square-well model of the impurity potential, and by Alfred and van Ostenburg,[18] based on an interpretation of NMR data.

We have shown how impurity-scattering phase shifts of dilute alloys can be determined from Dingle-temperature data by taking into account the renormalization of the wave function on the impurity site due to backscattering by the host lattice. Our results represent a consistent microscopic interpretation of the Dingle-temperature anisotropies of the dilute silver alloys Ag(Au) and Ag(Sn) taking proper account of the band structure of the host. The derived impurity phase shifts satisfy the optical theorem and the Friedel sum rule, and are consistent with a single set of backscattering coefficients for the silver lattice. We have assumed that off-diagonal elements of the scattering matrix are negligible, and have taken the diagonal elements to be as weak as possible consistent with the data. An investigation of these assumptions from first principles will be the subject of further work.

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[1]M. Springford, Advan. Phys. 20, 493 (1971).

[2]P. T. Coleridge, J. Phys. F: Metal Phys. 2, 1016 (1972).

[3]G. J. Morgan, Proc. Phys. Soc., London 89, 365 (1966).

[4]M. J. G. Lee, Phys. Rev. 187, 901 (1969), and Phys. Rev. Lett. 26, 501 (1971).

[5]P. T. Coleridge, Phys. Rev. B 7, 3508 (1973).

[6]H. R. Brown and A. Myers, J. Phys. F: Metal Phys. 2, 683 (1972).

[7]A. Myers, private communication.

[8]M. R. Halse, Phil. Trans. Roy. Soc. London 265, 507 (1969).

[9]G. Baym, *Lectures on Quantum Mechanics* (Benjamin, New York, 1969), p. 201.

[10]J. Friedel, Phil. Mag. 43, 153 (1952).

[11]As we have made only qualitative use of the Friedel sum rule, we have not attempted to correct Eq. (7) for the asphericity of the Fermi surface of silver. J. Langer and V. Ambegaokar, Phys. Rev. 121, 1090 (1961).

[12]R. Harris, J. Phys. C: Proc. Phys. Soc., London 3, 172 (1970).

[13]Because we are considering only s, p, and d scattering, and because d-wave scattering is very weak, we have not distinguished between the Γ_{12} and Γ_{25}' irreducible representations of the cubic group. The extension is trivial.

[14]N. Holzwarth and M. J. G. Lee, unpublished.

[15]K. Huang, Proc. Phys. Soc., London 60, 161 (1948).

[16]H. R. Brown and G. J. Morgan, J. Phys. F: Metal Phys. 1, 132 (1971).

[17]F. J. Blatt, Phys. Rev. 108, 285 (1957).

[18]D. A. van Ostenburg, private communication.

[19]M. J. G. Lee and V. Heine, Phys. Rev. B 5, 3839 (1972). Close to a scattering resonance (as in the noble metals) there is an ambiguity in the definition of the minimum perturbation pseudopotential. We refer to the pseudopotential for which the Friedel sum of the scattering phase shifts is zero.

[20]N. F. Mott, Proc. Cambridge Phil. Soc. 32, 281 (1936).

[21]L. C. R. Alfred and D. A. van Ostenburg, Phys. Rev. 161, 569 (1962).

Evaluation of Mott's Parameters for Hopping Conduction in Amorphous Ge, Si, and Se-Si

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The temperature dependence of electrical conductivity of rf-sputtered amorphous Ge, Si, and Ge-Si films as functions of annealing temperature and time have been investigated for $350 \gtrsim T \gtrsim 77$ K. Annealing shifts the hopping region to lower temperatures. We find that reasonable values of Mott's parameters are obtained only for properly annealed specimens in the true hopping-conduction region.

The band structure and transport properties of amorphous semiconductors have been subjects of increasing interest in recent years (for recent reviews and bibliographies, see Brodsky,[1] Tsay, Paul, and Mitra,[2] and others[3]). Though there is yet no agreement about a proper model for electron transport mechanisms,[1,3,4] certain basic experimental facts seem to be well established.[1,3]

From a series of extremely careful isothermal and step-annealing experiments we have investigated the annealing mechanisms of amorphous germanium,[5] Ge-Si (50% Ge and 50% Si), and Si

films.[6] We have systematically studied the influences of annealing on optical absorption and also on the temperature dependence of electrical conductivity in the range between annealing temperatures and 77 K for rf-sputtered Ge, Si, and Ge-Si films prepared in our laboratory. The conductivity of amorphous Ge measured as a function of temperature and time of annealing in the range between room temperature and temperature of annealing has been interpreted[7] as a function of two activation energies for electrical conduction due to intrinsic and extrinsic processes occuring simultaneously. At still lower temperatures conductivity can be explained by Mott's phonon-assisted tunneling or hopping process. In this Letter, we report the effects of annealing on the low-temperature conductivity of amorphous Ge, Si, and Ge-Si films. We believe this to be the first measurements reported on electrical properties of amorphous Ge-Si films. Also, using our expressions for Mott's parameters derived from Mott's equation[4] on hopping conductivity, we have evaluated $N(E_F)$ and γ, the density of localized states at the Fermi energy and the inverse rate of falloff of the wave functions associated with these states, respectively, for these materials.

The samples were prepared by rf sputtering on glass or optically polished quartz substrates in an argon atmosphere. The sputtering targets were of intrinsic quality. The sputtering parameters and subsequent characterization of the films were similar to those reported earlier.[5] Metal-contact–induced crystallization[8] in amorphous films severely restricts the choice of electrode materials for studying annealing effects on electrical properties. Presputtered molybdenum served as electrodes in our specimens for conductivity measurements. The electrical and optical properties were obtained from samples prepared in the same sputtering operation and subjected later to similar annealing conditions. We have also checked results from samples prepared identically (same sputtering parameters), but in two different sputtering operations. The differences observed were well within the overall accuracy ($\pm 3\%$) of our measurements. A lock-in amplifier and detection system[5] was used for conductivity measurements. At lower temperatures, as the sample resistance exceeds the input resistance limit of the lock-in amplifier, the voltage was measured across a suitable known resistance instead of that across the sample. A copper-Constantan thermocouple monitored temperature in this range. The lock-in frequency was chosen as 13 Hz. The frequency independence of conductivity at lower frequencies (below 10^4 Hz) for these materials assures that such data as obtained in our measurements can be taken as d.c. conductivity. Moreover, the use of lock-in system has totally eliminated some of the disadvantages (thermo-emf, lead capacitances, other noises, etc.) in the conventional d.c. conductivity measurements with electrometers. Through the use of ratiometric arrangements in a lock-in system, extremely high accuracy ($\pm 1\%$) and fine resolution are possible, which are a few of the prerequisites if one expects to observe small changes in the properties during the annealing process. Some of the specimens were annealed in vacuum and also in an He atmosphere, while others were immersed in silicon oil during annealing. No appreciable difference was observed in the general behavior for these different annealing environments.

The low-temperature conductivity data for sputtered Ge, Si, and Ge-Si films have been plotted as $\sigma\sqrt{T}$ versus $T^{-1/4}$ for $350 \gtrsim T \gtrsim 77$ K in Figs. 1(a), 1(b), and 1(c), respectively. Each of these figures also shows the effect of annealing. It is evident that at low temperatures, the conductivity of all these materials obeys Mott's relation[4]

$$\sigma = \sigma_0 \exp[-(T_0/T)^{1/4}] \tag{1}$$

for hopping conductivity. However, at high temperatures, as expected, they deviate from this law. Annealing, in general, lowers the conductivity by a few orders of magnitude. This has been interpreted[9] as due to a decrease by annealing in the number of "voids" or "dangling bonds" in the as-deposited films. We observe that an increase in annealing temperature or time shifts the hopping region to lower temperatures and increases the slope of the conductivity curve. Experimental data of Beyer and Stuke,[10] Chittick,[11] and Camphausen, Connell, and Paul[12] show similar behavior. We suggest, with Beyer and Stuke,[10] that (i) at low temperatures, a decrease in conductivity with annealing is due to diminishing hopping states, and (ii) at high temperatures, activation of electrons into other conducting states causes deviation from Mott's relation.

Following Miller and Abrahams,[13] Mott[4] has estimated the conductivity at low temperatures due to hopping processes as given in Eq. (1). Hill and others[14] have rigorously worked on Mott's original formulation under various conditions of

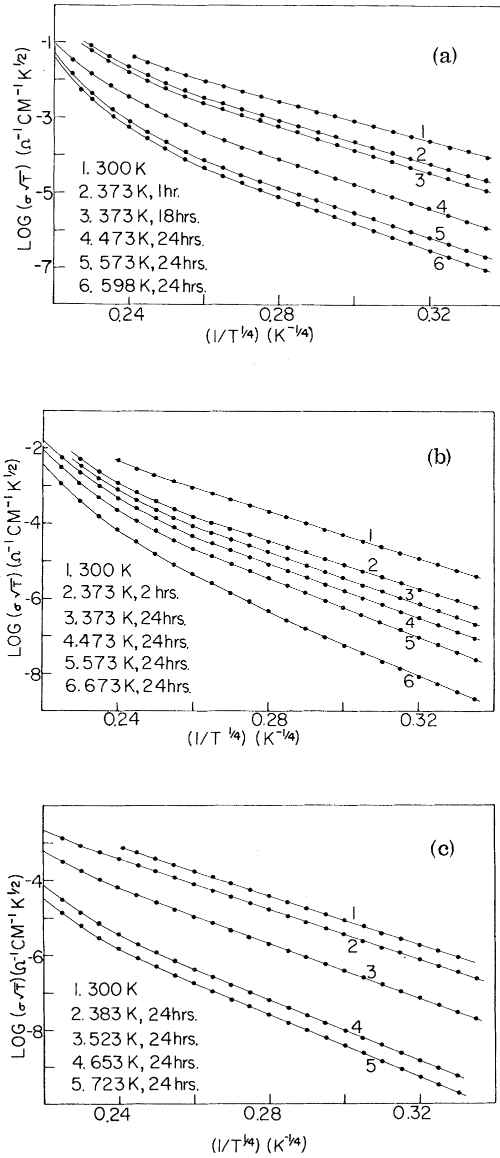

FIG. 1. Plots of $\sigma\sqrt{T}$ versus $T^{-1/4}$ for amorphous semiconductors as a function of annealing temperature; (a) Ge, (b) Ge-Si, and (c) Si films.

temperature, field, and distribution of hopping sites. The constants σ_0 and T_0 in Eq. (1) are expressed functionally as

$$\sigma_0 = e^2 a^2 \nu_{\rm ph} N(E_{\rm F}) \quad (2)$$

and

$$T_0 = \lambda\gamma^3/kN(E_{\rm F}), \quad (3)$$

where e is the electronic charge, a is the hopping distance, $\nu_{\rm ph}$ is a phonon frequency ($\sim 10^{13}$ sec^{-1}) obtained from the Debye temperature, and k is Boltzmann's constant. λ is a dimensionless constant (~ 18.1). Ambegaokar, Halperin, and Langer[14] have shown its lower limit to be 16. The constants σ_0 and T_0 have been found to depend on annealing history. Two other parameters, R and W, the hopping distance and the average hopping energy, respectively, due to Mott[4] and Hill,[14] are given as

$$R = [9/8\pi\gamma kTN(E_{\rm F})]^{1/4} \text{ cm} \quad (4)$$

and

$$W = [3/4\pi R^3 N(E_{\rm F})] \text{ eV}. \quad (5)$$

Substituting for a in Eq. (2) the average hopping distance R, we have

$$\sigma_0\sqrt{T} = A[N(E_{\rm F})/\gamma]^{1/2}, \quad (6)$$

where $A = 3e^2\nu_{\rm ph}/(8\pi k)^{1/2}$. Simultaneous solution[15,16] or equations (3) and (6) yields

$$N(E_{\rm F}) = (1.996\times10^{48}/\nu_{\rm ph}^{\ 3}) \times[(\sigma_0\sqrt{T})^3\sqrt{T_0}] \text{ cm}^{-3}\text{ eV}^{-1} \quad (7)$$

and

$$\gamma = (21.22\times10^{13}/\nu_{\rm ph})[(\sigma_0\sqrt{T})\sqrt{T_0}] \text{ cm}^{-1}. \quad (8)$$

We have evaluated Mott's parameters using Eqs. (4), (5), (7), and (8) and our experimental data from Figs. 1(a)-1(c). The results are listed in Table I for these materials. We have also analyzed the conductivity data of several workers on amorphous Ge and Si (unannealed as well as annealed) prepared by various techniques[1,3,9-12,16] at different laboratories. Quite unreasonable values of $N(E_{\rm F}) \gtrsim 10^{39}$ and $\gamma \gtrsim 10^{13}$ were obtained. Except for Beyer and Stuke,[10] other authors have not made any distinction between extrinsic conduction and true hopping regions. As for Lewis's[16] data on amorphous Si, even though W and γR are reasonable, we found unreasonably high values of $N(E_{\rm F})$ and γ in each case. On the other hand, Beyer and Stuke[10] annealed evaporated Ge films for a very short time (~ 15 min) only. The parameters evaluated from their data approached reasonable limits only for high-temperature annealing.[17] We observe from Table I that for true hopping conduction and properly annealed specimens, the parameters seem to be reasonable within Mott's requirements of the localized-state model, i.e., $\gamma R \gg 1$, $W \gg kT$. γ and $N(E_{\rm F})$, however, still seem to be somewhat larger than their expected values.[14] This deviation is most likely

TABLE I. Mott's parameters for amorphous Ge, Si, and Ge-Si films. Phonon frequency is calculated from the Debye temperature.

Material	Annealing History	T_o (10^7xK)	$\sigma_o\sqrt{T}$ (10^5xΩ^{-1}cm^{-1}K$^{1/2}$)	γ (10^{10}xcm^{-1})	$N(E_F)$ (cm^{-3}/eV)	R(150K) (10^{-10}xcm.)	W(150K) (eV)	γR
R.F. sputtered amorphous Si	300K	3.47	0.955	0.871	3.97×10^{27}	9.46	0.07	8.24
	383K,24hrs.	3.81	0.617	0.589	1.12×10^{27}	14.3	0.07	8.43
	523K,24hrs.	5.13	0.389	0.431	3.26×10^{26}	21.1	0.08	9.08
	653K,24hrs.	8.06	0.214	0.297	6.81×10^{25}	34.2	0.09	10.17
	723K,24hrs.	8.76	0.162	0.235	3.08×10^{25}	44.2	0.09	10.38
R.F. sputtered amorphous Ge	300K	1.30	1.52	1.52	5.70×10^{28}	4.23	0.06	6.44
	373K,1hr.	1.58	1.12	1.24	2.51×10^{28}	5.46	0.06	6.77
	373K,18hrs.	1.87	0.937	1.13	1.60×10^{28}	6.26	0.06	7.06
	473K,24hrs.	3.0	0.698	1.06	8.38×10^{27}	7.47	0.07	7.94
	573K,24hrs.	3.34	0.238	0.383	3.51×10^{26}	21.3	0.07	8.16
	598K,24hrs. } 623K,24hrs. }	3.70	0.202	0.342	2.26×10^{26}	24.5	0.07	8.37
R. F. sputtered amorphous Ge-Si	300K	2.40	2.14	2.09	7.89×10^{28}	3.60	0.06	7.51
	373K,2hrs.	3.27	1.76	2.02	5.12×10^{28}	4.05	0.07	8.11
	373K,24hrs.	4.31	1.54	2.01	3.94×10^{28}	4.32	0.07	8.69
	473K,24hrs.	4.59	0.939	1.27	9.22×10^{27}	6.98	0.08	8.83
	573K,24hrs.	5.17	0.631	0.902	2.97×10^{27}	10.1	0.08	9.10
	673K,24hrs.	6.28	0.250	0.394	2.04×10^{26}	24.2	0.08	9.55

due to the uncertainties involved in estimating σ_0 and T_0 from experimental data.

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[1]M. H. Brodsky, J. Vac. Sci. Technol. 8, 125 (1971), and the references therein.

[2]Y. F. Tsay, D. K. Paul, and S. S. Mitra, Phys. Rev. B (to be published).

[3]A large collection of papers in this field is in J. Non-Cryst. Solids 4 (1970).

[4]N. F. Mott, Advan. Phys. 16, 49 (1967), and Phil. Mag. 19, 835 (1969).

[5]S. Mardix and D. K. Paul, J. Electrochem. Soc. 120, 275 (1973).

[6]The annealing behavior and the annealing activation energies for amorphous Si and Ge-Si films will be published elsewhere.

[7]D. K. Paul and S. Mardix, "Annealing Effects on Electrical and Optical Properties of Amorphous Ge" (to be published).

[8]M. Toki, Y. Ogawa, and Y. Tujiki, Jap. J. Appl. Phys. 8, 1056 (1969); our unpublished data on contact materials in amorphous semiconductors also show onset of recrystallization of films around their eutectic temperatures.

[9]M. H. Brodsky, R. S. Title, K. Weiser, and G. D. Pettit, Phys. Rev. B 1, 2632 (1970); M. H. Brodsky and R. J. Gambino, J. Non-Cryst. Solids 8-10, 739 (1972).

[10]W. Beyer and J. Stuke, J. Non-Cryst. Solids 8-10, 321 (1972).

[11]R. C. Chittick, J. Non-Cryst. Solids 3, 255 (1970).

[12]D. L. Camphausen, G. A. N. Connell, and W. Paul, J. Non-Cryst. Solids 8-10, 223 (1972).

[13]A. Miller and E. Abrahams, Phys. Rev. 120, 745 (1960).

[14]R. M. Hill, Phil. Mag. 24, 1307 (1971); V. Ambegaokar, B. I. Halperin, and J. S. Langer, Phys. Rev. 34, 2612 (1971); M. Pollack, J. Non-Cryst. Solids 8-10, 486 (1972).

[15]Brodsky and Gambino (Ref. 9) were the first to suggest simultaneous solution of Mott's equation and obtained unphysical values for $N(E_F)$ and γ.

[16]Lewis [A. Lewis, Phys. Rev. Lett. 29, 1555 (1972)], used improper conversion factors [private communication, and also Phys. Rev. Lett. 30, 1238 (1973)] in his evaluation of the constants in these parameters, and claimed reasonable values using his incorrect expressions. We have re-evaluated the parameters from his experimental data and our Eqs. (7) and (8). The values obtained are highly unreasonable, $N(E_F) \gtrsim 10^{32}$ and $\gamma \gtrsim 10^{12}$. However, W and γR remain uneffected for obvious reasons.

[17]We have shown in Ref. 5 that the effect of annealing at high temperature for a shorter time is equivalent to that at low temperature for a much longer time.