ac conduction in sol-gel-derived glasses in the SiO_2-As_2O_3 system

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ac-resistivity measurements on sol-gel-derived glasses in the system $xAs_2O_3\cdot(1-x)SiO_2$ with $0.05 < x < 0.16$ have been carried out over the frequency range 2–100 kHz in the temperature range 80–400 K. The ac resistivity for all the glasses shows a sharp minimum at around 317 K. This is ascribed to a change in chemical equilibrium of the ratio $[As^{5+}]/[As^{3+}]$ as a function of temperature. In the temperature range 190–300 K the ac resistivity is shown to arise due to a correlated-barrier-hopping mechanism involving bipolarons. A small fraction of total arsenic sites is found to participate in the hopping conduction. The ac resistivity at temperatures below 190 K shows a frequency exponent s, the variation of which can be qualitatively explained on the basis of the overlapping-large-polaron model.

I. INTRODUCTION

Oxide glasses containing transition-metal ions have been the subject of considerable interest because of their semiconducting properties.[1-3] These glasses contain variable-valence ions such as V^{4+}-V^{5+}, Fe^{2+}-Fe^{3+}, and Cu^+-Cu^{2+}, respectively, which cause electron hopping between the localized sites represented by these ions. Silicate and borate glasses containing variable-valence ions such as Sb^{3+}-Sb^{5+} and As^{3+}-As^{5+} have been shown to have semiconducting properties.[4-7] The conduction in these glasses below 300 K has been ascribed to the hopping of a pair of electrons (bipolarons) between two ions of different valencies. All these studies have been carried out on melt-quenched glasses, and the ratio $[Sb^{5+}]/[Sb^{3+}]$ or $[As^{5+}]/[As^{3+}]$ has values varying from 0.03 to 0.36. We have now prepared silicate glasses containing arsenic oxide by the sol-gel technique. It has been possible to retain a much higher fraction of arsenic ions in the pentavalent state. The ac conductivity of the resulting glasses also is higher than those found earlier. The results are reported in this paper.

II. EXPERIMENTAL DETAILS

The starting compositions chosen for the three glasses studied were $90SiO_2\cdot10As_2O_3$, $80SiO_2\cdot20As_2O_3$, and $70SiO_2\cdot30As_2O_3$ in mol %. However, the final compositions as determined by chemical analyses were markedly different and their values are summarized in Table I.

Such a drastic change in the amount of arsenic present in the final glasses as compared with the starting value is due to the loss of some of the arsenic ions by volatilization during the heat-treatment schedule. The sol was prepared by mixing a solution of $AsCl_3$ in hydrochloric acid with another of silicon tetraethoxide in ethyl alcohol. The former was made by treating about 0.4 g AR-grade As_2O_3 in about 6 cm^3 of hydrochloric acid at 50 °C, and the latter was obtained by mixing about 2 cm^3 of $Si(OC_2H_5)_4$ in 10 cm^3 of ethyl alcohol, both solutions being stirred continuously for about 10 min. The exact amounts of As_2O_3 and $Si(OC_2H_5)_4$ were determined by the target composition of the glass sample as mentioned above. After adding some water (~ 2 cm^3) to the mixture, the solution was stirred at room temperature for 30 min. The sols were allowed to gel in a Petri dish for 4–5 days. The gels were kept at 50 °C for 2 days, after which they were heated at a rate of 1 °C/min to a temperature of 773 K where they were held for 2 h before being cooled down to room temperature. The density of the glass samples was measured by Archimedes' principle using acetone as the liquid. The last column in Table I gives the density values.

Amounts of As^{3+} and As^{5+} ions present in various glasses prepared by the sol-gel technique were determined by the following method.

For determining the trivalent arsenic content, 0.5 g of the glass sample was dissolved in a mixture of 2 cm^3 HF, 5 cm^3 $HClO_4$, and 5 cm^3 distilled water in a Teflon beaker and digested for 10 min. Water was added and the solu-

TABLE I. Compositions of glasses investigated and some physical parameters.

Glass No.	SiO_2 (mol %)	As_2O_3 (mol %)	Density (g/cm³)	Arsenic concentration N_t (cm⁻³)	Average intersite separation R_ω (Å)
1	94.2	5.8	1.97	2.0×10^{21}	7.9
2	90.8	9.2	2.29	3.5×10^{21}	6.6
3	84.6	15.4	2.43	5.5×10^{21}	5.7

TABLE II. Ratio $[As^{5+}]/[As^{3+}]$ for different glasses.

Glass No.	$[As^{5+}]/[As^{3+}]$	
	As prepared	After heating at 353 K for $\frac{1}{2}$ h
1	1.26	0.73
2	1.66	0.87
3	2.70	1.31

FIG. 2. Variation of ac resistivity as a function of temperature for glass 2: 2 kHz (X), 5 kHz (■), 10 kHz (▲), 20 kHz (△), 50 kHz (●), and 100 kHz (○).

tion stirred with excess H_3BO_3 for 10 min, maintaining the pH at ~ 1. Titration was carried out on this solution with $0.01N$ $KMnO_4$.[8] To determine the amount of pentavalent arsenic, 0.5 g of the glass sample was dissolved in a mixture of HF, H_2SO_4, and distilled water and digested for 10 min. Water was then added and the solution stirred with excess H_3BO_3 for 10 min. H_2SO_4 was then added to bring the pH of the solution to 1. About 5 g of potassium iodide was added to the solution. A small amount of sodium bicarbonate was dissolved in the mixture for creating an atmosphere of Co_2. The resulting solution was titrated with $0.02N$ sodium thiosulphate using starch solution as an indicator.[9] Table II summarizes the values of the ratio $[As^{5+}]/[As^{3+}]$ as obtained by the above chemical analysis for the three different glasses. The last column of this table shows the values of this ratio for glasses as estimated immediately after a heat treatment of the specimens at 353 K for $\frac{1}{2}$ h. The concentration of arsenic ions, N_t, and the average intersite separation R calculated from the equation

$$R = (1/N_t)^{1/3} \tag{1}$$

are shown in the last two columns of Table I.

Electrical measurements were carried out on specimens of about 0.4 mm thickness and having an area of around 0.5 cm^2. Gold electrodes were vacuum deposited on both the faces of the samples. The ac-resistivity measurements were carried out in a General Radio 1615-A capacitance bridge over a frequency range 2–100 kHz. The sample holder used was similar to the one described elsewhere.[4] Measurements were made in the temperature range 80–400 K with a stability of ±0.5 K.

Optical-absorption spectra of the glasses were taken in a Hitachi 330 spectrophotometer using air as reference in the wavelength range 2000–7000 Å.
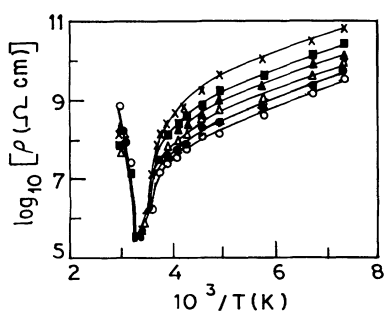
III. RESULTS

Figures 1, 2, and 3 show the variation of ac resistivities as a function of temperature at different frequencies for glasses 1, 2, and 3, respectively. It is evident that all the glass samples show a pronounced minimum in their ac resistivities at a temperature around 317 K. The minimum value of the resistivity varies from about 10^6 Ω cm in the case of glass 1 to approximately 10^2 Ω cm for glass 3, showing clearly that this value decreases as the arsenic content in the glass is increased. It should be noted that the ac-resistivity data in the range 80–290 K is reproducible on thermal cycling for all the glass compositions.

Figure 4 shows the variation of ac conductivity as a function of frequency for glass 2 at 184 K. The plot is typical of other glasses also. It is evident that conductivity obeys the relation $\sigma(\omega) \propto \omega^s$. The data were least-squares fitted to this equation, and the values of s were found to be less than 1. Figures 5, 6, and 7 give the variation of s as a function of temperature up to around 290 K for glasses 1, 2, and 3, respectively. The uncertainty in the exponent determination is indicated by the error bars
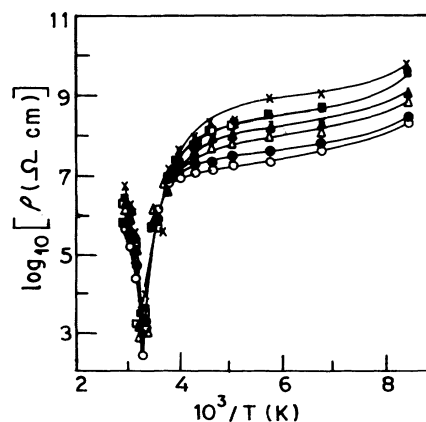

FIG. 1. Variation of ac resistivity as a function of temperature for glass 1: 2 kHz (X), 5 kHz (■), 10 kHz (▲), 20 kHz (△), 50 kHz (●), and 100 kHz (○).

FIG. 3. Variation of ac resistivity as a function of temperature for glass 3: 2 kHz (X), 5 kHz (■) 10 kHz (▲), 20 kHz (△), 50 kHz (●), and 100 kHz (○).
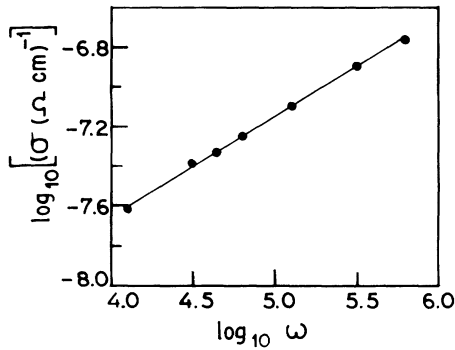
FIG. 4. Variation of conductivity as a function of frequency at 236 K for glass 2.

given to the data points in these plots. The implication of these results are discussed in the next section.

It is interesting to note that some of the s values estimated from the experimental results are quite small, being of the order of 0.2 at a temperature around 275 K. One explanation would be that the ac conductivity was being shunted by a parallel dc conduction process. Such a possibility is ruled out by the fact that the dc resistivity of all the glasses around 295 K is four orders of magnitude higher than the ac resistivity. The dc resistivities of glasses 1, 2, and 3 are 6.3×10^{10}, 1.8×10^{10}, and 7.4×10^{9} Ω cm, respectively, at this temperature.

In Fig. 8 is shown a plot of $(\alpha h v)^{1/2}$ as a function of $h v$ for glass 2, where α is the absorption coefficient and $h v$ the incident-photon energy. The figure is typical of other glasses. The optical band gap obtained from the intercept of the linear portion of the curve on the abscissa is 2.5 eV. The values obtained for the other glasses lie between 2.5 and 3.0 eV.

IV. DISCUSSION

The minimum in the ac resistivity observed for all the glasses at around room temperature is ascribed to a reaction of the type

$$As_2O_5 \ (\text{glass}) = As_2O_3 \ (\text{glass}) + O_2\uparrow \ . \tag{2}$$
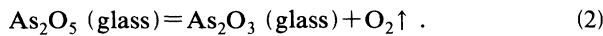
Differential thermal analyses of the present glasses in-

FIG. 5. Variation of s as a function of temperature for glass 1: Experimental data ($\bigcirc$), CBH model with $W_M = B$ (solid line), CBH model using W_M and τ_0 as parameters (dashed line), and OLP model (dot-dashed line).
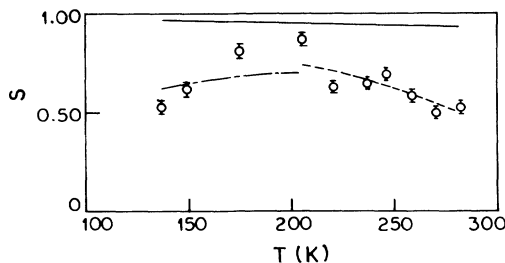

FIG. 6. Variation of s as a function of temperature for glass 2: Experimental data ($\bigcirc$), CBH model with $W_M = B$ (solid line), CBH model using W_M and τ_0 as parameters (dashed line), and OLP model (dot-dashed line).
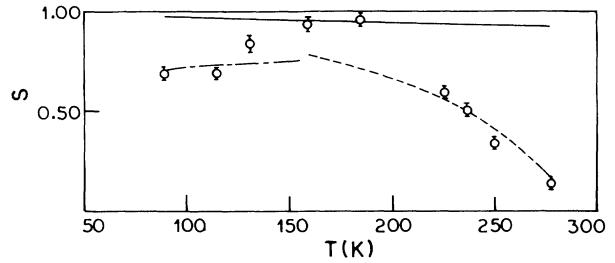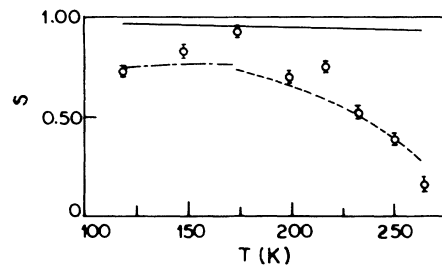

FIG. 7. Variation of s as a function of temperature for glass 3: Experimental data ($\bigcirc$), CBH model with $W_M = B$ (solid line), CBH model using W_M and τ_0 as parameters (dashed line), and OLP model (dot-dashed line).
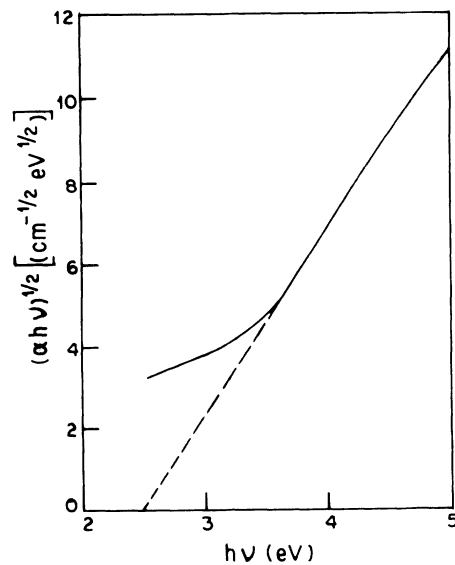

FIG. 8. Variation of absorption coefficient as a function of photon energy for glass 2.

dicate that the reaction sets in at around 310 K. This is similar to results reported earlier in the case of silicate glasses containing arsenic oxide prepared by the melt-quench method.[5,7] Chemical analysis carried out on samples heat treated at 353 K confirm the depletion of As^{5+} ions as described by Eq. (2) (see data in Table II). It should be noted that the ac-resistivity variation with temperature in the range 290–325 K can be reproduced during the cooling cycle of measurement only after holding the sample at these temperatures for a period of about 12 h. This is indicative of the fact that the above reaction is irreversible in nature. Data substantiating this aspect have been presented elsewhere in connection with dielectric permittivity and loss measurements for the present glass system.[10]

To explain the low-temperature ac resistivity of the present glass system, we apply the correlated-barrier-hopping (CBH) model with two electrons hopping simultaneously between the defect sites.[11] In the present case the latter are comprised of the As^{3+} and As^{5} sites. The ac resistivity in this model is given by

$$\rho(\omega)=\frac{12}{\pi^3 N^2 \epsilon\epsilon_0 \omega R_\omega^6} , \qquad (3)$$

where N is the spatial density of localized states, ϵ the dielectric constant of the glass, ϵ_0 the free-space permittivity, ω the angular frequency, and R_ω the hopping length. The latter is given by

$$R_\omega=\frac{2e^2}{\pi\epsilon\epsilon_0(W_M+kT\ln\omega\tau_0)} , \qquad (4)$$

where e is the electronic charge, W_M the barrier height at infinite intersite separation, k the Boltzmann constant, T the temperature, and τ_0 a characteristic relaxation time, which is assumed to have a value of the order of the inverse phonon frequency, viz., 10^{-13} sec. The frequency exponent s is expressed as

$$s=1-\frac{6kT}{W_M+kT\ln\omega\tau_0} . \qquad (5)$$

Taking $W_M=B$, where B is the optical band gap of the material, the value of N has been calculated from Eqs. (3) and (4) using the ac resistivity of the glass at a frequency $f=10^4$ cycles/sec. The results are shown in Table III. It is seem from these results that for both glasses 2 and 3 most of the arsenic sites contribute to the ac transport of the glasses. For glass 1 it appears that only a small fraction of these ions are participating in the conduction process. It should be mentioned here that the true dielectric constant of glass 1 would be a little higher than the measured value (~ 3.9) used in the calculation of R from Eq. (4). This is because glass 1 has some porosity, as is apparent from the measured density value of this sample.

The calculated s values for the three glasses as a function of temperature have been shown in Figs. 5–7 taking $W_M=B$ as the optical band gap. It is evident that the experimental data do not conform to the predicted values. The former show a maximum value of about 0.9 at around 190 K. It appears that the temperature variation of s in the temperature ranges 100–190 and 190–300 K

TABLE III. Density of states, N, calculated from Eq. (3) for different glasses.

Glass No.	Optical band gap B (eV)	T (K)	Calculated N (cm^{-3})	R_ω (Å)
1	2.95	245	4.4×10^{18}	11.9
2	2.50	250	2.9×10^{21}	1.6
3	2.50	250	2.7×10^{21}	1.5

are controlled by two different transport mechanisms. For fitting the experimental results at the higher-temperature region, we have used W_M and τ_0 as parameters. The values obtained are summarized in Table IV, and the least-squares-fitted curves are shown in these figures. The τ_0 value in all cases is reasonable. The W_M values ranging from 0.66 to 0.80 eV for these glasses suggest that the hopping arises due to the presence of localized states at the band edge, some 0.4 eV from the mobility edge. The fraction of arsenic-ion sites contributing to ac conduction in these glasses according to the CBH model is rather small, being of the order of 10^{-5} in the case of glass 1 and $\sim 10^{-3}$ for glasses 2 and 3.

The nature of the variation of s in the temperature range 100–190 K suggests that the same could arise as a result of the tunneling of large polarons for which the spatial extent of the polaron is large compared with the interatomic spacing.[12] According to the overlapping-large-polaron (OLP) model, the polaron-hopping energy W_H is given by

$$W_H=W_{H0}(1-r_0/R) , \qquad (6)$$

where r_0 is the large-polaron radius, W_{H0} is a constant, and R is the intersite distance.

The equation for ac resistivity $\rho(\omega)$ is

$$\rho(\omega)=\frac{12[2\alpha kT+W_{H0}r_0/R_\omega^2]}{\pi^4 e^2(kT)^2[N(E_F)]^2\omega R_\omega^4} , \qquad (7)$$

where α^{-1} is the spatial decay constant for the localized electron wave function, $N(E_F)$ the density of localized states at the Fermi level, and R_ω the tunneling distance at angular frequency ω and is given by

$$R_\omega=1/4\alpha([\ln(1/\omega\tau_0)-W_{H0}/kT]$$
$$+\{[\ln(1/\omega\tau_0)-W_{H0}/kT]^2$$
$$+(8\alpha r_0 W_{H0})/kT\}^{1/2}) . \qquad (8)$$

TABLE IV. Parameters obtained from CBH model by least-squares fitting in the temperature range 190–300 K.

Glass No.	τ_0 (sec)	W_M (eV)	R_ω (Å)	N (cm^{-3})
1	10^{-13}	0.80	83	1.3×10^{16}
2	10^{-13}	0.67	14	3.9×10^{18}
3	10^{-13}	0.66	14	3.2×10^{18}

TABLE V. Parameters obtained from OLP model by least-squares fitting in the temperature range 100–190 K.

Glass No.	W_{H0} (eV)	r_0 (Å)	α (Å^{-1})	R_ω (Å)	$N(E_F)$ (eV^{-1} cm^{-3})
1	0.12	0.1	1.1	5.1	4.5×10^{19}
2	0.07	1.0	1.0	8.1	5.5×10^{19}
3	0.06	1.1	1.0	8.5	1.0×10^{20}

The frequency exponent s is shown to be given by

$$s = 1 - \frac{(8R_\omega\alpha + 6r_0 W_{H0}/R_\omega kT)}{(2R_\omega\alpha + r_0 W_{H0}/R_\omega kT)^2} . \tag{9}$$

We have tried a least-squares fit for our experimental data for s in the temperature range 100–190 K using W_{H0}, r_0, and α as parameters. The theoretical curves obtained are shown in Figs. 5–7, and the values of these parameters are summarized in Table V. The number of arsenic sites participating in the OLP mode of conduction can be calculated from $kTN(E_F)$ with $T \sim 150$ K. This is found to be of the order of 10^{17} cm^{-3}, which is four orders of magnitude smaller than the total number of arsenic sites, indicating thereby that a small fraction of the latter are participating in this conduction mechanism. It should be noted, though, that the theoretical fits to experimental results are rather poor in this temperature range. However, this model predicts the correct variation of s with temperature.

In summary, we have reported that the ac resistivity of sol-gel-derived glasses in the system $x\mathrm{As_2O_3}(1-x)\mathrm{SiO_2}$ with a maximum x value of 0.154 show a sharp minimum at a temperature around 317 K. The latter arises because of a chemical reaction which involves conversion of As^{5+} ions to As^{3+} ions as a function of temperature. The ac resistivity in the range 190–300 K has been explained on the basis of a correlated-barrier-hopping model involving bipolarons. The latter are provided by the As^{3+} and As^{5+} sites. The density of states calculated from the experimental data indicates that a small fraction of the total arsenic sites participate in the conduction process and that these localized states are about 0.4 eV away from the mobility edge of the relevant band diagram. The frequency exponent s shows a maximum value of about 0.9 at around 190 K. The resistivity behavior below this temperature shows a trend which is qualitatively similar to that predicted by the overlapping-large-polaron model.

ACKNOWLEDGMENTS

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