Conduction in amorphous Mg_2X compounds (X = Ge and Sn)

J. J. Hauser

Bell Laboratories, Murray Hill, New Jersey 07974 (Received 6 January 1975)

Amorphous films of Mg₂Ge, Mg₂Sn, and Mg₂Ge_{1-x}Sn_x (x varying from 0 to 1) were prepared by sputtering at 77 °K. Mg₂Ge and Mg₂Sn, which are semiconductors in the crystalline state, showed semiconducting-type conduction in the amorphous state. The electrical resistivity of amorphous Mg₂Ge_{1-x}Sn_x is well fitted at low temperatures by the relation $\rho = \rho_0 \exp[(T_0/T)^{1/4}]$. The experimental value of the temperature coefficient T_0 is found to decrease exponentially with increasing x (the Sn concentration). On the other hand, T_0 was found to be inversely proportional to the impurity concentration when doping a -Sb or a -Ge with impurities forming localized impurity states. The exponential decrease in the present case is believed to be caused by the progressive decrease of the pseudogap as Mg₂Sn is substituted to Mg₂Ge.

I. INTRODUCTION

The electrical conductivity of many amorphous semiconductors can be described by a thermally activated hopping mechanism via localized states. These localized states are situated in a pseudogap which is not necessarily equal to the band gap of the crystalline semiconductor. For example, the pseudogaps estimated from the activation energies for conduction in the amorphous state are 0.58, 1.06, and 1.56 eV for InSb, ^{1,2} Ge, ¹ and Si, ¹ respectively, as compared to respective crystalline band gaps³ of 0.2, 0.8, and 1.12 eV. Even more striking is the behavior of Sb which is a semimetal in the crystalline state and a semiconductor with a 0.7-eV gap in the amorphous state.^{4,5} The change in a number of localized states at the Fermi level $[N(E_{\mathbf{F}})]$ as a result of doping with various impurities was investigated in both amorphous Ge $(a-Ge)^{6,7}$ and amorphous Sb (a-Sb).⁵ On the other hand, there has been to date no study of the dependence of the electrical conductivity on the magnitude of the pseudogap. Such a study can be best performed on a series of isostructural isoelectronic compounds differing only by their electrical band gaps. The isoelectronic requirement is essential as it has been established that isoelectronic impurities do not form localized impurity states at the Fermi level in both a-Sb (Ref. 5) and a-Ge.^{6,7} This was the reason for selecting the compounds Mg₂Ge and Mg_2Sn which are characterized in the crystalline state by energy gaps at absolute zero of 0.74 and 0.36 eV, respectively.^{8,9} The energy gaps of mixed crystals of Mg_2Ge and Mg_2Sn have also been reported.¹⁰ Furthermore, the atomic-size ratio which is 1.15 in the case of Mg₂Ge is favorable for the occurrence of the amorphous structure.¹¹

II. EXPERIMENTAL PROCEDURE

All amorphous films of the present study were getter sputtered onto sapphire substrates held at

77 °K in a vacuum system with a starting vacuum in the low- 10^{-7} -Torr range. The sputtering was performed at 2 W (1000 V, 2 mA) with an argon pressure of approximately 3×10^{-2} Torr. The sputtering targets were prepared by melting the components together in recrystallized alumina crucibles under an argon atmosphere. As a result of the relatively high melting points of the compounds (780 °C for⁹ Mg₂Sn and 1115 °C for⁸ Mg₂Ge) with respect to the boiling point of Mg (1107 °C) an appreciable amount of Mg is always lost by evaporation during melting. Stoichiometric compounds can nevertheless be obtained by ascribing the weight loss of the charge to Mg and adjusting the initial amounts of Mg and Sn (or Ge) in the charge accordingly. The targets were then polished with alundum in alcohol (water must be avoided because of the high reactivity of all these compounds even with atmospheric humidity⁸). In order to remove any surface oxide, all targets were presputtered 1 h at 4.5 W and $\frac{1}{2}$ h at 2 W prior to actual film deposition. The amorphous nature of the films was established with an x-ray diffractometer trace obtained at 77 °K. The film thickness was determined using weight gain and the bulk densities (3.09 and 3.59 $g \text{ cm}^{-3}$ for Mg₂Ge and Mg₂Sn, respectively).⁸ An interpolated value of the density was used for the mixed compounds $Mg_2Ge_{1-r}Sn_r$ which is justified by the fact that their lattice parameter varies linearly with concentration.¹⁰ As the density of most amorphous films is usually lower than $bulk^{4,5}$ by about 10%, the use of crystalline densities will tend to underestimate the film thickness. Following deposition, the films are transferred under liquid nitrogen onto the resistivity holder which is then immersed in liquid helium. The resistance of the film is then measured in helium gas by warming up to room temperature. The resistance is obtained by measuring on a Keithley 615 electrometer the current flowing as a result of a constant applied voltage

3860

TABLE I. X-ray fluorescence analysis of $Mg_2Ge_{1-x}Sn_x$ sputtering targets.

Target	Ge counts	Sn counts	Fractional Sn counts ^a
Mg ₂ Ge	36 604	•••	0
$Mg_2Ge_{0.75}Sn_{0.25}$	20 665	4 889	0.19
$\mathrm{Mg_2Ge_{0.5}Sn_{0.5}}$	10164	9600	0,48
	11 368	9 420	0.45 ^b
$Mg_2Ge_{0.4}Sn_{0.6}$	9606	10711	0.53
$\mathrm{Mg_2Ge_{0.3}Sn_{0.7}}$	6 0.88	12354	0.67
	6204	12 506	0,67 ^b
	6 384	12189	0.65 ^b
$Mg_2Ge_{0.15}Sn_{0.85}$	2 925	15174	0.84
Mg_2Sn	•••	16 471	1

^aObtained by taking the ratio of Sn counts to the total Ge and Sn counts.

^bThese various sets of data were obtained after successive sputtering of the target.

corresponding to an electric field smaller than 10^2 V/cm .

The Mg₂X tunnel junctions were prepared identically to the previously described *a*-Ge junctions.⁷ A narrow Al strip (0.019 cm wide) is evaporated from a tungsten filament and oxidized for 15 min in dry oxygen at 125 °C. The Mg₂X target was presputtered as described above, but the vacuum system was opened to air for about 3 min in order to introduce the oxidized Al strip prior to the Mg₂X deposition. The *a*-Mg₂X film was then sputtered at 77 °K without further presputtering as a small disk 0.13 cm in radius. The counterelectrode is a Pb strip (0.019 cm wide) which is evaporated at 77 °K in situ, thus defining a junction with an active cross-sectional area of 3.6×10^{-4} cm². The junctions are then measured without warming up above 77 °K. The conductance-voltage curves were obtained by hand differentiating the I-V curves. The junctions were measured by a four-probe technique which eliminates lead resistance.

III. EXPERIMENTAL RESULTS AND DISCUSSION

Since the bulk of this study is concerned with a-Mg₂Ge_{1-x}Sn_x films, it is most important to control the composition. Accordingly, the composition of the targets was checked by x-ray fluorescence analysis and the results are shown in Table I. It is clear from Table I that both Ge and Sn counts vary monotonically with the nominal compositions of the targets. Furthermore, the fractional Sn counts are in quite good agreement with the nominal Sn concentration (compare the first and last column of Table I). Since the composition of the targets is close to nominal, one can expect the composition of the films to be close to nominal as well, as it has been demonstrated several times that sputtering is a steady-state process.⁷ This point will be further established by the fact that the electrical properties of $Mg_2Ge_{1-x}Sn_x$ vary monotonically with concentration.

The amorphous nature of Mg_2Ge and Mg_2Sn films deposited at 77 °K is established by the x-ray diffractometer traces shown in Figs. 1 and 2. The annealing behavior of Mg_2Sn is however quite different from that of Mg_2Ge . As shown in Fig. 1, Mg_2Ge remains amorphous upon annealing to room temperature despite some differences in the amorphous structure as revealed by the differences in the x-ray diffractometer traces at low angles. This annealing behavior is quite similar to that of *a*-Ge films deposited at 77 °K.¹² On the other hand,



FIG. 1. X-ray diffractometer traces for an Mg_2Ge film deposited at 77 °K; the top trace was obtained at 77 °K on the as-deposited film, the bottom trace at 300 °K on the same film. The crystalline lines are indicated by arrows.



FIG. 2. X-ray diffractometer traces for an Mg₂Sn film deposited at 77 °K; the bottom trace was obtained at 77 °K on the as-deposited film, the top trace shows annealing at successively higher temperatures with the progressive appearance of the (111) line at an angle of 22.7°.

it is clear from Fig. 2 that while Mg_2Sn films deposited at 77 °K are amorphous, these films recrystallize with a (111) preferred orientation upon warming up to room temperature as shown by the progressive appearance of the (111) line at 22.7° as the temperature is raised above 183 °K.

Let us now turn our attention to the temperature dependence of the resistivity of $a-Mg_2Ge_{1-x}Sn_x$ films. It is clear from Figs. 4 and 5 that the resistivity of all these films can be fitted quite accurately at low temperatures by the relation

$$\rho = \rho_0 \exp[(T_0/T)^{1/4}], \tag{1}$$

where T_0 is given by¹³

3862

$$T_0 = 16\alpha^3 / k N(E_F),$$
 (2)

where α is the coefficient of exponential decay of localized-state wave functions and $N(E_F)$ is the density of states at the Fermi level. This temperature dependence suggests a thermally activated hopping conductivity via localized states¹⁴ similar to the one described in amorphous semiconductors.^{2,4,12} As a matter of fact the data shown for a-Mg₂Ge in Fig. 3 are very similar to those reported for *a*-Ge films.¹² The data between 30 and 110 °K are reversible and are fitted by relation (1) with values of T_0 , ρ_0 , and $N(E_F)$ (listed in Table II) very close to those for *a*-Ge.^{12,15} The films anneal at around 110 °K as shown by the deviation from the low-temperature data towards higher re-





	Film			
Sample	thickness (Å)	Т ₀ (°К)	$N(E_F)^{a}(eV cm^3)^{-1}$	$ ho_0(\Omega { m cm})$
Mg ₂ Ge No. 1	10600	5.3 $\times 10^{7}$	3.5×10^{18}	3.1×10 ⁻⁸
Mg_2Ge No. 2	25 000	5.3 $\times 10^{7}$	3.5×10^{18}	5.9×10^{-8}
$Mg_{0.66}Ge_{0.34}$ No. 1	14600	5.3×10^{7}	3.5 $\times 10^{18}$	6.2×10^{-8}
$Mg_2Ge_{0.75}Sn_{0.25}$ No. 1	4119	9.9×10^{6}	1.9×10^{19}	7.6×10^{-6}
$Mg_2Ge_{0.75}Sn_{0.25}$ No.2	3 338	1.1×10^{7}	1.7×10^{19}	6.5×10^{-6}
$Mg_2Ge_{0.75}Sn_{0.25}$ No. 3	13800	1.7×10^{7}	1.1×10^{19}	1.9×10^{-5}
$Mg_2Ge_{0.5}Sn_{0.5}$ No. 3	1842	9.2×10^{6}	2.0×10^{19}	3.3×10^{-6}
$Mg_2Ge_{0.5}Sn_{0.5}$ No. 4	3 276	8.7×10^{6}	2.1×10^{19}	1.9×10^{-6}
$Mg_2Ge_{0.5}Sn_{0.5}$ No. 5	2252	1.09×10^{7}	1.7×10^{19}	1.8×10^{-6}
$Mg_2Ge_{0.4}Sn_{0.6}$ No. 1	5715	2.8×10^{6}	6.6×10^{19}	4.7×10^{-5}
$Mg_2Ge_{0.4}Sn_{0.6}$ No. 2	6186	$1.2 imes 10^{6}$	1.5×10^{20}	8.4×10^{-4}
$Mg_2Ge_{0.4}Sn_{0.6}$ No. 3	5984	1.3×10^{6}	$1.4 imes 10^{20}$	3.3×10^{-4}
$Mg_2Ge_{0.3}Sn_{0.7}$ No. 1	4625	5.6×10^{5}	3.3×10^{20}	3.2×10^{-4}
$Mg_2Ge_{0.3}Sn_{0.7}$ No. 2	2643	9.7×10^{5}	$1.9 imes 10^{20}$	6×10^{-5}
Mg ₂ Ge _{0.3} Sn _{0.7} No. 3	2840	8.8×10^{5}	2.1×10^{20}	8.1×10 ⁻⁵
$Mg_2Ge_{0.15}Sn_{0.85}$ No. 1	3237	4.1×10^{5}	4.5 $\times 10^{20}$	4.9×10^{-4}
Mg ₂ Ge _{0.15} Sn _{0.85} No. 2	26 000	2.1×10^{5}	8.8×10^{20}	4.7×10^{-3}
Mg ₂ Ge _{0.15} Sn _{0.85} No. 3	$22\ 000$	$7.2 imes 10^5$	2.6×10^{20}	1.5×10^{-3}
Mg ₂ Sn No. 2	5255	1.4×10^{5}	1.3×10^{21}	5.6 $\times 10^{-3}$
Mg_2Sn No. 3	5890	$2.7 imes 10^{5}$	6.9×10^{20}	2.6×10^{-2}
Mg_2Sn No. 6	2342	9.6×10 ⁴	1.9×10^{21}	$2.7 imes 10^{-3}$
Mg ₂ Sn No. 8	6 500	1.3×10^{5}	1.4×10^{21}	$1.5 imes 10^{-3}$
Mg_2Sn No. 13	5 507	$1.1 imes10^5$	1.7×10^{21}	$2.9 imes 10^{-3}$
Mg ₂ Sn No. 14	3 988	1.3×10^{5}	1.4×10^{21}	1.7×10^{-3}
Mg _{0.64} Sn _{0.36} No. 1	5317	1.5×10^{5}	1.2×10^{21}	1.8×10 ⁻³
Mg _{0.70} Sn _{0.30} No. 1	4350	1.5×10^{4}	1.2×10^{22}	6.5×10^{-2}

TABLE II. Properties of Mg₂Ge_{1-x}Sn_x films.

^aCalculated from relation (2) with $\alpha = 10^7$ cm⁻¹.

sistance. After annealing at room temperature, the resistance can again be fitted by relation (1) but with a much higher value of T_0 which implies via relation (2) a lower density of localized states. This is consistent with the x-ray diffractions shown in Fig. 1 which suggest a more distorted structure at 77 °K, where atoms would be frozen in during deposition thus resulting in a greater density of localized states.

The properties of Mg₂Sn films shown in Fig. 4 and Table II are quite different. Although the data can be fitted between 6 and 77 $^{\circ}$ K by relation (1) the value of T_0 is approximately three orders of magnitude smaller than for Mg₂Ge, i.e., the density of localized states is about three orders of magnitude larger if one assumes that α remains unchanged which as we shall discuss below is quite unlikely. In agreement with the x-ray diffraction shown in Fig. 2, the annealing behavior of the resistance of Mg₂Sn is quite different from that of Mg₂Ge. Mg₂Sn films (and Mg₂Ge_{1-x}Sn_x films rich in Sn as well) anneal shortly above the deposition temperature of 77 °K.¹⁶ This anneal is accompanied by a deviation from the low-temperature data towards lower resistance which results from the progressive recrystallization of the film. After annealing at room temperature, the resistance of the film can no longer be fitted by relation (1).

The temperature dependence of the resistance for a few selected Mg₂Ge_{1-r}Sn_r films is plotted in Fig. 4. It is clear from Fig. 4 that the data for all these films can be adequately represented by relation (1). These data can be summarized by plotting the values of T_0 as a function of composition (Fig. 5); the actual experimental values of T_0 are listed in Table II. The variation of T_0 with concentration is not as monotonic as implied by Fig. 4; as shown in Fig. 5 some scatter does exist as exemplified by the slight overlap of certain neighboring compositions. There is no obvious explanation for the deviation shown by the $Mg_2Ge_{0.5}Sn_{0.5}$ data since the x-ray fluorescence analysis for the corresponding target seems well behaved (Table I). The explanation may be related to the miscibility gap which exists for the bulk material in this composition range.¹⁰ Indeed, while the lattice parameter varies linearly with concentration for x < 0.2 and x > 0.6, the x-ray lines are broadened and split up^{10} for 0, 2 < x < 0, 6. Nevertheless, two conclusions can be drawn from the data shown in Fig. 5. First. as stated above the composition of the films must be fairly close to the nominal composition of the targets, the lat-



FIG. 4. Temperature dependence of the resistance for $Mg_2Ge_{1-x}Sn_x$ films (x varying from 0 to 1) deposited at 77 °K.

ter being rather well confirmed by the x-rayfluorescence analysis of Table I. Second, T_0 decreases exponentially with increasing Sn concentration.

One may at this point worry about the influence of stoichiometry on the data shown in Figs. 4 and 5. As shown in Table II by Mg_{0.66}Ge_{0.34} and $Mg_{0.64}Sn_{0.36}$ it is clear that the value of T_0 is unaffected by off-stoichiometry on the Ge- or Sn-rich side. On the other hand, off-stoichiometry on the Mg-rich side leads as shown by Mg_{0.70}Sn_{0.30} to a reduction in T_0 by about an order of magnitude. These off-stoichiometries were attained by deliberately adding the requisite amounts of Ge, Sn, or Mg. However, as discussed in the experimental procedure, the natural off-stoichiometry for these compounds is a deficiency of Mg as a result of the heavy Mg evaporation during melting. One can therefore rest assured that the data presented in Fig. 5 are totally unaffected by a possible small off-stoichiometry.

The exponential decrease of T_0 with increasing Sn concentration (Fig. 5) cannot be explained by the introduction of localized states as a result of substituting Sn for Ge in Mg₂Ge for the following two reasons. First, T_0 was found to be inversely

proportional to the impurity concentration when doping a-Sb or a-Ge with impurities forming localized impurity states.⁵⁻⁷ Second, it was established that isoelectronic impurities do not produce localized impurity states. $^{5-7}$ This point is further confirmed by the present self-doping experiments $(Mg_{0.66}Ge_{0.34} \text{ and } Mg_{0.64}Sn_{0.36} \text{ in Table II})$. In other words, one may not conclude that the exponential decrease in T_0 with x will result via relation (2) and a fixed value of α ($\simeq 10^7$ cm⁻¹) in an exponential increase of $N(E_F)$ with x. We will now proceed to show that while a formulation in terms of $N(E_F)$ is quite valid for Mg₂Ge, it becomes increasingly poorer as one approaches Mg₂Sn. Although the gap in Mg₂Ge is only known with certainty in the crystalline state^{8,9} (0.74 eV), the tunneling experiments to be discussed below suggest that the pseudogap in the amorphous state has approximately the same value. Consequently, a value of $\alpha \simeq 10^7$ cm⁻¹ seems quite appropriate for *a*-Mg₂Ge especially in view of the fact that this value of α leads to less than a factor-of-5 variation in $N(E_F)$ for *a*-semiconductors with pseudogaps ranging¹ from 0.6 to 1.6 eV.¹⁷ This value of $\alpha ~(\simeq 10^7 \text{ cm}^{-1})$ corresponds via relation (2) to 3.5×10^{18} states $(eV cm^3)^{-1}$ for Mg₂Ge. The values of these parameters satisfy the consistency requirement for the assumption of localized states to be valid¹³:

$$T_0 > 200 U/k, \tag{3}$$



FIG. 5. Dependence of the temperature coefficient T_0 on Sn concentration (x) for Mg₂Ge_{1-x}Sn_x films.



FIG. 6. Tunneling conductance as a function of bias voltage at 77 °K for Al-Mg₂Ge_{1-x}Sn_x-Pb junctions and one Al-Sb-Pb junction all deposited at 77 °K. The Sb and Mg₂Ge_{1-x}Sn_x films are approximately 3000 Å thick. The Al-Sb-Pb junction is the junction Al-Sb-Pb No. 1 shown in Fig. 8 of Ref. 5 where the conductance was divided by 10 to allow easier comparison with other curves.

where U is an energy of the order of the binding energy of a trap ($\simeq 0.3$ eV for a large pseudogap a-semiconductor such as a-Ge). The right-hand side of (3) is of order 10^6 °K and the inequality is well satisfied by a-Mg₂Ge ($T_0 = 5.3 \times 10^7$ °K). On the other hand, the inequality (3) is barely satisfied for Mg₂Sn even if one uses a smaller binding energy $(U \simeq 0.1 \text{ eV})$ which may be more appropriate for the smaller energy gap; the right-hand side of (3) is equal to 2×10^5 °K which is about the value of T_0 (Table II). Consequently, some delocalization is certainly present in Mg₂Sn and it is unrealistic to calculate $N(E_F)$ from relation (2) with a fixed value of $\alpha(10^7 \text{ cm})$ as was done in Table II. One may not rule out that Mg₂Sn may possess intrinsically a greater number of localized states than Mg₂Ge, but as discussed above for the large-gap semiconductors¹⁷ this is not expected to contribute more than a factor of 5 in $N(E_F)$ which is insufficient to explain the three orders of magnitude change in $N(E_F)$ shown in Table II. The most likely explanation for the decrease in T_0 as one proceeds from Mg₂Ge to Mg₂Sn is therefore a progressive increase in α^{-1} as a result of the closing of the pseudogap, until finally in Mg₂Sn the localized

states become delocalized into extended states. This may be stated more precisely by substituting relation (2) into (3) which results in the consistency relation

3865

$$12.5N(E_F)U < \alpha^3. \tag{4}$$

Therefore, using $U \simeq 0.1$ eV and $N(E_F) = 3.5 \times 10^{18}$ states (eV cm³)⁻¹ in relation (4) one concludes that the states can remain localized if $\alpha^{-1} < 60$ Å. An increase of α^{-1} from 10 to 60 Å is sufficient to explain the observed decrease in T_0 with increasing Sn concentration.

In retrospect, this explanation may be pertinent to some previous experiments. In doping a-Ge films with impurities forming localized impurity states, ⁷ it was found that while $N(E_F)$ increases linearly with concentration below the localization limit, it increases exponentially in the vicinity of the limit. The tunneling experiments suggested that close to the localization limit, the pseudogap was reduced to about half the value for undoped a-Ge. Possibly more related to the present study are experiments with a-Sb films doped with Bi.⁵ Although Bi does not form localized impurity states in a-Sb, T_0 was found to decrease exponentially with increasing Bi content up to 30 at. %. The pseudogap is expected to decrease from its value for pure a-Sb (0.7 eV) to zero in this concentration range since a-Sb films with 30-at. % Bi are metallic and even superconducting.

The energy-gap values for Mg₂Ge_{1-x}Sn_x compounds have been previously reported.¹⁰ It would be helpful for the present discussion to estimate the actual values of the pseudogaps in the a-Mg₂Ge_{1-x}Sn_x films. We shall attempt to do this with tunneling experiments. Tunneling experiments with *a*-semiconductor films deposited at 77 $^{\circ}$ K are usually obscured by the fact that the tunneling density of localized states is higher than the density of localized states estimated from resistivity measurements.⁷ This was explained⁷ by the fact that tunneling only probes the surface layer which conceivably contains more localized states (e.g., more dangling bonds). This out-of-equilibrium surface layer which only differs by the number of localized states in the cases of a-Si and a-Ge, ⁷ could also be nonstoichiometric in the present case of the deposition of a compound. Keeping these restrictions in mind, the voltage dependence of the tunneling conductance for a-Mg₂Ge_{1-x}Sn_x junctions is shown in Fig. 6. The concentration range studied in Fig. 6 is limited to $0 \le x \le 0.7$ as it was impossible for some unknown reason to obtain good tunnel junctions with higher Sn content. Since the tunneling-conductance-versus-voltage curves are nearly symmetric with respect to zero bias, we only show the positive-bias side of the curve (Al negative). The voltage drop across the

3866

 $a - Mg_2Ge_{1-x}Sn_x$ films was less than 5% of the total bias. The various Mg₂Ge_{1-x}Sn_x junctions are compared in Fig. 6 with a previously studied a-Sb tunnel junction.⁵ The analysis of the a-Sb junction^{5,7} led to the conclusion that the voltage dependence of the conductance was consistent with a 0.7-eV pseudogap. The similarity between $a - Mg_2 Ge_{1-x} Sn_x$ junctions and the a-Sb junction suggests that the pseudogaps for $a - Mg_2Ge_{1-r}Sn_r$ with $0 \le x \le 0.7$ are approximately 0.7 eV. These data would therefore suggest that the pseudogap for Mg_2Ge is 0.7 eV in good agreement with the crystalline energy gap.^{8,9} However, Fig. 6 also suggests that this pseudogap remains essentially unchanged for Sn concentrations as high as 0.7 which contradicts the crystalline energy-gap results.¹⁰ This contradiction is actually not as severe as one may think as the crystalline energy gap of Mg₂Ge is only decreased¹⁰ by 11% for x = 0.5 and by 21% for x = 0.7. The discrepancy between crystalline energy gap and tunneling amorphous pseudogap could be the result of a non-steady-state deposition of the first few layers of $\mathrm{Mg}_2\mathrm{Ge}_{1-x}\mathrm{Sn}_x$ which would result in an initially higher Ge concentration. The validity of this speculation is supported by the fact that the tunneling value of T_0 for all Mg₂Ge_{1-x}Sn_x junctions is different from the value of T_0 obtained

from resistivity measurements. Although it was pointed out in the introduction that there is not a one to one correspondence between amorphous pseudogaps and crystalline band gaps amongst various semiconductors, there is a relationship between these quantities for semiconductors of the same type. For example, the ratio of the pseudogaps¹ for a-Si and a-Ge (1.47) is approximately equal to the ratio of the crystalline band gaps³ (1.40). Although it is still true for GaSb and GaAs with a ratio of 1.79 for both the amorphous¹ and crystalline³ states, it is not true for the III-V compounds in general. Nevertheless, a decreasing crystalline band gap corresponds in III-V compounds to a decreasing amorphous pseudogap. Consequently, despite the shortcomings of the tunneling results, it is quite reasonable to expect, based on the crystalline band-gap measurements¹⁰, that the pseudogap of a-Mg₂Sn is smaller than that of a-Mg₂Ge.

IV. CONCLUSIONS

The resistivity of a-Mg₂Ge_{1-x}Sn_x films depends exponentially on $T^{-1/4}$ suggesting a thermally activated hopping conductivity via localized states. The temperature exponent T_0 decreases exponentially with increasing Sn concentration. Tunneling experiments suggest that a-Mg₂Ge has a pseudogap of 0.7 eV close in value to the crystalline band gap. This fact, in conjunction with the crystalline band-gap measurements, suggests that the pseudogap of a-Mg₂Ge_{1-x}Sn_x films decreases with increasing Sn content. The exponential decreases of T_0 with increasing Sn concentration can therefore best be explained by a progressive delocalization (increasing α^{-1}) as a result of the decreasing pseudogap.

ACKNOWLEDGMENT

I would like to thank C. M. Antosh for his able technical assistance in obtaining the data.

- ¹J. Stuke, Proceedings of the Tenth International Conference on the Physics of Semiconductors, Cambridge, Massachusetts, 1970, edited by S. P. Keller, J. C. Hensel, and F. Stern (U. S. Energy Commission, Washington, D. C., 1971), p. 14.
- ²J. J. Hauser, Phys. Rev. B 8, 2678 (1973).
- ³S. M. Sze, *Physics of Semiconductor Devices* (Wiley, New York, 1969).
- ⁴J. J. Hauser, Phys. Rev. B 9, 2693 (1974).
- ⁵J. J. Hauser, Phys. Rev. B <u>11</u>, 738 (1975).
- ⁶J. J. Hauser, Solid State Commun. <u>13</u>, 1451 (1973).
- ⁷J. J. Hauser, Phys. Rev. B 9, 2544 (1974).
- ⁸U. Winkler, Helv. Phys. Acta 28, 633 (1955).
- ⁹R. F. Blunt, H. P. R. Frederikse, and W. R. Holser, Phys. Rev. <u>100</u>, 663 (1955).
- ¹⁰G. Busch and U. Winkler, Helv. Phys. Acta <u>26</u>, 578 (1953).
- ¹¹S. Mader, J. Vac. Sci. Technol. 2, 35 (1965).
- ¹²J. J. Hauser, Phys. Rev. B 8, 607 (1973).

- ¹³V. Ambegaokar, B. I. Halperin, and J. S. Langer, Phys. Rev. B 4, 2612 (1972).
- ¹⁴N. F. Mott, Philos. Mag. 19, 835 (1969).
- ¹⁵P. A. Walley and A. K. Jonscher, Thin Solid Films <u>1</u>, 367 (1968).
- ¹⁶The difference between apparent recrystallization temperatures as measured by x rays (190 °K) and by resistance (80 °K) can be explained by two factors: (i) the rate of heating was approximately four times as fast for x-ray measurements than for resistance measurements, (ii) resistance measurements are more sensitive to small amounts of crystalline phase than x-ray measurements.
- ¹⁷The values of $N(E_F)$ using $\alpha = 10^7$ cm⁻¹ in relation (2) are are 2×10^{18} , 4×10^{18} , 10^{19} , and 10^{19} states (eV cm³)⁻¹, respectively, for *a*-Ge (Ref. 7), *a*-Si [J. J. Hauser, Phys. Rev. B <u>8</u>, 3817 (1973)], *a*-InSb (Ref. 2), and *a*-Sb (Refs. 4 and 5).