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Hopping conductivity in amorphous antimony

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Amorphous Sb films ranging in thickness between 170 and 14 000 Å were prepared at 77 °K in three different ways: getter sputtering, evaporation from Sb, and evaporation from PtSb. The electrical resistivity of these various films is well fitted between 30 and 160 °K by the relation $\rho=\rho_0 \exp[(T_0/T)^{1/4}]$ with $T_0 \simeq 10^7$ °K.

Suhrmann and Berndt[1] reported that Sb films, ranging in thickness between 35 and 325 μm, deposited at 77 °K were amorphous and displayed a negative temperature coefficient of resistance between 77 and 270 °K. Above 270 °K these films transformed irreversibly to the crystalline form of Sb as evidenced by a sharp decrease of the resistance by about three orders of magnitude. Sommer[2] reported different properties in 70-Å amorphous Sb films evaporated at room temperatures from pure Sb or from a PtSb alloy. The different properties were ascribed to the fact that Sb evaporated as Sb_4 from elementary Sb and predominantly as monoatomic Sb_1 from PtSb. Raman-spectra experiments[3] on thick Sb films (500–1000 Å) deposited at 77 °K also reported a different Raman spectrum for films evaporated from Sb and for films evaporated from PtSb. It would therefore be of interest to study the temperature dependence of the resistivity for amorphous Sb and compare it with other amorphous materials. Furthermore, one should also study whether different methods of preparation of amorphous Sb films will result in similar or dissimilar electrical properties.

The amorphous Sb films were always deposited at 77 °K on sapphire substrates in a vacuum system with a starting vacuum in the low 10^{-7}-Torr range. Three different methods were used to deposit the films. Films ranging in thickness between 170 and 14 000 Å were getter sputtered[4] from an arc-melted Sb target at a rate of 170 Å/min. The sputtering was performed at 2 W (1000 V, 2 mA) with an argon pressure of 1.5×10^{-2} Torr. Films ranging in thickness between 860 and 4150 Å were flash evaporated at rates varying between 60 and 400 Å/sec. These films were evaporated from either Sb or PtSb beads heated in a tungsten filament at about 1000 °C. Following deposition the film is transferred under liquid nitrogen onto the resistance holder, which is then immersed in liquid helium. The resistance of the film is then measured in helium gas at atmospheric pressure by warming up to room temperature. The resistance is measured by a four-probe technique with electric fields smaller than 10^2 V/cm. 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 density of Sb (6.62 g cm^{-3}). As the density of most amorphous films is usually lower than bulk[5] by about 10%, the previous assumption will tend to underestimate the film thickness.

The most striking result of the present study is that the low-temperature resistivity of all amorphous Sb films regardless of the method of deposition can be fitted quite accurately by the relation

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

where T_0 [given by $16\alpha^3/N(E_F)k]^6$ is approximately 10^7 °K, α is the coefficient of exponential decay of localized states, $N(E_F)$ is the density of localized states at the Fermi level, and k is Boltzman's constant. This temperature dependence suggests a thermally activated hopping conductivity via localized states[7] similar to the one described in amorphous semiconductors [Ge (Refs. 8 and 9) and Si (Refs. 10 and 9)]. The theoretical calculation of the prefactor ρ_0 is on much less solid ground than that of T_0. Mott's model[7] establishes the following relation:

$$\rho_0=[T\alpha/N(E_F)]^{1/2}, \tag{2}$$

which predicts theoretical values many orders of magnitude larger than the experimental values observed in Ge,[8,9] and in Si.[9,11] Recently, Brenig *et al.*[12] have derived the following different expression for the prefactor which is in good agreement with the Ge data[8,9]:

$$\rho_0=[256\alpha^2/9e^2N(E_F)\gamma_0](T/T_0)^{3/4}, \tag{3}$$

where $\gamma_0 \simeq 4\times10^{19}$ sec^{-1}. On the other hand, although Lewis[13,14] mistakenly reported good agreement between Mott's expression [relation (2)] and the experimental prefactors for annealed amorphous Si films, Paul and Mitra[15] have shown that annealed Ge, Si, and Ge-Si films display parameters approaching those given by Mott's theory.[7]

It is clear from Fig. 1 that the data are well fitted by relation (1). In the case of the sputtered films (solid symbols) the $T^{-1/4}$ dependence is well

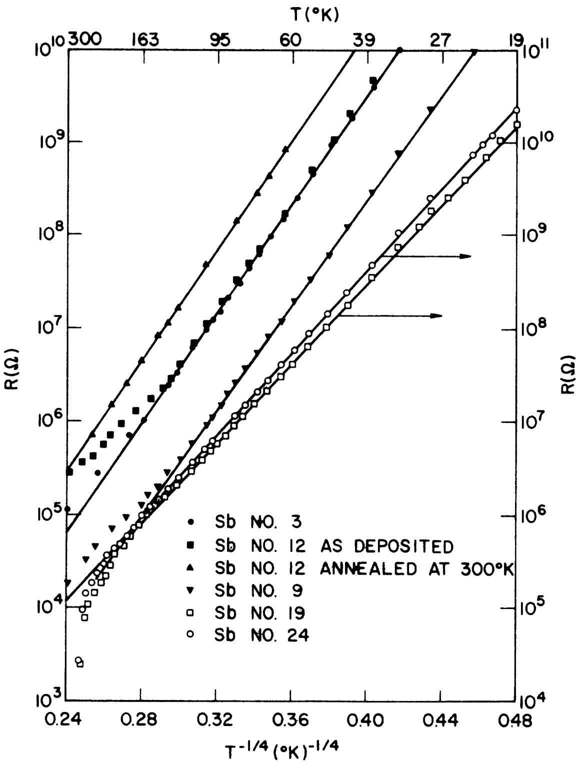

Fig. 1. Temperature dependence of the resistance for sputtered Sb films (solid symbols) and evaporated Sb films (open symbols); note that the data for evaporated films are plotted against the right ordinate axis. Sb No. 19 was evaporated from pure Sb while Sb No. 24 from PtSb.

obeyed up to about 160 °K (lower temperatures for thinner films) where the films anneal as shown by the deviation from the low-temperature data towards higher resistance. The resistance versus temperature curves are completely reversible between 30 and 160 °K. Above 160 °K one observes an irreversible increase in resistance which results in the deviation from Mott's law [relation (1)]. However, as we shall further discuss below, even a sample fully annealed at room temperature with a resulting fivefold irreversible increase in resistance (see Sb No. 12 in Table I) still satisfies Mott's law upon cooling (see Sb No. 12 in Fig. 1). Despite the anneal, the sputtered films remain amorphous up to 300 °K as shown by x-ray diffractions; recrystallization can be achieved by annealing at 40 °C and leads, in agreement with previous experiments,[1,2] to a large decrease in resistance. As shown in Fig. 1 (by Sb No. 12) and in Table I annealing leaves T_0 (and therefore the density of localized states) essentially unchanged. The increase in resistance is almost accounted for by a corresponding increase in the prefactor. Although the reasons for this effect are not clear, it may be caused by microcracks which are almost always visible under the microscope in annealed films; in certain films the microcracks become connected in such a way that the conductivity can no longer be measured. The microcracks are never visible under the microscope at 77 °K in films deposited at 77 °K; this observation coupled with the reversibility of the resistance data between 160 and 30 °K suggests that the microcracks develop in the films as a result of annealing above 160 °K. The annealing effects observed could also result from a redistribution of the Ar normally trapped in a low-temperature sputtered film. The electrical properties of all sputtered films irrespective of thickness are very similar (Table I): T_0 varies between 1.2×10^7 °K and 2.4×10^7 °K while the resistivity at 77 and 300 °K is, respectively, a few hundred Ω cm and 1 Ω cm. The scatter in the prefactor ρ_0 is much larger: ρ_0 varies from 5×10^{-9} to 1.2×10^{-6} Ω cm, the larger values being observed in the annealed films. These experimental values of ρ_0 can be compared with the following theoretical estimates: ρ_0 varies between 4.7×10^{-6} and 6.5×10^{-6} Ω cm for Mott's model[7] and between 1.4×10^{-9} and 1.6×10^{-9} Ω cm for the Brenig *et al.*[12] model as T_0 increases from 1.2×10^7 to 2.4×10^7 °K. Consequently, most experimental values of ρ_0 fall between the theoretical estimates, with the values for the annealed films approaching Mott's predictions. Although the last observation seems to support Paul's and Mitra's results on annealed Ge, Si, and Ge-Si films,[15] the trend may be observed here for just the opposite reason. Indeed, while annealed Si films[13] were supposed to be void-free, most annealed Sb films contain microcracks. Consequently, as suggested above, ρ_0 may reflect to a much greater extent than T_0 the defect structure of the films.

Let us now turn our attention to evaporated amorphous Sb films. The temperature dependence of the resistance is again well represented by relation (1) and as shown in Fig. 1, this is true whether the Sb film is evaporated from pure Sb (Sb No. 19) or from PtSb (Sb No. 24). On the other hand, the annealing behavior of the evaporated films is drastically different from that of the sputtered films. While sputtered films increased in resistance at about 160 °K and remained amorphous at room temperature, the resistance of evaporated films starts to decrease around 180 °K and decreased sharply at 270 °K as a result of the recrystallization of the film which is complete at room temperature. Although Sommer[2] reported that the resistance of a 70-Å film evaporated from PtSb decreases from 10^8 to 10^3 Ω, whereas the resistance of a 70-Å film evaporated from pure Sb remains unchanged at 10^8 Ω, the change in resistance upon annealing for the two types of film seems identical when the films

TABLE I. Properties of Sb films.

Sample	Film thickness (Å)	Deposition method	T_0(°K)	ρ_0(Ω cm)	ρ_{RT} (Ωcm)	$\rho_{77\,°K}$ (Ω cm)
Sb No. 4	14 900	Sputtering	1.8×10^7	6.9×10^{-8}	...	245
Sb No. 16[a]	10 950	Sputtering	1.2×10^7	1.2×10^{-6}	1.1	515
Sb No. 6	8900	Sputtering	1.3×10^7	2.1×10^{-7}	...	134
Sb No. 2	6300	Sputtering	1.6×10^7	2×10^{-7}	1.3	380
Sb No. 10	5390	Sputtering	2×10^7	5.9×10^{-8}	0.8	377
Sb No. 10	5390	Annealed at 300 °K	1.6×10^7	3.2×10^{-7}	0.8	606
Sb No. 9	5220	Sputtering	1.8×10^7	4.4×10^{-8}	0.25	157
Sb No. 3	5000	Sputtering	2×10^7	8.8×10^{-8}	1.5	562
Sb No. 7	2400	Sputtering	2×10^7	5.6×10^{-8}	0.75	360
Sb No. 8	2160	Sputtering	2×10^7	2.3×10^{-8}	0.8	151
Sb No. 11	1720	Sputtering	2.4×10^7	7.8×10^{-9}	0.9	142
Sb No. 12	870	Sputtering	2.4×10^7	8.9×10^{-9}	0.6	163
Sb No. 12	870	Annealed at 300 °K	2.2×10^7	4×10^{-8}	0.6	435
Sb No. 13	520	Sputtering	2.5×10^7	5.1×10^{-9}	...	120
Sb No. 14	170	Sputtering	2.2×10^7	1.1×10^{-8}	...	94
Sb No. 17	4150	Sb evaporation	7.1×10^6	2.4×10^{-6}	10^{-2}	89
Sb No. 24	1300	PtSb evaporation	1.9×10^6	1.9×10^{-6}	8×10^{-4}	49
Sb No. 25	1200	PtSb evaporation	7.5×10^6	2.4×10^{-6}	5×10^{-4}	112
Sb No. 20	1065	Sb evaporation	7.5×10^6	4.2×10^{-7}	...	20
Sb No. 19	930	Sb evaporation	6×10^6	1.3×10^{-6}	10^{-4}	23
Sb No. 23	860	Sb evaporation	6.7×10^6	9×10^{-7}	...	26
SB[b]	350 000	Sb evaporation	6.5×10^5	4×10^{-4}	10^{-2}	6

[a] Film annealed 1 h at 300 °K before measurement.

[b] Data of Suhrmann and Berndt (Ref. 1).

are about 1000 Å thick (see Table I and Fig. 1). One is therefore led to conclude that the differences reported by Sommer[2] only apply to ultrathin films deposited at room temperature. It is also clear from Table I that the properties of all evaporated films are quite similar and distinct from sputtered films. Namely, T_0 varies between 6×10^6 and 7.5×10^6 °K which is lower than the lowest value of 1.2×10^7 °K found in sputtered films. The same qualitative difference between evaporated and sputtered films was reported for amorphous Ge,[9] and was ascribed to the smaller particle size present in sputtered films. The resistivity at 77 °K of the evaporated films is a few ten-ohm-centimeters as compared to a few hundred-ohm-centimeters for the sputtered films, while the room-temperature resistivity of the evaporated films is only a fraction of an ohm centimeter as a result of the recrystallization. Although the Raman spectra for amorphous Sb films evaporated from PtSb and from pure Sb onto substrates kept at 77 °K were quite different,[3] it is obvious from Table I that the electrical properties of the two types of film are undistinguishable. Consequently, the difference between Sb evaporating as Sb_1 or Sb_4 may be important to the electrical properties of very thin films[2] or to the Raman spectrum of thicker films,[3] but it is immaterial to the electrical properties of thicker films. Finally, the experimental prefactor values for evaporated films range between 4×10^{-7} and 2.4×10^{-6} Ω cm which is larger, in general, than the values observed for sputtered films and is therefore closer to the theoretical value predicted by Mott[7]: $\rho_0(\text{Mott}) = (3.3 \text{ to } 3.6)\times10^{-6}$ Ω cm as T_0 varies between 6×10^6 and 7.5×10^6 °K. Consequently, the prefactor ρ_0 can agree with Mott's theoretical value even for unannealed films and the safest conclusion that one can draw from this and previous studies[11,13] is that ρ_0 is strongly structure sensitive. Thus, agreement or disagreement of ρ_0 with theoretical predictions may not be too meaningful unless the detailed defect structure of the amorphous film is fully understood.

The limited data of Suhrmann and Berndt[1] can be fitted approximately by relation (1). The resulting parameters T_0 and $\rho_{77\,°K}$ are much lower than the corresponding values for thinner films (Table I). As it is generally more difficult to make a fully amorphous thick film than a fully amorphous thin film,[3,14] it is likely that the low values of T_0 and $\rho_{77\,°K}$ are the result of microcrystallization. As these parameters are also generally lower for evaporated films than for sputtered films (Table I), this may indicate that evaporated films have a greater extent of short-range order than sputtered films or may even contain microcrystals. This would also be consistent with the fact that the evaporated films recrystallize much more easily than the sputtered films. In conclusion, the conductivity mechanism in amorphous Sb films regardless of the method of deposition is well described by thermally activated hopping via localized states. The exponent T_0 of the $T^{-1/4}$ temperature dependence of the conductivity is approximately 10^7 °K which corresponds to 10^{19} states/eV cm^3. These parameters as well as the exponential prefactor ρ_0 have approximately the same order of magnitude as those reported for amorphous semiconductors.[8-11,16]

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