10^{36}$  cm<sup>-6</sup> and  $N_c N = 2.9 \times 10^{35}$  cm<sup>-6</sup> are erroneous: using the previous parameters one obtains the curves reported in Fig. 2, which



FIG. 1. Temperature dependence of  $\sigma(\omega)$  in rf sputtered SiO<sub>2</sub> film. Experimental data (open circles) are from our paper Ref. 3. Calculated curves are from Shimakawa and Kondo (Ref. 2). The dashed and dotted lines I and II are results for processes I and II, respectively. The total ac conductivity is shown by the solid lines.



FIG. 2. Temperature dependence of  $\sigma(\omega)$  calculated with formula (1) and (2) and the data given by Shimakawa and Kondo in Ref. 2: n=1,  $\epsilon=3$ ,  $\tau_0=10^{-12}$  s,  $W_M=2.5$  eV, and  $N_cN=7\times10^{36}$  cm<sup>-6</sup> for process I;  $W_M=1.4$  eV and  $N_cN=2.9\times10^{35}$  cm<sup>-6</sup> for process II. The dashed and dotted lines I and II are calculated results for processes I and II, respectively. The total ac conductivity is shown by the solid lines.  $\bigcirc$ ,  $\bigcirc$ ,  $\square$ ,  $\blacksquare$ : our experimental results.

differ from those obtained by SK; however, other values of  $N_c N$  give curves of  $\sigma(\omega)$  analogous to those of Fig. 1. This is the case, for example, with  $N_c N = 7 \times 10^{37}$  cm<sup>-6</sup> and  $N_c N = 10^{35}$  cm<sup>-6</sup> for processes I and II, respectively (Fig. 3).

The problem of the uniqueness of the solution was not approached in Ref. 2, but it must be emphasized that there is not just one set of parameters which allow the fitting of experimental data at high temperatures; there are a multitude. For example, the curves reported in Fig. 4 have been



FIG. 3. Temperature dependence of  $\sigma(\omega)$  calculated with formula (1) and (2) and the following data: n=1,  $\epsilon=3$ ,  $\tau_0=10^{-12}$  s,  $W_M=2.5$  eV, and  $N_c N=7\times 10^{37}$  cm<sup>-6</sup> for process I;  $W_M=1.4$  eV and  $N_c N=10^{35}$  cm<sup>-6</sup> for process II. The dashed and dotted lines I and II are calculated results for processes I and II, respectively. The total ac conductivity is shown by the solid lines.  $\bigcirc$ ,  $\bigcirc$ ,  $\square$ ,  $\blacksquare$ : our experimental results.



FIG. 4. Temperature dependence of  $\sigma(\omega)$  calculated with formulas (1) and (2) and the following data: n = 1,  $\epsilon = 3.8$ ,  $\tau_0 = 10^{-12}$  s,  $W_M = 2$  eV, and  $N_c N = 9 \times 10^{36}$  cm<sup>-6</sup> for process I;  $W_M = 1.73$  eV and  $N_c N = 9 \times 10^{36}$  cm<sup>-6</sup> for process II. The dashed and dotted lines I and II are calculated results for process I and II, respectively. The total ac conductivity is shown by the solid lines.  $\bigcirc$ ,  $\bigcirc$ ,  $\Box$ ,  $\blacksquare$ : our experimental results.

calculated with the following set:

$$n = 1, \ \epsilon = 3.8, \ \tau_0 = 10^{-12} \text{ s}$$

 $N_c N = 9 \times 10^{36}$  cm<sup>-6</sup> and  $W_M = 2$  eV for the process I.  $N_c N = 9 \times 10^{36}$  cm<sup>-6</sup> and  $W_M = 1.73$  eV for the process II. (The usual value of  $\epsilon$  in SiO<sub>2</sub> is 3.8 and we measured  $\epsilon = 3.8$  in our films, which is the reason why we have chosen this value here.)

We also should like to make the following digression: a model considering only the CBH of one type of carrier gives an almost similar fitting of experimental data; curves reported in Fig. 5 have been calculated with formulas (1) and (2) but with only one process [so that  $\sigma(\omega) = \sigma_{\rm I}(\omega)$ ] and the parameters n=1,  $\epsilon=3.8$ ,  $\tau_0=10^{-12}$  s,  $W_M=1.75$  eV, and  $N_c N=1.2 \times 10^{37}$  cm<sup>-6</sup>.

The principal weakness of the CBH model with two types



FIG. 5. Temperature dependence of  $\sigma(\omega)$  calculated with formula (1) and (2) and the following data: n=1,  $\epsilon=3.8$ ,  $\tau_0=10^{-12}$  s,  $W_M=1.75$  eV, and  $N_c N=1.2 \times 10^{37}$  cm<sup>-6</sup> for process I; process II not considered. The total ac conductivity  $[\sigma(\omega)=\sigma_I(\omega)]$  is shown by the solid lines. O,  $\Phi$ ,  $\Box$ ,  $\blacksquare$ : our experimental results.



FIG. 6. Total ac conductivity calculated with formulas (1) and (2) and the data given by Shimakawa and Kondo in Ref. 2: n=1,  $\epsilon=3$ ,  $\tau_0=10^{-12}$  s,  $W_M=2.5$  eV, and  $N_cN=7\times10^{37}$  cm<sup>-6</sup> (instead of  $7\times10^{36}$  cm<sup>-6</sup> of SK) for process I;  $W_M=1.4$  eV and  $N_cN=10^{35}$  cm<sup>-6</sup> (instead of  $2.9\times10^{35}$  cm<sup>-6</sup> of SK) for process II. O,  $\bullet$ ,  $\Box$ ,  $\blacksquare$ : ac conductivity measured in our films in the (77–570)-K range.

of carriers proposed by SK is that it does not allow the explanation of the experimental results in the whole temperature range 77-570 K. Figures 6 and 7 show that the variations of calculated  $\sigma(\omega)$  with temperature are still strong below 320 K. This is in contradiction with experimental facts. The same results are observed with the CBH model with only one type of carrier.

We also envisaged two contributions to conductivity: the CBH of bipolarons, dominating at low temperatures; and the QMT of polarons, dominating at high temperatures. For 77 K < T < 320 K,  $\sigma(\omega)$  obeys an equation of the form  $\sigma_1(\omega) \propto \omega$  [Fig. 8(a)]; this was interpreted in terms of Elliott's model<sup>14</sup> where two electrons simultaneously hop between two oppositely charged sites not randomly distributed but paired, as first considered by Kastner, Adler, and



FIG. 7. Total ac conductivity [calculated with formulas (1) and (2) and the data used for Fig. 6] vs frequency. Open circles: our experimental results.



FIG. 8. (a) Variations of conductivity  $\sigma_1(\omega)$  with frequency in the temperature range 77-320 K. Open circles: our experimental results. (b) Variations of conductivity  $\sigma_2(\omega)$  with frequency at different temperatures.  $\sigma_2(\omega)$  is obtained by subtracting  $\sigma_1(\omega)$  from the total conductivity  $\sigma(\omega)$  given in Fig. 2 of Ref. 3.  $\blacktriangle$ ,  $\bullet$ ,  $\circ$ ,  $\circ$ ,  $\Delta$ : experimental results. —:: theoretical curves calculated from  $C \exp(-W/kT)\omega[\ln(\nu/\omega) - W_H/kt]^4$  with  $\nu = 10^{13} \text{ s}^{-1}$ , W = 0.28eV,  $W_H = 0.35$  eV, and  $C = 6.9 \times 10^{-14} \Omega^{-1} \text{ cm}^{-1} \text{ s}$ .

Fritzsche in the case of lone-pair semiconductors.<sup>15</sup> In this case

$$\sigma(\omega) = \frac{N^2}{24} \pi^2 \epsilon \left( \frac{8e^2}{\epsilon W_M} \right)^6 \frac{\omega}{(\omega \tau_0)^\beta} \exp \left( \frac{W_M}{8kT_g} \right) \\ \times \exp \left[ -\frac{T}{8T_g} \ln \left( \frac{1}{\omega \tau_0} \right) \right] , \qquad (3)$$

where  $\beta = 6kT/W_M$ ;  $\epsilon$  is the dielectric constant, N the density of defects,  $W_M$  the maximum thermal barrier height for the two carriers, and  $T_g$  the glass transition temperature.  $\tau_0$  is of the order of an atomic vibrational period. Equation (3) is easily rewritten in the form  $\sigma(\omega) = A\omega^s$  with  $s = 1 - 6kT/W_M + T/8T_g$  and A a temperature-independent parameter. It is seen that a practically temperature-independent  $\sigma(\omega)$  and a linear-frequency behavior occurs when  $W_M \sim 48kT_g$ . For SiO<sub>2</sub>  $T_g = 1500$  K so  $W_M = 6.2$  eV was obtained. For 320 K < T < 570 K, it was found that  $\sigma(\omega)$  resulted from two contributions:  $\sigma_1(\omega)$  previously discussed, and  $\sigma_2(\omega)$  due to the QMT of polarons.

The following formula of Austin and Mott<sup>16</sup> was used to fit data:

$$\sigma(\omega) = a(T)\omega[\ln(\nu/\omega) - W_H/kT]^4 .$$
(4)

 $\nu$  is the phonon frequency,  $W_H$  the polaron hopping energy, and  $a(T) = C \exp(-W/kT)$  to take account of the thermally activated process. A good fit to experimental data is obtained for W = 0.28 eV,  $W_H = 0.35$  eV, and  $\nu = 10^{13}$  s<sup>-1</sup> (or W = 0.3 eV,  $W_H = 0.3$  eV, and  $\nu = 10^{12}$  s<sup>-1</sup>) [Fig. 8(b)].

It is interesting to note that this model, CBH of bipolarons at low temperatures and, added to it, QMT of polarons at high temperatures, allows a fitting of the entire range of experimental results. The latter interpretation has the advantage of explaining the experimental data in the whole temperature range used for the experiments, which the CBH model with one or two carriers does not do.

### **III. DESCRIPTION OF CHARGE TRANSPORT**

It is now desirable to be more precise about the nature of charge transport. The points to discuss are the following: the possibility of a connection of values of  $W_M$  chosen by SK with defects known in SiO<sub>2</sub>, and the eventual impossibility of values of  $N_c N$  chosen for our films.

SK thought that the defects present in our films could be  $C_1^{-}(1T), C_3^{+}(3T), C_1^{0}(1T), \text{ and } T_3^{0}(3C)$  defects determined by Lucovsky in irradiated v-SiO<sub>2</sub>; they proposed that  $\sigma_{\rm I}(\omega)$  was due to CBH of holes between  $C_{\rm I}^0(1T)$  and  $C_1^-(1T)$  and  $\sigma_{II}(\omega)$  to CBH of electrons between  $T_3^0(3C)$ and  $C_3^+(3T)$ .  $W_M = 2.5 \text{ eV} = W_1$  and  $W_M = 1.4 \text{ eV} = W_2$ would then be the thermal energies to transfer the trapped hole from  $C_1^0(1T)$  and the trapped electron from  $T_3^0(3C)$ to their respective bands. This point deserves attention. The optical levels of  $C_1^-(1T)$  and  $C_1^0(1T)$  are located, respectively, at 1.5 and 7.5 eV above the valence band;<sup>8</sup> so when  $C_1^{-}(1T)$  captures a hole and  $C_1^{0}(1T)$  is formed, the lattice distortion associated with  $C_1^0(1T)$  is  $W_p = 3$  eV and the thermal-reexcitation energy of the hole trapped is necessarily 4.5 eV in Lucovsky's model [dotted line level in Table II]. The value  $W_1 = 2.5$  eV chosen by SK to fit with CBH of two carriers is rather far from the last one. In this case it seems perhaps daring to affirm that  $\sigma_{I}(\omega)$  is due to the hopping of holes between neutral and negative nonbridging oxygen defects of Lucovsky. Concerning  $W_2$ , a precise value cannot be deduced from Lucovsky's model; however, it can be estimated. An energy of 1.5 eV would be necessary to transfer the electron captured by  $C_3^+(3T)$  in the conduction band if the capture were not accompanied by lattice distortion; this is not the case here but from Lucovsky's model it is not possible to determine the lattice distortion associated with the capture of an electron by the defect  $C_3^+(3T)$ . Following Lucovsky, it is thought that when an electron is added to  $C_3^+(3T)$  to form  $C_3^0(3T)$ ,  $C_3^0(3T)$  is unstable and the generation of  $T_3^0(3C)$  occurs via the reaction

$$T_4^0(4C) + C_3^0(3T) \rightarrow C_2^0(2T) + T_3^0(3C)$$

The added electron has now to be thermally excited from  $T_3^0(3C)$  to the conduction band. The optical level of  $T_3^0(3C)$  lies at about 5.8 eV below the conduction band so the thermal energy necessary to transfer the electron from  $T_3^0(3C)$  to the conduction band is at least equal to 2.9 eV; this is far from  $W_2 = 1.4$  eV, the parameter chosen in Ref. 2 to calculate  $\sigma_{II}(\omega)$  with the model of CBH with two carriers. It seems difficult again here to conclude that  $\sigma_{II}(\omega)$  is due

### COMMENTS

$$T_3^0(3C) + C_3^+(3T) \rightleftharpoons C_3^+(3T) + T_3^0(3C)$$

 $T_3^0(3C)$  and  $C_3^+(3T)$  being the defects proposed by Lucovsky.

With the two mechanisms envisaged in Ref. 2,  $N_c N = 7 \times 10^{37}$  and  $N_c N = 10^{35}$  cm<sup>-6</sup> represent  $N(C_1^0)N_T/2$  and  $N(T_3^0)N_T/2$ , respectively;  $N(C_1^0)$  and  $N(T_3^0)$  are the densities of  $C_1^0(1T)$  and  $T_3^0(3C)$ , and  $N_T$  the density of the total charged defects; that leads to  $N(C_1^0)/N(T_3^0) = 700$ . The ESR signal obtained on our films shows that  $N(T_3^0)$  is higher than  $N(C_1^0)$ :<sup>10</sup> the spectrum given in Fig. 9 displays a central narrow-resonance characteristic of E' center and coupled on its left, little features due to a mixture of "wet" and "dry" oxygen-hole centers (OHC); E', OHC "wet," and OHC "dry" are the terms used in ESR measurements, but E' is  $T_3^0(3C)$ ; OHC "wet" is  $C_1^0(1T)$  and OHC "dry" the peroxy radical.<sup>8,17-20</sup> From Fig. 9 it is sure that the ratio

$$N(OHC "wet")/N(E') = N(C_1^0)/N(T_3^0) \sim 700$$

is impossible in our films annealed at 403 K. Films used for the conductivity measurements are annealed at 570 K,<sup>3</sup> but it was shown that OHC "wet" and E' annealed together up to 700 K.<sup>21</sup> Then the ratio  $N(C_1^0)/N(T_3^0)$  should not vary much betweeen films annealed at 403 and 570 K.  $N(C_1^0)/N(T_3^0) \sim$  700 then is not convenient for our films. This latter discussion can also be applied to the set of parameters used to calculate the curves of the Fig. 4. With the parameters  $W_1$ ,  $W_2$ , and  $\epsilon$  chosen by SK, we tried to fit data with defect concentrations such as  $N(C_1^0)/N(T_3^0) < 1$ , but the fitting is absolutely impossible in these conditions. Parameters  $W_1$ ,  $W_2$ ,  $N(C_1^0)$ ,  $N(T_3^0)$ , with  $N(C_1^0)/N(T_3^0) < 1$ , fitting data at high temperatures can be found but again one comes up against the difficulty of binding the values of  $W_1$  and  $W_2$  to thermal levels of  $C_1^0(1T)$  and  $T_3^0(3C)$ , as found in literature.

We also considered that defects reported by Lucovsky



FIG. 9. Room-temperature ESR spectrum obtained for a film annealed at 403 K in vacuum for 9 h.

could be present in our films, but with the structure of a v-SiO<sub>2</sub> target being destroyed during sputtering, we envisaged that defects in our films could differ from those of v-SiO<sub>2</sub>, especially since it is well known that rf sputtered films are irradiated during fabrication. So we did not eliminate, a priori, the  $D^-$ ,  $D^+$ ,  $D^0$  proposed by Mott for oxygen non-bridging defects in SiO<sub>2</sub> at the Si-SiO<sub>2</sub> interface [Table I(a)]. We envisaged that  $\sigma_1(\omega)$  could be due to CBH of bipolarons between  $D^-$  and  $D^+$ , and  $\sigma_2(\omega)$  to QMT of holelike polarons between  $D^0$  and  $D^-$ . A long discussion on the choice of the defects reported by Mott instead of those reported by Lucovsky was given in Ref. 1 and we will not develop it again here. We will only summarize the principal facts.

The contribution  $\sigma_1(\omega)$  is due to CBH of bipolarons according to  $D^- + D^+ \rightleftharpoons D^+ + D^-$ . Let  $W_M$  be the energy to transfer two electrons from  $D^-$  to the conduction band. According to Mott, Davis, and Street<sup>22</sup>

$$W_{M} = B - (E_{1} + W_{p}) + E_{1}' + W_{p}' \quad . \tag{5}$$

B is the band gap,  $E_1$  and  $E'_1$  the energy levels (without distortion) with respect to the valence and conduction bands of the acceptor  $D^-$  and donor  $D^+$ , and  $W_p$  and  $W'_p$  the distortion energies associated with  $D^0$  and  $D^+$ . From levels given by Mott [Table II(a)] and from our experimental results  $W_M = 6.2$  eV, one obtains the thermal energy level of  $D^0$ donor  $E'_1 + W'_p = 2.8$  eV, that is a possible value though a little too small, since Mott suggested 2.6 eV for the distortion energy  $W'_p$ .<sup>11</sup> If we consider the model of Lucovsky, the interconversion of defects  $C_1^-(1T)$  and  $C_3^+(3T)$  is not possible and the hopping process of two electrons would be more complicated; indeed, when two electrons hop from one  $C_1^-(1T)$  to one  $C_3^+(3T)$ ,  $C_1^-(1T)$  does not become  $C_3^+(3T)$  but  $C_3^+(2T, 1C)$  and  $C_3^+(3T)$  does not become  $C_1^-(1T)$  but  $T_3^-(3C)$ . In this case  $C_1^-(1T)$ ,  $C_1^0(1T)$ ,  $C_3^+(2T, 1C)$  replace  $D^-$ ,  $D^0$ ,  $D^+$ ; from Eq. (5), the energy levels reported Table II(b), and  $W_M = 6.2$  eV, the distortion associated with  $C_1^0(1T)$  would be greater than that associated with  $C_3^+$  (2T, 1C).<sup>1</sup> This is not reasonable since a true covalent bond appears in the last case. Finally, there is nothing to oppose a CBH of bipolarons according to  $D^- + D^+ \rightleftharpoons D^+ + D^-$ . If one tries to analyze the QMT of polarons operating at high temperatures, one is obliged to choose the defects given by Mott. Indeed, taking into account the experimental value of hopping energy  $W_H = 0.35$ eV, the only possible process is a hopping of holelike polarons between neutral and negative oxygen nonbridging defects described by Mott, according to  $D^0 + D^- \rightleftharpoons D^- + D^0$ , since he proposed an activation energy of 0.4 eV for this process; the same hopping between  $C_1^0(1T)$  and  $C_1^-(1T)$ with levels estimated by Lucovsky would necessitate considerably greater activation energy, of the order of 1.5 eV.<sup>1,8</sup> As the contribution  $\sigma_2(\omega)$  is thermally activated it is necessary to consider the creation of neutral defects at high temperatures according to

$$D^- + D^+ + |U_{\rm eff}| \to 2D^0$$
 . (6)

 $U_{\text{eff}}$  is the negative effective correlation energy corresponding to the reverse reaction. The activation energy W = 0.28eV and the law of mass action applied to Eq. (6) lead to the value  $U_{\text{eff}} = -0.56$  eV. Finally, from this analysis the negative defect level was located at 4.1 eV below the conduction band; this can be compared with 4.4 eV estimated by Mott for  $D^-$  and is far from 7.5 eV proposed by Lucovsky for  $C_1^-(1T)$ . It seems that all these facts allow us to affirm that ac conductivity is controlled by  $D^-$ ,  $D^+$ ,  $D^0$ , oxygen nonbridging defects, proposed by Mott for SiO<sub>2</sub>.

#### **IV. CONCLUSION**

Two descriptions of ac charge transport in rf sputtered SiO<sub>2</sub> films were recently proposed. As they are different, it seemed desirable in this paper to examine them both and see if one proved more advisable than the other. The first important point to emphasize was their ability or inability to explain the entire range of experimental data. The model of CBH with two types of carriers does not fit these data below 350 K with parameters  $W_1$  and  $W_2$  chosen in Ref. 2; the model using the CBH of bipolarons and QMT of polarons is superior in that it explains  $\sigma(\omega)$  obtained in our films in the (77-570)-K range.

To precise the charge transport, the second important point was to discuss the possible connection of parameters used for fitting experiments, with possible defects in rf sputtered SiO<sub>2</sub> films. In the model of CBH with two carriers, the thermal energy levels of defects controlling transport have been chosen in Ref. 2, 2.5 and 1.4 eV, and have been connected with  $C_1^0(1T)$  and  $T_3^0(3C)$  of Lucovsky. These values are almost half of those which can be deduced from optical levels proposed by Lucovsky for these defects. So it seems to us that the affirmation that  $\sigma(\omega)$  is controlled by

\*Associated with CNRS.

- <sup>1</sup>R. Meaudre and M. Meaudre, Philos. Mag. B <u>46</u>, 647 (1982).
- <sup>2</sup>K. Shimakawa and A. Kondo, Phys. Rev. B <u>27</u>, 1136 (1983).
- <sup>3</sup>M. Meaudre and R. Meaudre, Philos. Mag. B 40, 401 (1979).
- <sup>4</sup>G. Lucovsky, Philos. Mag. B <u>39</u>, 513 (1979).
- <sup>5</sup>G. Lucovsky, Philos. Mag. B <u>39</u>, 531 (1979).
- <sup>6</sup>R. A. Street and G. Lucovsky, Solid State Commun. <u>31</u>, 289 (1979).
- <sup>7</sup>G. Lucovsky, J. Non-Cryst. Solids <u>35&36</u>, 825 (1980).
- <sup>8</sup>G. Lucovsky, Philos. Mag. B <u>41</u>, 457 (1980).
- <sup>9</sup>R. Meaudre and M. Meaudre, J. Non-Cryst. Solids <u>46</u>, 71 (1981).
- <sup>10</sup>M. Meaudre, R. Meaudre, J. Tardy, and B. Tribollet, J. Phys. (Paris) <u>42</u>, 1013 (1981).
- <sup>11</sup>N. F. Mott, Adv. Phys. <u>26</u>, 363 (1977).
- <sup>12</sup>G. E. Pike, Phys. Rev. B <u>26</u>, 1572 (1972).
- <sup>13</sup>S. R. Elliott, Philos. Mag. B <u>36</u>, 1291 (1977); <u>37</u>, 553 (1978).
- <sup>14</sup>S. R. Elliott, Philos. Mag. B <u>40</u>, 507 (1979).
- <sup>15</sup>M. Kastner, D. Adler, and H. Fritzsche, Phys. Rev. Lett. <u>22</u>,

such defects is unfounded.

Concerning the alternative model, bipolaron CBH and QMT of polarons, a discussion has been opened on the relation of parameters obtained from fitting to defects possible in SiO<sub>2</sub>. The hopping energy of 0.35 eV has been unambiguously connected with the QMT of holelike polarons between  $D^0$ ,  $D^-$  of Mott. The position of thermal energy of  $D^0$  donor was obtained at 2.8 eV below the conduction band, this value is acceptable. The  $D^-$  level was obtained at 4.1 eV below the conduction band; this value agrees with 4.4 eV estimated by Mott.<sup>11</sup>

Finally, a point deserves particular attention: the position of a negative defect below the conduction band and the distortion associated with the capture of a hole by this defect deduced from our analysis are 4.1 and 0.7 eV (Mott has estimated these parameters as 4.4 and 0.8 eV, respectively). This constitutes a very favorable situation for dc conduction in our metal-insulator-metal structures: the barrier energy existing at the Au-SiO<sub>2</sub> contact being 4.1 eV,<sup>23</sup> the dc conduction can only be explained with defect levels at about the same height.<sup>9,24</sup> Our results, thus, give a coherent description of ac and dc transport in rf sputtered SiO<sub>2</sub> films, and it seems possible to conclude that this transport is controlled by defects  $D^+$ ,  $D^-$ ,  $D^0$ . The aim of this paper is not to say which interpretation is correct but to consider which of them, up to now, gives the best account of experimental data obtained on our films whilst taking into account, faithfully, the different results concerning SiO<sub>2</sub> found in the literature.

1504 (1976).

- <sup>16</sup>I. G. Austin and N. F. Mott, Adv. Phys. <u>18</u>, 41 (1969).
- <sup>17</sup>D. L. Griscom, G. H. Sigel, Jr., and E. J. Friebele, in *Glass*, proceedings of the XI International Congress on Glass, Prague, 1977, edited by J. Götz (North-Holland, Amsterdam, 1977), p. 3.
- <sup>18</sup>D. L. Griscom, J. Non-Cryst. Solids <u>31</u>, 241 (1978).
- <sup>19</sup>E. J. Friebele and D. L. Griscom, in *Treatise on Materials Science and Technology, Vol. 17: Glass II*, edited by Herbert Herman (Academic, New York, 1979), p. 257.
- <sup>20</sup>D. L. Griscom, J. Non-Cryst. Solids <u>40</u>, 211 (1980).
- <sup>21</sup>M. Stapelbroek, D. L. Griscom, E. J. Friebele, and G. H. Sigel, Jr., J. Non-Cryst. Solids <u>32</u>, 313 (1979).
- <sup>22</sup>N. F. Mott, E. A. Davis, and R. A. Street, Philos. Mag. <u>32</u>, 961 (1975).
- <sup>23</sup>B. E. Deal, E. H. Snow, and G. A. Mead, J. Phys. Chem. Solids <u>27</u>, 1873 (1966).
- <sup>24</sup>M. Meaudre, R. Meaudre, and J. J. Hauser, J. Non-Cryst. Solids <u>58</u>, 145 (1983).