Conductivity (ac and dc) in III-V amorphous semiconductors and chalcogenide glasses

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Variable-range hopping, as evidenced by a resistivity proportional to $\exp(T^{-1/4})$, has been induced in many III-V amorphous semiconductors (InSb, AlSb, and GaAs) and even in chalcogenide glasses (As_2Te_3, $As_2Te_{3-x}Se_x$, and GeTe) by depositing films at 77 K. It is therefore remarkable that the same procedure failed to generate variable-range hopping in GaSb, which is one of the less ionic III-V semiconductors. Besides differences in the dc conductivity, there are also different behaviors in the ac conductivity of amorphous semiconductors. The low-temperature ac conductivity of all amorphous semiconductors is proportional to $\omega^s T^n$ with $s \simeq 1$ and $n < 1$, which is consistent with a model of correlated barrier hopping of electron pairs between paired and random defects. However, in the case of a-SiO_2 and a-$GeSe_2$ one finds, in addition, that the capacitance obeys the scaling relation $C = A\ln(T\omega^{-1})$, which would suggest a conduction mechanism by tunneling relaxation. Furthermore, this scaling relation cannot be fitted to the data for a-As_2Te_3, a-InSb, and a-GaSb although the functional dependence of C on T and ω are similar.

I. INTRODUCTION

Annealed III-V amorphous semiconductors and chalcogenide glasses are characterized by an exponential dependence of the conductivity on $1/T$. The absence of variable-range hopping [i.e., conductivity proportional to $\exp(-T^{-1/4})$] has been linked,[1] in the case of the chalcogenide glasses, to the absence of neutral dangling bonds (D^0 defects). However, variable-range hopping has been induced in many amorphous semiconductors by depositing films at 77 K: a-InSb,[2] a-AlSb and a-GaAs,[3] and a-As_2Te_3,[4] a-$As_2Te_{3-x}Se_x$, and a-GeTe.[5] Such experiments were interpreted[5] by assuming that the strains created by the low-temperature deposition results in an overlap of donor and acceptor states in the III-V compounds, and to an overlap of D^+ and D^- states in the chalcogenides. On the other hand, Gheorgiu *et al.*[6] reported the absence of variable-range hopping in GaSb films annealed at 300 K. These films display instead a conductivity proportional to $\exp(-T^{-1/2})$. This observation does not necessarily contradict the results described above on other III-V semiconductors since in most cases[2,3] variable-range hopping disappears upon annealing at 300 K. It is therefore necessary to examine the conductivity of GaSb films as-deposited at 77 K before drawing any further conclusions. This will be the subject of the first part of this paper.

In the second part the ac conductivity of a-As_2Te_3, a-InSb, and a-GaSb will be examined in the light of a scaling relation recently observed[7] in a-SiO_2 and a-$GeSe_2$. The scaling relation $C = A\ln(T\omega^{-1})$ fitted the data for frequencies between 10^2 and 10^5 Hz and for temperatures ranging from 4.2 to 73 K (a-SiO_2) and 4.2 to 93 K (a-$GeSe_2$). Since the low-temperature ac conductivity of a-As_2Te_3 (Ref. 8) has essentially the same functional dependence as that of a-$GeSe_2$ (Ref. 9) and a-SiO_2 (Ref. 7) ($\sigma_{ac} \propto \omega^s T^n$ with $s \simeq 1$ and $n < 0.1$ in all cases), it would be interesting to investigate whether the scaling relation will apply to a-As_2Te_3 and to the III-V amorphous semiconductors as well.

II. EXPERIMENTAL PROCEDURE

The GaSb films were getter-sputtered from a single-crystal target at a power of 2 W (1000 V, 2 mA) onto sapphire substrates held at 77 K. The films were then transferred onto a four-point contact-resistivity holder without warming, and the dc conductivity was measured by first cooling down to 4.2 K and then warming up to above 77 K in a helium-gas atmosphere to study the annealing behavior of the films. The amorphous structure of the films and their crystallization temperature were determined by x-ray diffraction. The ac-conductivity measurements were performed in the transverse geometry by sputtering the various amorphous semiconductors [As_2Te (Ref. 4), GaSb and InSb (Ref. 2)] at 77 K between two cross leads (1000 Å thick, 0.019 cm wide) evaporated at 77 K. The lead material was Au for As_2Te_3, and GaSb and Pb for InSb. The whole deposition of the samples is performed at 77 K with a sliding mask without breaking the vacuum. The ac conductivity is then measured[8] in a manner similar to the dc conductivity using a General Radio type 1615 capacitance bridge in conjunction with a Princeton Applied Research model 124-A lock-in amplifier.

III. EXPERIMENTAL RESULTS AND DISCUSSION

A. dc conductivity

The conductivity of GaSb films as-deposited at 77 K or annealed at 300 K can be fitted (Figs. 1—3 and Table I) either by an exponential dependence on temperature,

$$\sigma = \sigma_0 \exp(-E/kT) , \tag{1}$$

or by the relation

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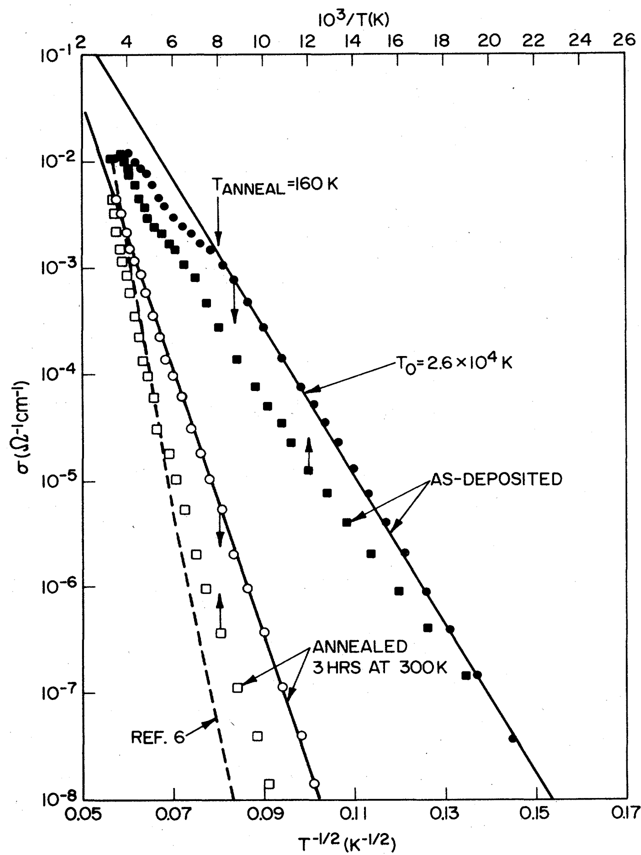

FIG. 1. Temperature dependence of the conductivity for an 8440-Å-thick GaSb film deposited at 77 K: the solid symbols pertain to the as-deposited film and the open ones to the annealed film; the circles (open and solid) refer to the $T^{-1/2}$ scale and the squares as well as the dashed line refer to the T^{-1} scale.

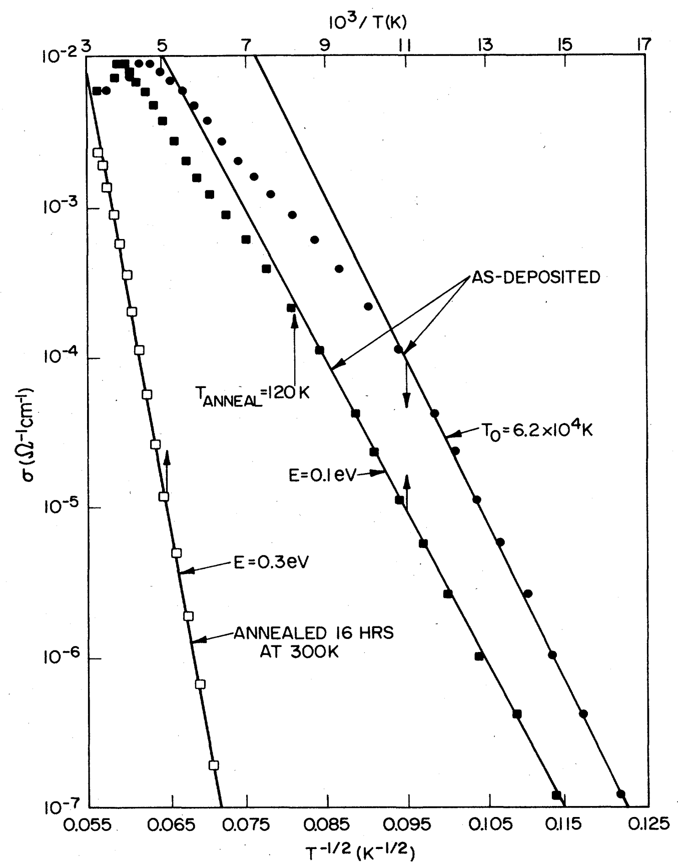

FIG. 2. Temperature dependence of the conductivity for an 8120-Å-thick GaSb film deposited at 77 K: the solid symbols pertain to the as-deposited film (circles for $T^{-1/2}$ scale and squares for T^{-1} scale) and the open squares refer to the annealed film on the T^{-1} scale.

TABLE I. dc electrical properties of *a*-GaSb films.

Sample	Thickness (μm)	Treatment	T function	T_0 (K)	E (eV)
Fig. 1	0.84	as-deposited[a]	$\exp(-T^{-1/2})$	2.6×10^4	
	0.84	annealed, 300 K	$\exp(-T^{-1/2})$	8.3×10^4	
	0.84	annealed, 300 K	$\exp(-T^{-1})$		0.22
Ref. 6		annealed, 300 K	$\exp(-T^{-1})$		0.25
Fig. 2	0.81	as-deposited	$\exp(-T^{-1/2})$	6.2×10^4	
	0.81	as-deposited	$\exp(-T^{-1})$		0.1
	0.81	annealed, 300 K	$\exp(-T^{-1})$		0.3
Fig. 3	1.00	as-deposited	$\exp(-T^{-1})$		0.08
		annealed, 440 K	$\exp(-T^{-1})$		0.31
		annealed, 530 K	$\exp(-T^{-1})$		0.31
Ref. 6		annealed, 420 K	$\exp(-T^{-1})$		0.31

[a]Meaning as-deposited at 77 K and cooled at 4.2 K.

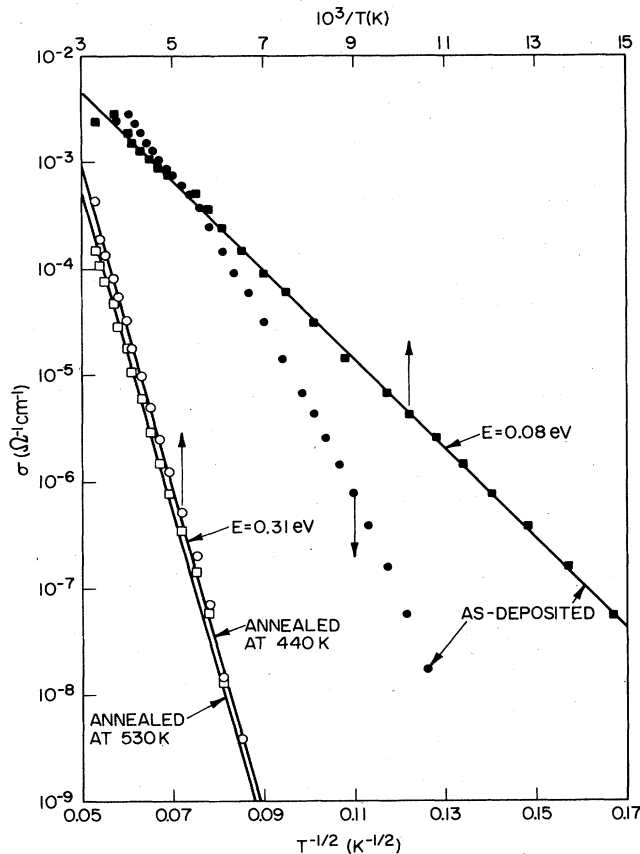

FIG. 3. Temperature dependence of the conductivity for a 1-μm-thick GaSb film deposited at 77 K: the solid symbols pertain to the as-deposited film (circles for $T^{-1/2}$ scale and squares for T^{-1} scale) and the open symbols refer to the annealed film on the T^{-1} scale.

$$\sigma = C \exp[-(T_0/T)^{1/2}] , \qquad (2)$$

which has been taken[6] to imply hopping conduction in localized states in the pseudogap away from the Fermi level, as, for example, at a band edge with a linear density of states.[10] Indeed, the as-deposited data shown in Fig. 1 are best fitted up to the annealing temperature (160 K) by relation (2) (note the upward curvature when the same data are plotted versus T^{-1}; it is also true that when the same data are plotted versus $T^{-1/4}$ one observes a downward curvature. This latter fit is not shown in Fig. 1 for the sake of clarity, and also because the $T^{-1/4}$ fit will be ruled out more convincingly in the subsequent experiments). After annealing at 300 K, in agreement with Ref. 6, the data are again best represented by relation (2) and are close to those obtained on flash-evaporated films (dashed line in Fig. 1). On the other hand, the data for a film of the same thickness ($\simeq 0.8\ \mu$m) deposited under identical conditions can be fitted as well in the as-deposited state by relation (1) or (2) (Fig. 2). Furthermore, for still another similar film (Fig. 3), the data in the as-deposited state are much better fitted by relation (1) (note the downward curvature when the same data are plotted versus $T^{-1/2}$). The last two experiments reinforce the inadequacy of a $T^{-1/4}$ fit.

It is surprising that films deposited under essentially identical conditions display different functional dependences for their conductivity. This result is not understood at present since this would require the understanding of the mechanism responsible for relation (2), which, as discussed below, cannot be firmly established. One possible reason for this irreproducibility may reside in the fact that annealed III-V compounds[2,3] and chalcogenide glasses[4,5] always fit relation (1), while deviations from relation (1) such as variable-range hopping are attributed to some type of defect.[4,5] Since, as shown by the conductivity data of Figs. 1 and 2, as-deposited films display pronounced annealing effects in the temperature range 120—160 K, it is possible that more subtle annealing effects take place just above the deposition temperature of 77 K and are responsible for the erratic functional dependence of the conductivity.

Anyhow, whether the as-deposited conductivity is proportional to $\exp(-T^{-1})$ or $\exp(-T^{-1/2})$, it was never found to be proportional to $\exp(-T^{-1/4})$, thus ruling out conduction by variable-range hopping near the Fermi level. Although one may argue that a fit to relation (2) could imply conduction by variable-range hopping at the Fermi level in a density of states which varies quadratically with energy,[11] such a possibility cannot be firmly established for the following reasons. First, besides the two mechanisms already mentioned, there are many other mechanisms which yield the functional dependence of relation (2), e.g., the correlation effects on variable-range hopping by Efros and Shklovskii,[12] and the hopping conductivity in granular materials.[13] The first theory has been criticized,[14] while the second should apply to metal particles embedded in a dielectric which is not appropriate to the present experiments. As far as hopping at a band edge with a linear density of states, or at the Fermi level into a density of states varying quadratically with energy, neither theory has been firmly established in an unambiguous experiment. At any rate, even if a fit to relation (2) implied some form of hopping, it is not always observed and is different from the variable-range hopping at E_F observed in all other III-V compounds[2,3] deposited in a similar manner [the difference is particularly striking in the case of InSb, which has a similar activation energy[2,15] (0.29 eV)]. One should also point out that this is not the first occurrence for the absence of variable-range hopping in an amorphous semiconductor deposited at 77 K, since the conductivity of a-$Cd_{0.5}Mn_{0.5}Te$ as-deposited at 77 K is well fitted[16] by relation (1). However, while this was expected in $Cd_{0.5}Mn_{0.5}Te$ because it is a large-gap (2.1 eV), strongly ionic ($f_i \simeq 0.72$ on Phillips's scale[17]) semiconductor, it is surprising for GaSb, which is one of the less ionic III-V semiconductors ($f_i = 0.261$). One would expect this low ionicity to promote disorder, especially in samples deposited at 77 K, and, indeed, such disorder-induced variable-range hopping in AlSb (Ref. 3) ($f_i = 0.256$) deposited at 77 K. It is also interesting to note that the conductivity of a-GaSb annealed overnight at 300 K (Fig. 2 and Table I) and at 440 K (Fig. 3 and

Table I) are well fitted by relation (1) with $E=0.3$ eV and σ_0, respectively, 300 and 44 Ω^{-1} cm^{-1}; these values are in good agreement with those reported[6] for $T<273$ K for flash-evaporated films annealed at 420 K ($E=0.31$ eV and $\sigma_0=90$ Ω^{-1} cm^{-1}). One slight difference between the two types of GaSb films is reflected in the crystallization temperature, which, as usual, is higher in the sputtered films (580 K) than in the evaporated films (430–470 K). The absence of variable-range hopping in GaSb films deposited at 77 K (the pertinent evidence is summarized in Table I) suggests that the type of defects created by this low-temperature deposition is different in GaSb than in other III-V semiconductors, such as InSb, AlSb, and GaAs. Interestingly, thermoelectric-power experiments[15] suggested the same: the thermopower is n type for all tetrahedrally coordinated materials, including InSb and GaAs, except for GaSb, which is p type like all chalcogenide glasses. One should stress that the absence of variable-range hopping applies only to stoichiometric GaSb films since, e.g., as-deposited a-$Ga_{0.4}Sb_{0.6}$ films are characterized[18] by a variable-range-hopping conductivity which disappears upon annealing at room temperature. This behavior is undoubtedly linked with the excess Sb since a-Sb itself displays a variable-range-hopping conductivity.[19]

B. ac conductivity

The temperature dependence of the conductivity (σ_{ac}) as a function of frequency is shown in Fig. 4 for an as-deposited and annealed a-As_2Te_3 film. The data are quite similar to those previously reported[8] and are well fitted by the relation

$$\sigma_{ac} \propto \omega^s T^n \ , \tag{3}$$

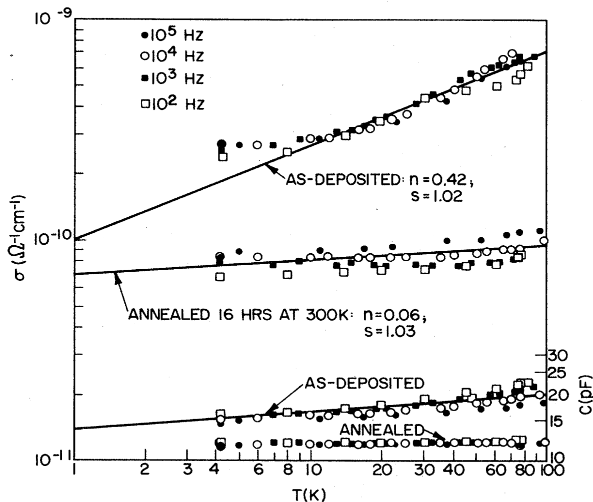

FIG. 4. Low-temperature $\sigma_{ac}(\omega)$ (two upper curves) for as-deposited and annealed As_2Te_3 film. Note that the ordinate-axis scale corresponds to 10^2 Hz only and should be multiplied by $\omega/10^2$ for the other frequencies. The bottom two curves show the corresponding variations of the capacitance.

with $s \simeq 1$. Such a relation was interpreted[8] in terms of correlated barrier hopping[20,21] (CBH) of electron pairs between both paired and random defects. The temperature dependence of the capacitance as a function of frequency is also shown in Fig. 4, where it is clear that C has a weak temperature dependence (defined as $T^{n'}$) in the as-deposited state which essentially disappears with annealing. It is also clear from Fig. 4 that the frequency dependence is more pronounced in the as-deposited state and increases with increasing temperature. The latter point is better seen in Fig. 5 which shows a double-logarithmic plot of the relation

$$C \propto \omega^{s'-1} \ . \tag{4}$$

The values of all ac parameters are listed in Table II for a-As_2Te_3 and the other amorphous semiconductors. The values of the exponent $s'-1$ for the annealed sample are quite close to those reported[7] for a-SiO_2 and annealed a-$GeSe_2$, and are therefore in disagreement with the CBH model. Briefly, restating the argument previously made[7] for a-SiO_2, since the conductance at low temperatures is proportional to ω^s, the ratio of the imaginary to real conductance is equal to $\omega^{s'-s}$, which for many models, including the CBH of bipolarons, has the form[2] $-A\ln(\omega\tau_0)$, where τ_0 is of the order of an inverse phonon frequency (10^{-12}–10^{-13} s^{-1}). This leads to the expression

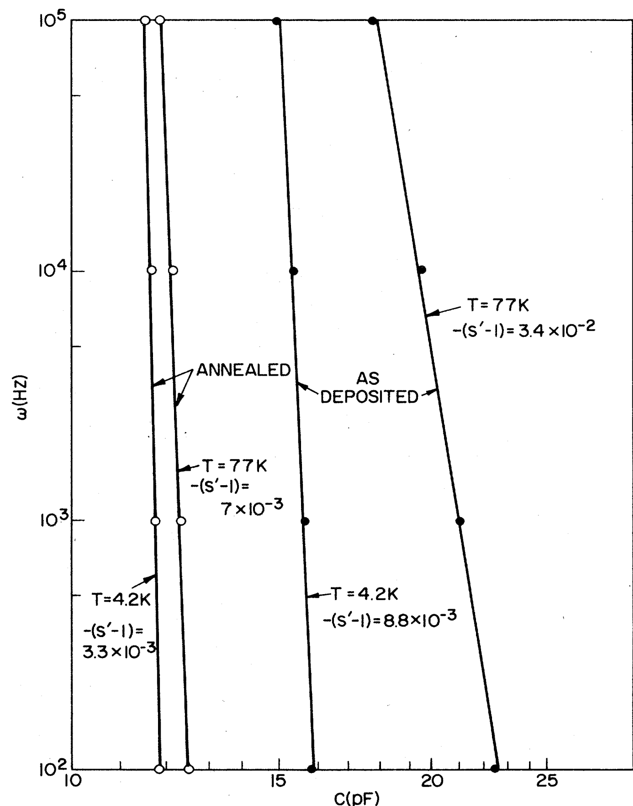

FIG. 5. Frequency dependence of the capacitance at 4.2 and 77 K for the As_2Te_3 film described in Fig. 4.

TABLE II. ac loss parameters at 4.2 K for various amorphous semiconductors.

Sample	Treatment	n	s	n'	$-(s'-1)$
As_2Te	as-deposited[a]	0.42	1.02	0.07	8.8×10^{-3}
	annealed	0.06	1.03	0.00	3.3×10^{-3}
InSb	annealed	0.11	0.98	0.05	1.3×10^{-2}
GaSb	annealed	0.15	1.00	0.01	2.3×10^{-3}
SiO_2[b]	deposited at 300 K	0.02	0.99	0.00	3.5×10^{-3}
$GeSe_2$[b]	as-deposited[a]	0.31	1.05	0.05	1.8×10^{-2}
	annealed at 533 K	0.08	0.98	0.00	2.65×10^{-3}

[a]Same meaning as in Table I.
[b]Data from Ref. 7

$$s'-s=[\ln(\omega\tau_0)]^{-1} . \quad (5)$$

For $\omega=10^4$ Hz, relation (5) gives a value of 4.8×10^{-2} for $-(s'-s)$, which is much larger than the value of 3.3×10^{-3} observed at 4.2 K for annealed As_2Te_3 (Fig. 5), assuming s to be unity. Even if one chose, for s, the superlinear value of 1.03 (Fig. 4), $-(s'-s)$ would be equal to 3.33×10^{-2}, which would require, in relation (5), the unphysical value of 10^{-17} for τ_0. In the case of a-SiO_2 and a-$GeSe_2$, this difficulty was partially answered by invoking relaxation by atomic tunneling, which leads to

$$s'-s=[\ln(\omega B/kT)]^{-1} , \quad (6)$$

where B contains details of the interaction. It is clear that relation (6) can yield, at low temperatures, the low experimental values of $s'-s$. However, such a model further implies a scaling relation for the capacitance,

$$C \propto \ln(kT/\omega B) . \quad (7)$$

This scaling relation was an excellent fit to the capacitance data for a-SiO_2 and an approximate one to that of a-$GeSe_2$. It is clear, however, from Fig. 6 that scaling relation (7) does not fit the capacitance data for annealed a-As_2Te_3 (of course, the fit is even worse for the as-

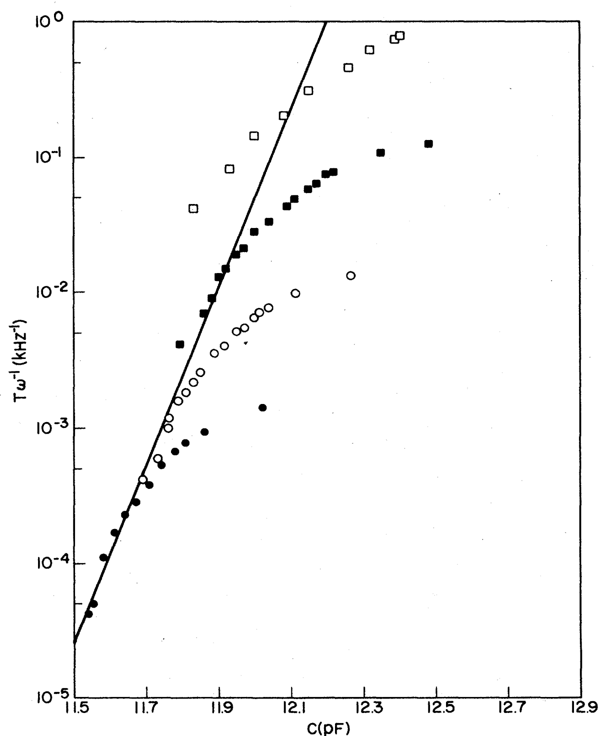

FIG. 6. Capacitance vs T/ω for the annealed As_2Te_3 film described in Figs. 4 and 5. The symbols have the same meaning as in Fig. 4. All the points should be close to the solid line for relation (7) to apply.

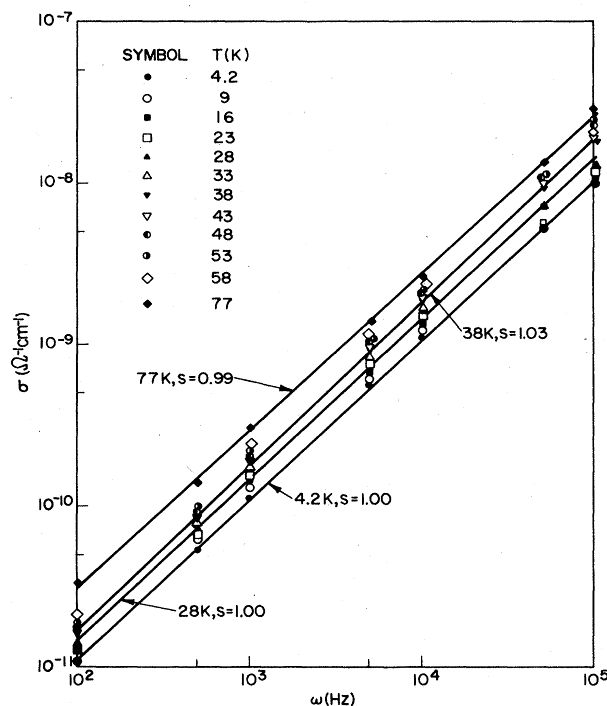

FIG. 7. Frequency dependence of the ac conductivity for an a-GaSb film deposited at 77 K and annealed in vacuo for 24 h at 300 K. The lines represent the best fit at selected temperatures.

deposited film). Consequently, although the frequency dependence of the capacitance is not explained by the CBH model [relation (5)], contrary to a-SiO_2 and a-$GeSe_2$, the relaxation model is not a likely alternate.

In the case of a-InSb, the capacitance of a film annealed overnight at 300 K is essentially temperature independent ($\propto T^{0.05}$ for $T<50$ K), but shows a pronounced frequency dependence similar to that of as-deposited a-As_2Te_3 or a-$GeSe_2$ annealed below its glass-transition temperature ($T_g=443$ K): $-(s'-1)$ decreases from 2.3 to 1.3×10^{-2} as T decreases from 77 to 4.2 K. Although variable-range hopping disappears in both InSb (Ref. 2) and As_2Te_3 (Ref. 8) films annealed at 300 K, the high value of $-(s'-1)$ in annealed InSb films would imply[7] that defects which affect ac conduction are still present. Nevertheless, assuming $s=1.00$, the value of 1.3×10^{-2} for $-(s'-1)$ is still too small to fit relation (5) (using the measured value of 0.98 for s would only worsen the fit). It is not surprising that, with such a high value of $-(s'-s)$, an attempt to fit the capacitance data for a-InSb to scaling relation (7) yields an even worse fit than that shown in Fig. 6 for a-As_2Te_3.

This study will now be completed by examining in greater detail σ_{ac} for a-GaSb, which is similar in many respects to the chalcogenide glasses. Since deviations from unity of the exponent s are important in the analysis of the frequency dependence of the capacitance, $\log_{10}\sigma_{ac}$ is plotted for GaSb versus $\log_{10}\omega$ (instead of $\log_{10}T$ as in Fig. 4 for As_2Te_3) in Fig. 7. The lines have been drawn at selected temperatures in order to display both unity fits and maximum deviations from unity, and it is clear that, for $T\leq77$ K, s is very close to 1.00. Furthermore, similar to As_2Te_3 (Fig. 4), Fig. 8 shows that for $T\leq33$ K the capacitance has a very small temperature dependence at all measured frequencies. More importantly, similar to As_2Te_3 (Fig. 5) and other chalcogenide glasses such as SiO_2 and $GeSe_2$ (Table I of Ref. 7 and Table II here for a few typical examples), Fig. 9 displays a fit to relation (4) with very similar values of the exponent $s'-1$. One is again confronted with the fact that, with $s=1.00$, relation (5)—which is based on the CBH of bipolarons—yields a value for $-(s'-s)$ which is much larger than the value observed in Fig. 9. It is particularly clear from the data shown in Fig. 7 that an attempt to reduce this discrepancy by the choice of a superlinear value for s is unreasonable. Furthermore, as previously mentioned for As_2Te_3, even the choice for s of 1.03 (unique fit at 38 K in Fig. 7) would still require an unphysical value for τ_0. In order to check whether this difficulty can be alleviated by invoking relaxation by atomic tunneling, a fit of the capacitance

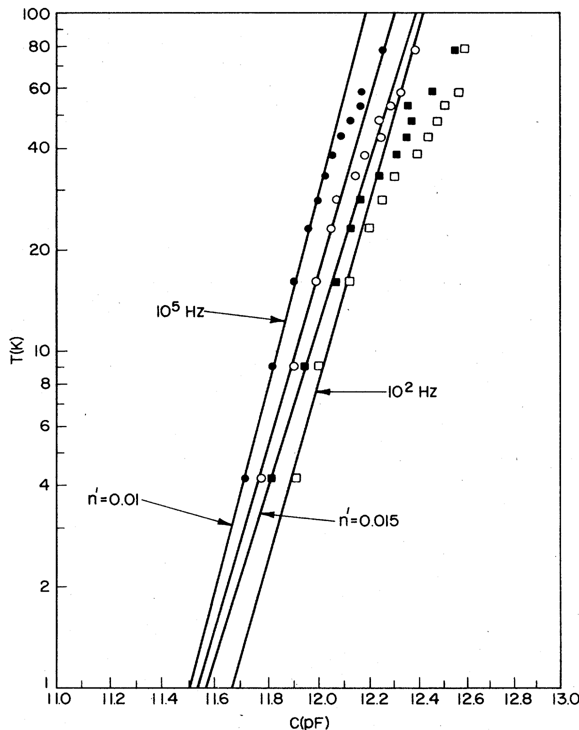

FIG. 8. Temperature dependence of the capacitance measured at 10^2, 10^3, 10^4, and 10^5 Hz on the same GaSb film described in Fig. 7.

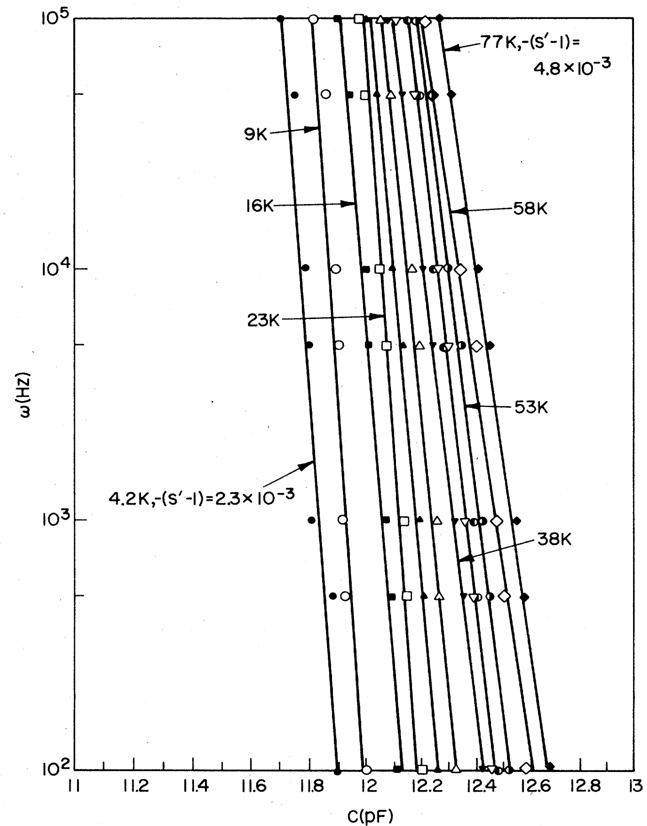

FIG. 9. Frequency dependence of the capacitance measured at temperatures ranging from 4.2 to 77 K on the same GaSb film described in Fig. 7 (the same temperature symbols were used as well).

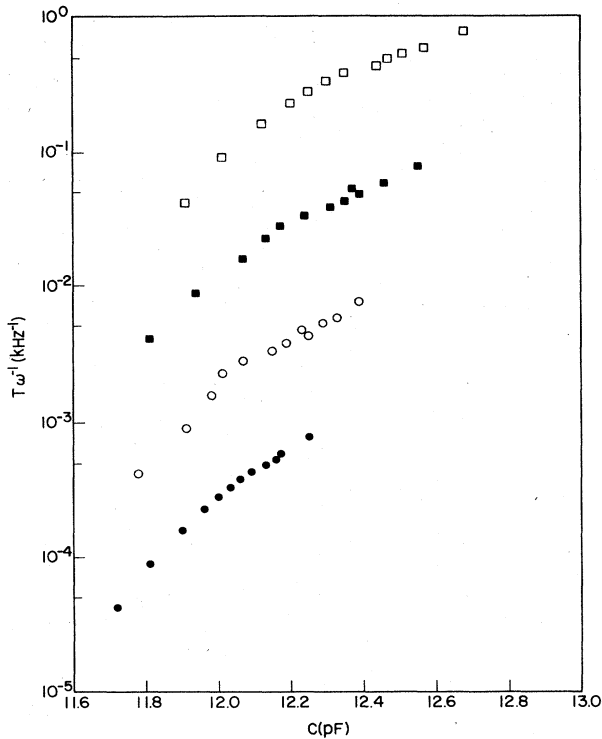

FIG. 10. Capacitance vs T/ω for the annealed GaSb film described in Fig. 7. The symbols have the same meaning as in Fig. 4.

data to the scaling relation (7) is attempted in Fig. 10. The fit to relation (7) is obviously worse than the fit for As_2Te_3 shown in Fig. 6 since the data for each frequency lie on a completely separate curve (Fig. 10). Therefore, despite the similar magnitude and functional dependence of C on T and ω for all these amorphous semiconductors, scaling relation (7) can only be fitted by the capacitance data of SiO_2 on $GeSe_2$.

IV. CONCLUSIONS

Despite the low ionicity of GaSb, it was not possible to induce variable-range hopping in GaSb films deposited at 77 K. This result, as well as the thermoelectric power, sets GaSb aside for all other III-V amorphous semiconductors. The frequency dependence of the capacitance of all amorphous III-V semiconductors and chalcogenide glasses is an order of magnitude smaller than that predicted by the CBH of bipolarons. This discrepancy can only be partially resolved in the case of a-SiO_2 and a-$GeSe_2$, where the capacitance obeys a scaling relation which implies a conduction mechanism based on relaxation by atomic tunneling.

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