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Direct evidence for ambient-controlled hopping conduction in inhomogeneous *a*-Si and *a*-Si:H from gas-diffusion experiments

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The previously reported ambient effect—namely, with decreasing temperature in the range $T \leq 140$ K the dc electrical hopping conductivity σ of sputtered *a*-Si and *a*-Si:H films steadily increases above the values predicted by the $\ln\sigma \propto T^{-1/4}$ law (whose behavior is well followed in gas ambient) upon evacuation of the ambient gas (e.g., He, Ar, N_2, CH_4, or air)—is investigated further. It is now clearly demonstrated to arise from the presence of gas molecules in the film's voids. The diffusion constant of gas molecules (atoms) into the film is shown to vary linearly with ambient-gas pressure, just as expected for gas diffusion into a porous medium.

It is usually observed[1] that the temperature (T) dependence of the dc electrical conductivity σ in amorphous germanium (*a*-Ge) and amorphous silicon (*a*-Si) follows the $T^{-1/4}$ law,

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

where T_0 and σ_0 are experimentally determined constants. As to the theoretical explanation, the variable-range hopping model of Mott[2] is commonly accepted.

However, several confusing experimental results have been reported in the literature. An upward deviation from the $T^{-1/4}$ law has been observed[3-6] at low temperatures (≤ 90 K) in some *a*-Ge and *a*-Si films which was used[5] as a strong argument against Mott's theory. As shown in our previous work,[7,8] such deviations could simply be ascribed to a second-path conduction, possibly tunneling through microvoids, which can be easily eliminated by carrying out measurements in gas ambient; it was argued that the presence of gas molecules in the voids is responsible for this conductivity change, called the *ambient effect*. Therefore, the upward deviations should not be considered as an intrinsic property of the hopping conduction, but merely as the consequence of the film's inhomogeneity.

In the present work, direct evidence is obtained from gas-diffusion experiments showing that it is indeed the penetration of gas molecules into the film's microvoids which modifies the second-path conduction. This observation is felt elucidating to the understanding of the ambient effect mechanism.[8]

Two samples—one pure *a*-Si and one hydrogenated *a*-Si film—are described. They were rf sputtered onto high-purity (purity $\geq 99.9999\%$) fused-quartz substrates, held at room temperature (RT) by water cooling. Table I contains some deposition parameters. Conductivity measurements were carried out using the planar geometry with typical electrode spacing ≈ 2 mm. Both silver paint and evaporated Al films were used as electrodes. These remained perfectly Ohmic up to an electric field ≈ 500 V/cm. The experiments presented below were carried out with an electric filed of ≈ 100 V/cm. Details of the measurement setup and sample preparation have been described elsewhere.[7,8]

To understand the ambient effect, detailed knowledge of the film structure is essential. For this purpose, transmission electron microscopy (TEM) experiments were carried out of which details have been presented previously.[8] Figures 1(a) and 1(b) show the TEM pictures of the films S1 and S2, respectively. Clearly, S1 is much less inhomogeneous than S2. Owing to the thickness of the film, the resolution of the TEM does not suffice to reveal a clear structure of film S1.

Gas in-diffusion[9] experiments have been carried out by first evacuating the measuring chamber at RT to a base pressure of $\approx 10^{-4}$ Torr which takes about 2 h. After this the system was cooled down to ≈ 80 K via a mechanical thermal contact and thermal radiation. Subsequently, the pump was shut off and pure He gas (purity $> 99.999\%$) to a pressure p_a was quickly admitted into the vacuum chamber through a leakage valve. The change of σ with time was followed by a computer-controlled system. The outgassing of chamber walls was tested by shutting off the vacuum pump and was shown to be sufficiently slow on the time scale of gas diffusion experiments. Figures 2(a) and 2(b) present the He gas diffusion results represented by the current (I) versus time (t) behavior for samples S1 and S2 carried out at 85 and 90 K, respectively, for various ambient pressures in the

TABLE I. Sample preparation characteristics of sputtered *a*-Si and *a*-Si:H films. W is the rf power, p the ambient pressure, d_r the film growth rate, and d_{Si} the thickness of the film.

Sample	Ambient	W(W)	p (Torr)	d_r (nm/s)	d_{Si} (μm)
S1	Ar	100	0.008	0.030	0.52 ± 0.02
S2	99%Ar+1%H_2 (vol%)	100	0.01	0.024	0.75

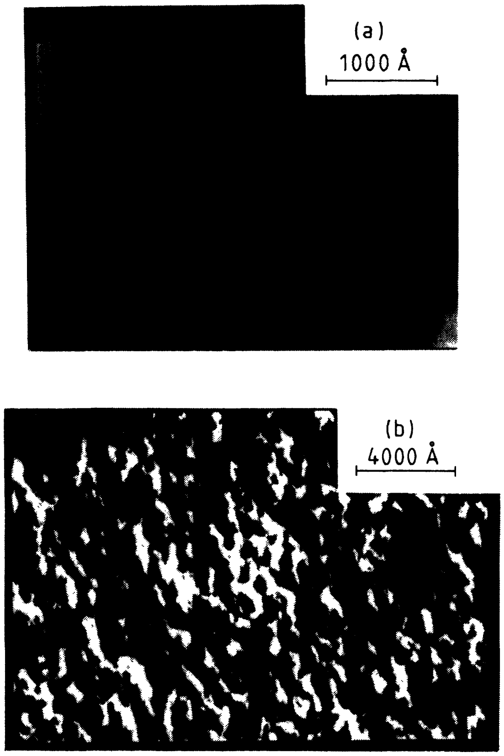

FIG. 1. (a) Bright-field electron transmission micrograph of film S1 (cf. Table I) and (b) of film S2. Notice the remarkable difference in structure inhomogeneity.

range $0.01 \leq p_a \leq 0.2$ Torr. Time zero corresponds to the moment of gas admission. Clearly, the rate of change of σ depends on p_a. The same experiments were repeated with pure Ar (99.9999%) and N_2 (> 99.9999%). They all exhibit the same effect and the σ vs T behavior is essentially the same for all these gases. Also, air and CH_4 had similar effects.

Supposing it is the penetration of gas molecules into the film's voids that causes the conductivity change, then, into first-order approximation, σ will depend linearly on the gas concentration n in the film. If, on macroscopic scale, gas molecules are distributed homogeneously throughout the film, then σ is given by

$$\sigma_v = \sigma_{\text{bulk}} + \sigma_a \frac{n_0 - n}{n_0} ; \tag{2}$$

σ_v represents the conductivity in vacuum, σ_{bulk} is the ordinary hopping conduction (i.e., $\ln\sigma_{\text{bulk}} \propto T^{-1/4}$) measured in gas ambient with sufficiently high p_a (> 1 Torr), σ_a is the maximum additional conductivity in vacuum (i.e., "second" conductivity path), and n_0 is the gas concentration needed to totally eliminate the additional conduction. Equation (2) is a good approximation as long as $n < n_0$. Obviously, n is proportional to p_a and during the gas in-diffusion its local value will depend on the site distance from the film's free surface. As appears from Fig. 2, n is indeed smaller than n_0 in our experiment since the residual current (when $t \rightarrow \infty$) decreases as the applied p_a increases. Diffusion in a *porous medium* can be approximately described[10] by the classical diffusion equation

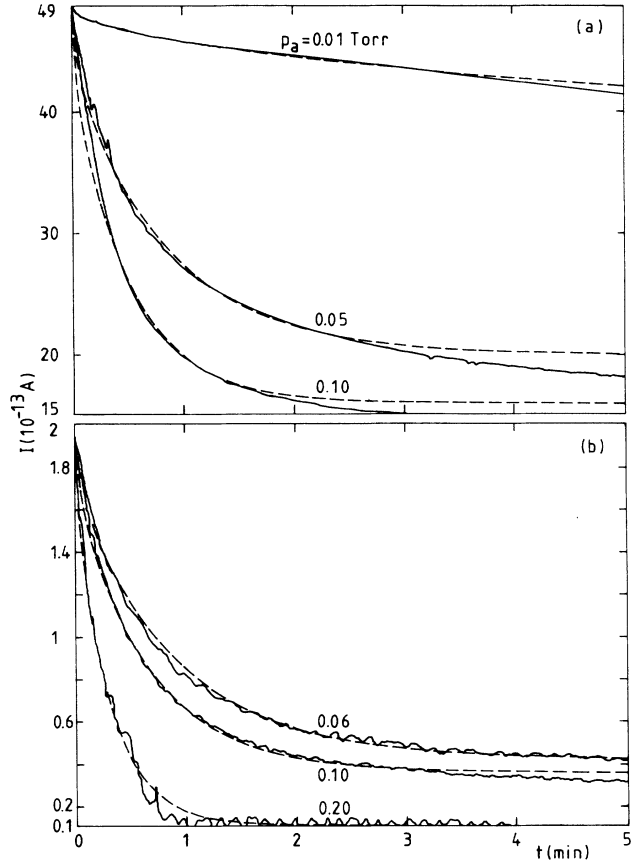

FIG. 2. Change of conductivity (a) in film S1 (T = 85 K) and (b) in film S2 (T = 90 K), represented by the current, is plotted vs t during He gas in-diffusion for various ambient pressures (p_a) indicated in the figure. The origin of the time scale corresponds to the moment at which He was admitted into the measuring chamber. The dashed lines represent theoretical calculations based on the general diffusion equation and using the parallel-resistance scheme. The deduced diffusion constant D is given in Table II. The growing difference between the fitted and experimental curves at larger time is due to the increasing influence of temperature changes.

$$\frac{\partial n}{\partial t} = D \frac{\partial^2 n}{\partial x^2} , \tag{3}$$

where D represents the diffusion constant and x is the distance (perpendicularly) from the film's main free surface into the bulk. The total conductivity versus t behavior can then easily be calculated using (2) and (3), supposing that the gas pressure outside the film is always p_a and inside the film is zero at $t = 0$, which is a good description of the present experimental situation. In this calculation, the film is divided into identical layers (of infinitesimal thickness) parallel with the film's free surface and σ is calculated using the parallel-resistance scheme. The results are also plotted in Figs. 2(a) and 2(b) as the dashed lines. The fitting is satisfactory for sample S2 but, apparently, somewhat less for S1. This, in fact, is not surprising. It was noticed that by gas admission the system temperature decreases about 1 to 2 K after a few minutes (contact gas effect), which also causes a decrease of σ. Since the gas-influenced σ change is more significant in film S2 than in S1 (cf. Fig. 2), this temperature effect will be relatively more disturbing in film S1 such as to become apparent a few minutes after the start of the diffusion experiment. Hence, for sample S1 only the initial part of the experimental curves has been fitted.

The possibility that the ambient effect arises by some measurement-induced artifacts has been dealt with at length previously.[7,8] They were all found irrelevant. In particular, as regards the present work, T gradients are excluded. Also, that the changes in σ observed in the present work upon introducing gas into the measuring chamber cannot all be due to a cooling effect simply follows from the "static" observation; the ambient effect is there under static ambient conditions, i.e., either vacuum or 1-atm gas ambient.

Derived diffusion constants are given in Table II. Clearly, D is proportional to p_a in both samples. In support of this result, we should emphasize that the relative error on D is small (see Table II); indeed, the fitting quality is very sensitive to the D value applied. The proportionality between D and p_a is in excellent agreement with the theory for (nondissociative) gas diffusion into a porous medium.[10] This is convincing evidence that gas molecules really *penetrate into the film's voids and are responsible for the σ change.*

One can also observe from Table II that D—in our case effectively "describing" the diffusion into "conduction-sensitive" voids—is roughly the same in both films despite the fact that the two films have quite different morphology; the diffusion experiments in S1 were carried out at a slightly lower T than in S2 which explains the small difference in D. This fact supports our former[8] suggestion that the mechanism of the second-path conduction, which can be influenced by free[8] gas molecules (atoms) in the voids, is electron tunneling through microvoids. Since tunneling is rather sensitive to the tunneling distance, the larger voids in film S2 do not contribute to the ambient effect at all. We do expect, however, that the number of "conduction-sensitive" microvoids is larger in S2 than in S1 which explains the larger relative change of σ in S2.

TABLE II. Diffusion constants for He into sputtered a-Si and a-Si:H films at various He ambient pressures p_a.

Sample	p_a (Torr)	D (10^{-11} cm^2/s)
S1 (T=85 K)	0.01	0.33 ± 0.02
	0.05	2.0 ± 0.1
	0.10	3.5 ± 0.2
S2 (T=90 K)	0.06	3.3 ± 0.3
	0.10	5.0 ± 0.3
	0.20	10.0 ± 0.8

The above analysis clearly demonstrates that the ambient effect originates from the film inhomogeneity. The additional conductivity measured in vacuum can be diminished by gas molecules penetrating into the film's voids, where the diffusion constant is found proportional to the gas pressure. All these observations are consistent with the mechanism of electron tunneling through microvoids.

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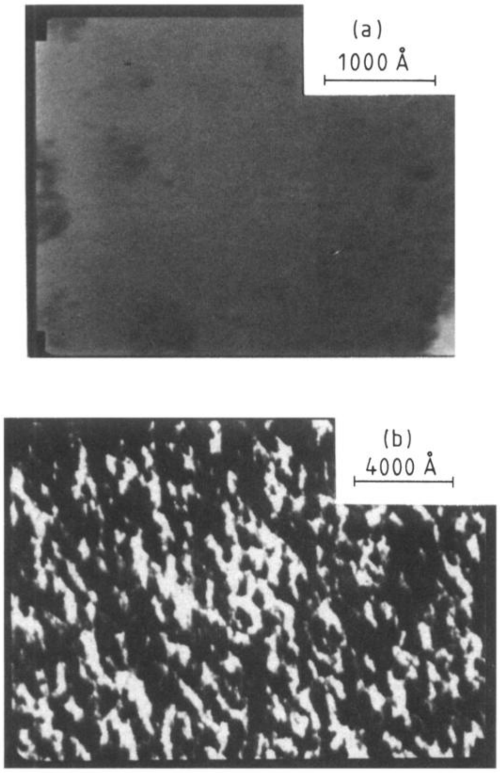
[9] Gas out-diffusion experiments were also tried but reliable results were prevented by the interference of outgassing from the measuring chamber walls. Clearly, these are likely to interfere much more severely when carrying out an out-diffusion experiment starting at, e.g., $p_a = 0.1$ Torr (and hence, fully absorbed walls), than when starting an in-diffusion experiment from a *prolonged* outgassed system in which p_a is suddenly increased from $< 10^{-4}$ to 0.1 Torr.

[10] R. E. Cunningham and R. J. J. Williams, *Diffusion in Gases and Porous Media* (Plenum, New York and London, 1980).



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