

Evidence for the Mott Model of Hopping Conduction in the Anneal Stable State of Amorphous Silicon*

Adam Lewis†

Department of Physics and Astronomy, University of Maryland, College Park, Maryland 20742

(Received 5 July 1972; revised manuscript received 25 October 1972)

The temperature dependence of the dc conductivity and the room-temperature optical absorption were measured for a series of vacuum-evaporated amorphous Si films. Both properties were strongly dependent on annealing up to about 400°C, but insensitive from 400 to 600°C. We find a $\ln(\sigma\sqrt{T}) \propto T^{-1/4}$ behavior which gives reasonable parameters for Mott's localized-state model for conductivity by hopping only for films that have been annealed at least to 400°C.

The optical and electrical properties of amorphous Si and Ge films grown on room-temperature substrates show definite annealing effects.^{1,2} One interpretation¹ of this behavior is that annealing reduces the number of electrically active imperfections caused by "voids" or "dangling bonds." Any attempt to measure the intrinsic properties of amorphous Ge or Si films must be made on films prepared free of defects³ or on films in which the defects have been annealed away.

This paper is a report of measurements on a series of five amorphous Si films deposited onto room-temperature substrates. I find that the electrical and optical properties depend on annealing temperature up to 400°C, but are insensitive to further annealing until crystallization⁴ occurs above 600°C. There is clear evidence for the Mott model⁵ of conduction by hopping only for samples annealed at least to 400°C.

The samples were grown on optically polished disks of fused quartz and crystalline sapphire by electron-beam bombardment of crystalline Si at a source-to-substrate distance of 30 cm. The oil-pumped evaporator was liquid-nitrogen trapped to a base pressure of $\sim 1 \times 10^{-7}$ Torr. The films were deposited at average rates of 7–21 Å/sec and were 0.24–1.16 μm thick. During deposition, the pressure rose to $\sim 4 \times 10^{-6}$ Torr. Annealing periods were for two hours⁶ and were carried out in a vacuum of $\sim 1 \times 10^{-6}$ Torr. The resistivities of the crystalline evaporant were 10 $\Omega\text{ cm}$ (one film), 800 $\Omega\text{ cm}$ (one film), and 5000 $\Omega\text{ cm}$ (three films). I could not see any dependence of the optical and electrical properties on film thickness, resistivity of evaporant, substrate material, or previous number of anneals.

Figure 1 shows the Ohmic conductivity⁷ of one of these samples. The conductivity shows an initial rapid decrease with annealing, but is stable for the 440 and 530°C anneals. The curve for

725°C is for a crystallized film. The other four samples reproduce this behavior, and indicate that the region of stabilization to further annealing is from 400 to 600°C.

The conductivity in this anneal stable state has a knee at about 350 K sample temperature. At higher sample temperatures, the plot of $\ln\sigma$ versus T^{-1} gives a slope of ~ 0.70 eV and an intercept at $T^{-1} = 0$ of $\sim 100\text{--}500\ \Omega^{-1}\text{ cm}^{-1}$. I suggest, with Mott and Davis,⁸ that this conductivity is due to carriers excited into extended states in the conduction band across a band gap of ~ 1.4 eV. This interpretation is supported by the optical data presented later. For sample temperatures lower than 350 K, the plot of $\ln\sigma$ versus T^{-1} is not linear. We will discuss this region below.

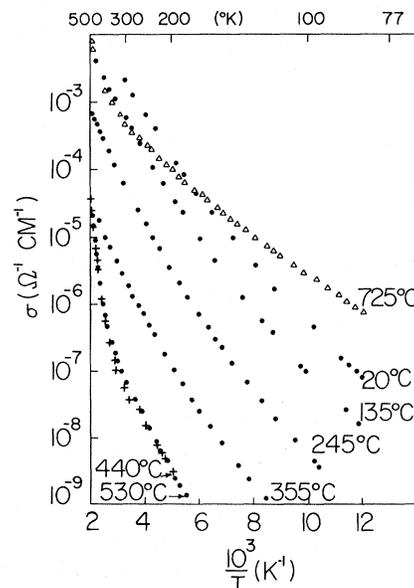


FIG. 1. Conductivity versus reciprocal temperature for an evaporated amorphous Si film taken after annealing to the indicated centigrade temperatures.

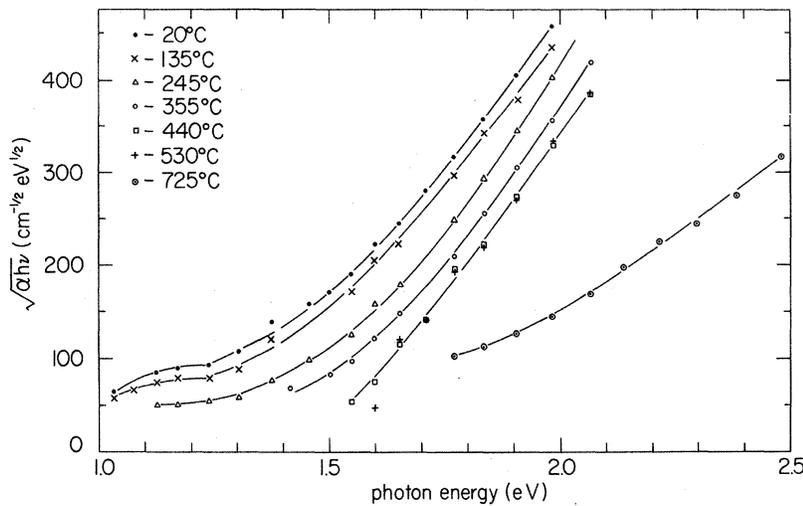


FIG. 2. Room-temperature optical absorption spectra versus photon energy for the same film and conditions as in Fig. 1. α (cm^{-1}) is the absorption constant.

Stabilization is also seen in the optical absorption, as shown in Fig. 2. For anneals below 300°C , these data agree with the results of Brodsky *et al.*,¹ except that we also see the weak structure at 1.0–1.2 eV reported by Grigorovici and Vancu.⁹ By extrapolation to zero absorption, the band gap in the anneal stable state is ~ 1.4 eV, in agreement with the conductivity data. The optical absorption for all five samples is the same in the anneal stable state within a few percent. The infrared index of refraction also stabilizes at about 3.7.

The low-temperature conductivity of the five samples in the anneal stable state is plotted in Fig. 3 on a logarithmic scale as a function of $T^{-1/4}$ for $165 \leq T \leq 350$ K. At sample temperatures less than 165 K, the Ohmic resistance is $>10^{11} \Omega$ and out of the range of our equipment. It is important to note that all of the curves lie within a factor of 5 of each other even after the change of 5 orders of magnitude in the values which occurs upon annealing from 20 to $\geq 400^\circ\text{C}$.

The data shown in Fig. 3 fit Mott's relation⁵

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

to the 3% accuracy of the measurements.¹⁰ This relation was derived by Mott for conductivity by hopping to distant sites via localized states near the Fermi energy. In his derivation, Mott uses two parameters, γ (cm^{-1}), the inverse rate of falloff of the wave function associated with the localized states near the Fermi energy, and $N(E_F)$ ($\text{cm}^{-3} \text{eV}^{-1}$), the density of localized states at the Fermi energy. The expected value¹¹ of γ

is $\sim 10^8 \text{cm}^{-1}$, and $N(E_F)$ is expected to be $\sim 10^{19-20} \text{eV}^{-1} \text{cm}^{-3}$.

Values for γ and $N(E_F)$ can be deduced from the data by simultaneously solving Mott's equations¹² for σ_0, T_0 . The results are

$$\gamma = (\sigma_0 \sqrt{T}) \sqrt{T_0} (2.16 \times 10^{-3}) \text{cm}^{-1}, \tag{2}$$

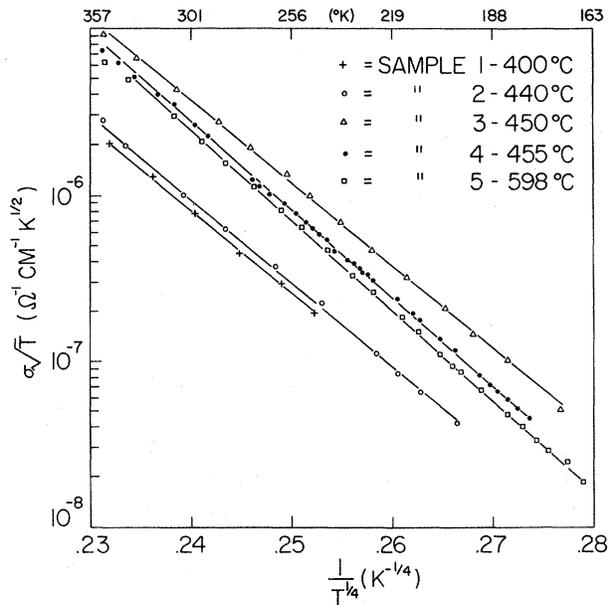


FIG. 3. $T^{-1/2}$ times the low-temperature conductivity of the five samples after annealing to at least 400°C , plotted versus $T^{-1/4}$. The straight lines are least-squares fits with Eq. (1) of the text.

and

$$N(E_F) = (\sigma_0 \sqrt{T})^3 \sqrt{T_0} (2.04 \times 10^{-3}) \text{ cm}^{-3} \text{ eV}^{-1}, \quad (3)$$

where T and T_0 are in Kelvin and σ_0 is in $\Omega^{-1} \text{ cm}^{-1}$. We can also evaluate two other important quantities introduced by Mott,⁵ the hopping distance, R (cm), and the average hopping energy, W (eV). These are

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

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

where k is the Boltzman constant. The results are listed in Table I, where $T = 200$ K was used in Eq. (4). (R and W are relatively insensitive to T .)

For conductivity by hopping to distant sites, Mott requires $\gamma R \geq 8$ and $W \gg kT$. Our observations are consistent with these, since $\gamma R \sim 12$ and $W \sim 8kT$.

When we judge the values of γ and $N(E_F)$ in Table I to see if they are "reasonable," we must keep in mind the experimental and theoretical uncertainties in the value of σ_0 . Experimentally we estimate the value of σ_0 to be accurate to a factor¹³ of 3. The theoretical estimate of σ_0 is expected to be order-of-magnitude correct.¹⁴ Therefore, from Eqs. (2) and (3), we should not expect to determine γ to better than an order of magnitude and $N(E_F)$ to better than a factor of 10^3 . Within these uncertainties, the values listed in Table I are compatible with the expected values of γ ($\sim 10^8 \text{ cm}^{-1}$) and $N(E_F)$ ($\sim 10^{19-20} \text{ eV}^{-1} \text{ cm}^{-3}$).

When we try to fit the conductivity for $T < 300$ K with Eq. (1) for any of the five films, the fit is within experimental error only for films annealed at least to 400°C . If we still try to extract values for γ and N from the 20°C data, we obtain the unphysical values $\gamma \sim 10^{14} \text{ cm}^{-1}$ and $N \sim 10^{39} \text{ cm}^{-3} \text{ eV}^{-1}$, even though the "best-fit" value of the slope, T_0 , is $\sim 10^8$ K, a reasonable number¹¹ in the hopping theory. Even for a film annealed to 355°C , the deduced values are $\gamma > 10^{10} \text{ cm}^{-1}$ and

$N > 10^{27} \text{ cm}^{-3} \text{ eV}^{-1}$. This latter value cannot be reconciled with Mott's model even allowing for the factor of 10^3 uncertainty in the determination of $N(E_F)$.

My interpretation of the observed annealing behavior of these films is that voids and defects which give rise to an extrinsic conductivity can be annealed away so that residual low-temperature conductivity in the anneal stable state arises solely from the amorphous nature of the material. I have ruled out oxygen contamination as a possible effect because I have looked for and not seen any absorption at $9 \mu\text{m}$ due to the Si-O vibrational mode in both unannealed and fully annealed Si films in agreement with Brodsky *et al.*¹

Similar annealing effects were observed in amorphous Ge by Theye.² She found that the infrared value of the index of refraction and the room-temperature resistivity were stable from 300 to 400°C . Above 400°C , the film crystallized.

These observations on Ge and Si cast doubt on earlier interpretations of an observed $\ln \sigma \propto T^{-1/4}$ dependence. Morgan and Walley¹⁵ plotted $\ln(\text{resistance})$ versus $T^{-1/4}$ for unannealed Ge and Si films grown onto room-temperature substrates. They used the straight-line fit as evidence for Mott's process without any evaluation of the parameters. Clark's data¹⁶ replotted by Mott and Davis¹⁷ was also taken on unannealed Ge films. They obtained a slope of $\sim 10^8$ K but, as we have seen, this is not an adequate test of the model. Brodsky and Gambino¹ used slightly annealed Si films, obtained a straight line for $\ln(RT^{-1/2})$ versus $T^{-1/4}$, and criticized Mott's model because they obtained reasonable numbers for γ and N . Finally, it is well known that the *same* conductivity data can be plotted against various temperature dependences to yield "reasonable fits."^{18,19} Therefore, while necessary, it is not sufficient to test Mott's model by observing that $\ln \sigma \propto T^{-1/4}$ "reasonably fits" the data. We have tested the model by seeing that within the uncertainties of the model the data yields physically acceptable

TABLE I. Evaluation of Mott's parameters using Eqs. (2)–(5) in text and experimental data from Fig. 3.

Sample	$\sqrt{T}\sigma_0$ ($\Omega^{-1} \text{ cm}^{-1} \text{ K}^{1/2}$)	T_0 (K)	$N(E_F)$ ($\text{cm}^{-3} \text{ eV}^{-1}$)	γ (cm^{-1})	$1/\gamma$ (\AA)	$R(200 \text{ K})$ (\AA)	$W(200 \text{ K})$ (eV)	γR
1	9.52×10^5	1.80×10^8	2×10^{18}	2.8×10^7	3.6	42	0.13	12
2	1.38×10^6	1.86×10^8	7×10^{19}	4.1×10^7	2.5	29	0.13	12
3	3.00×10^6	1.70×10^8	7×10^{20}	8.4×10^7	1.2	13	0.13	12
4	1.21×10^7	2.17×10^8	5×10^{22}	3.9×10^8	0.26	3.2	0.14	12
5	2.46×10^7	2.42×10^8	5×10^{23}	8.3×10^8	0.12	1.5	0.14	13

values of the model parameters and that the data fit the model to experimental accuracy. This is the first report, to the author's knowledge, of such a complete test of Mott's model.

The author acknowledges valuable discussions with Dr. R. Glosser, Dr. R. E. Glover, III, Dr. S. K. Bahl, and Dr. M. H. Brodsky. I would like to thank Dr. David Beaglehole for suggesting the problem and for his patient guidance throughout the stages of this work.

*Work supported in part by the U. S. Army Research Office, Durham, and the Advanced Research Projects Agency.

†Present address: Division of Engineering and Applied Physics, Harvard University, Cambridge, Mass. 02138.

¹M. H. Brodsky, R. S. Title, K. Weiser, and G. D. Pettit, *Phys. Rev. B* **1**, 2632 (1970); M. H. Brodsky and R. I. Gambino, *J. Non-Cryst. Solids* **8-10**, 321 (1972).

²M. L. Theye, *Mater. Res. Bull.* **6**, 103 (1971).

³Evidently, films of amorphous Ge can be formed free of large (> 100 Å) voids by evaporation onto heated substrates [see T. M. Donovan and K. Heineman, *Phys. Rev. Lett.* **27**, 1794 (1971)].

⁴Crystallization was determined by looking for the onset of sharp structure in the reflectivity at 3.4 eV, the Γ -point transition in crystalline Si. This method can detect a crystallinity as small as 2% by volume.

⁵N. F. Mott, *Phil. Mag.* **19**, 835 (1969).

⁶Anneals below 225°C could be done in the measurement cryostat. By monitoring resistance versus annealing time, I found that all significant changes took place in 2 h or less.

⁷I used coplanar evaporated silver electrodes with a gap of a few hundred microns. They were removed before annealing and redeposited over a fresh part of the film after annealing.

⁸N. F. Mott and E. A. Davis, *Electronic Processes in Non-Crystalline Materials* (Clarendon Press, Oxford, England, 1971), p. 200 ff.

⁹R. Grigorovici and A. Vancu, *Thin Solid Films* **2**, 105 (1968).

¹⁰Measurements of sample temperature are accurate to $\pm 0.3\%$. The uncertainty in σ is $\pm 3\%$. If the deviation of a data point from the least-squares fit with Eq. (1) is, on the average, less than 3%, we say that the data fit Eq. (1) to within experimental error.

¹¹V. Ambegaokar, B. I. Halperin, and J. S. Langer, *Phys. Rev. B* **4**, 2612 (1971); B. I. Halperin, private communication.

¹² σ_0 contains $T^{-1/2}$, and so $\sigma_0\sqrt{T}$ is temperature independent.

¹³Small uncertainties in T_0 produce relatively large uncertainties in σ_0 .

¹⁴E. A. Davis, private communication.

¹⁵M. Morgan and P. A. Walley, *Phil. Mag.* **23**, 661 (1971).

¹⁶A. H. Clark, *Phys. Rev.* **154**, 750 (1967).

¹⁷Ref. 8, p. 285.

¹⁸K. L. Chopra and S. K. Bahl, *Phys. Rev. B* **1**, 2545 (1970).

¹⁹D. Adler, *Crit. Rev. Solid State Sci.* **2**, 317 (1971).

Luminescence of Cu_2O —Excitonic Molecules, or Not?*

Y. Petroff,† P. Y. Yu,‡ and Y. R. Shen

Department of Physics, University of California, Berkeley, California 94720, and Inorganic Materials Research Division, Lawrence Berkeley Laboratory, Berkeley, California 94720

(Received 21 August 1972)

Luminescence spectra of Cu_2O excited at various temperatures by a tunable dye laser showed no evidence of the existence of excitonic molecules (or biexcitons) as suggested recently by Gross and Kreingol'd. A pair of previously unreported peaks with an exceptionally strong temperature dependence has been observed below 3°K.

The existence of excitonic molecules (or biexcitons) in a crystal was first suggested by the results of Haynes on Si.¹ Since then, the subject has attracted much attention. Recently Gross and Kreingol'd² reported the existence of excitonic molecules in Cu_2O . It is well established³ that the absorption edge of Cu_2O consists of two hydrogenic series, known as the "yellow" and the "green" series, due to the excitons formed by the lowest conduction band and the two top valence bands (split by spin-orbit coupling) at the

center of the Brillouin zone. These excitons are said to be forbidden because the conduction and valence bands involved have the same parity, so that the $n=1$ excitons cannot be excited by dipole transition. Gross and Kreingol'd² observed an inverted hydrogenic series in the luminescence spectrum of Cu_2O at 2°K, with a Rydberg constant equal to that of the green exciton series. They concluded that this inverted series in the luminescence spectrum should result from the decay of excitonic molecules, each of which was com-