Influence of microstructure on the $T^{-1/4}$ conductivity law of slowly deposited sputtered a-Si and a-Si:H

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The electrical dc conductivity σ of slowly deposited sputtered a-Si and a-Si:H films has been measured in the temperature range $77 \leq T \leq 500$ K. In all films, deviations from the $T^{-1/4}$ law were observed in vacuum ambient at low temperatures—σ increases above the values predicted by the $T^{-1/4}$ law—which were found to be totally absent in He-gas ambient. This is tentatively ascribed to electron tunneling across microvoids which can be significantly lowered by scattering at gas molecules. An unexpected strong increase of the conductivity was observed in a-Si:H over the whole T range after an annealing treatment at 340 °C, whereas the density of dangling bonds decreases. This is demonstrated to be the consequence of the prevailing structural inhomogeneity, which influences both the preexponential factor σ_0 and T_0 of the $T^{-1/4}$ law.

I. INTRODUCTION

The dc electrical conductivity σ in amorphous germanium (a-Ge) and amorphous silicon (a-Si) exhibits a nonactivated σ versus temperature (T) behavior.[1] Based on the model of variable-range hopping occurring in a partially filled band of localized states near the Fermi level, Mott[2] succeeded in showing that at sufficiently low T, σ follows the relation

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

referred to as the $T^{-1/4}$ law. This theory has since been put on a more rigorous basis by other authors[3-5] using percolation methods. More particularly, we mention the results of Kirkpatrick[5] in which T_0 and σ_0 are given as

$$T_0=19\alpha^3/kN(E_F) , \tag{2}$$

$$\sigma_0=0.022\alpha^3C(T_0/T)^{0.35} , \tag{3}$$

where α is the inverse of the falloff constant of the wave function of a localized state near the Fermi level; C is a constant which depends only on the material's bulk properties, namely, the deformation potential, the density, the velocity of sound, and the dielectric constant; $N(E_F)$ ($\mathrm{cm}^{-3}\,\mathrm{eV}^{-1}$) represents the density of states at the Fermi level, and k is Boltzmann's constant. Mott's theory[2] assumes, among others, (i) an energy-independent density of states $N(E)$ near the Fermi level, (ii) a phonon-activated transition rate in which the multiphonon processes are neglected, and (iii) a homogeneous film structure. The linearity of the $\log\sigma$ versus $T^{-1/4}$ plot predicted by Mott has been confirmed in many reports;[6-8] it was shown that such behavior could extend over more than 8 orders of magnitude and down to very low T (<14 K) without any sign of deviation. However, although Mott's theory predicts a reasonable T_0 value, it fails to give a physically realistic σ_0 value.[7,9] Hence, there have been several attempts to overcome this difficulty. Emin[10] takes into account the multiphonon processes in the calculation of the hopping rates. Others[11] invoke a nonconstant density of states. Despite successes of these theories in some aspects, they all fail to produce an essentially temperature-independent σ_0 in Eq. (1).

The present work reports on new observations relevant to this matter. After annealing a-Si:H films at the temperature $T_A=340$ °C, it was observed that T_0 in Eq. (1) decreases attendant with an *overall* increase (relative to the asdeposited sample case) of σ. However, electron spin resonance (ESR) shows that the number of dangling-bonds (DB's) *does not increase* during annealing. This is just opposite to what Eq. (2) predicts and conflicts with the general annealing behavior of pure a-Si so far reported. It will be shown that this effect clearly demonstrates that an inhomogeneous structure not only has an influence on σ_0 but also on T_0. A small influence on T_0 will cause a drastic change of σ_0 which makes the measured σ_0 value quite unreliable.

Another confusing experimental result reported in the literature is the observation[7,9,12,13] of an upward deviation from the $T^{-1/4}$ law at low T (≤ 90 K) in some a-Ge and a-Si films which was used[12] as a strong argument against Mott's theory. This, however, should not be considered as an intrinsic property of the hopping conduction because it does not appear universally. In the present work, such "deviations" have been systematically observed and analyzed, and they were found to relate strongly to the measuring ambient, e.g., vacuum, He gas, etc. The results indicate that the upward bending in the $\log\sigma$ versus $T^{-1/4}$ plot (thus deviating from the linear behavior of the $T^{-1/4}$ law) may simply be ascribed to tunneling of electrons across void surfaces which can be partly diminished by the presence of gas molecules in the voids.

II. EXPERIMENTAL

Three samples were studied—one pure a-Si and two weakly hydrogenated a-Si films. They were rf sputtered onto high-purity (purity $\geq 99.9999\%$) fused-quartz sub-

TABLE I. Sample preparation characteristics of the sputtered *a*-Si and *a*-Si:H films.

Sample	*S*1	*S*2	*S*3
Ambient	Ar	99% Ar + 1% H_2 (vol %)	97% Ar + 3% H_2 (vol %)
p_a (Torr)[a]	0.008	0.01	0.008
d_r (nm/s)[b]	0.030	0.024	0.028
d_{Si} (μm)[c]	0.52±0.02	0.75	0.80

[a] p_a denotes ambient pressure.
[b] d_r represents the *a*-Si film growth rate.
[c] d_{Si} is the film thickness.

strates, held at room temperature (RT) by water cooling. The 2 in. diam. targets were polycrystalline Si with RT resistivity $\rho_{RT}=150\ \Omega$ cm, and were positioned 7.5 cm away from the substrates. After the system was pumped to a base pressure $<10^{-6}$ Torr, the substrates were plasma-etched *in situ* with an rf power $P_{rf}=150$ W in a 10 mTorr Ar (99.9999% pure) ambient for 15 min prior to the *a*-Si deposition. The films were fabricated in either pure Ar or a mixture of Ar and (1–3) vol % H_2 (99.9999% pure) at constant $P_{rf}=100$ W. Table I contains some deposition parameters. Of each sample set, a film from the same batch was annealed at 247, 340, or 450 °C in vacuum (pressure $p_a \leq 10^{-5}$ Torr for 30 min). Part of the ESR characteristics have been published previously.[14]

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 over the whole T range measured. Using a high thermally conductive paint, the sample was cemented on thin Teflon sheet (100 μm thick) which in turn is cemented on the top of a copper cylinder with a diameter of 22 mm. The sample was covered with a copper radiation shield with an inner diameter of 22 mm and a height of 10 mm. The sample is thus fully enclosed by a solid Cu box, assuring a homogeneous sample temperature. A copper-constantan thermocouple was mounted in the copper cylinder inside the copper shield and was calibrated against a standard platinum resistance thermometer. The copper support was enclosed by a double-walled vacuum system which could be immersed in cooling liquids. The Cu support was cooled either via mechanical (thermal) contacts or exchange gas contact. A Keithley 617 electrometer with an internal voltage source was used for current (I) measurements. The leakage resistance of this system is higher than $10^{15}\ \Omega$ and the error in current measurements is less than 2×10^{-15} A.

III. RESULTS AND ANALYSIS

A. Measurement procedure

The temperature dependence of σ is shown in Figs. 1, 2, and 3. For each film, σ was first measured in He ambient. This comprised a degassing during several hours in a vacuum $\approx 10^{-4}$ Torr at RT for the as-deposited samples, and at 200 °C for the annealed ones. Subsequently, dry He gas (>99.999% pure; $p_a=1$ atm) was admitted in the measuring chamber through a liquid-nitrogen H_2O trap, whereupon σ was measured from 77 K to beyond RT. In a second step σ was remeasured, but this time in vacuum, after an identical degassing process. The vacuum was kept at $p_a \approx 10^{-4}$ Torr during the whole measurement. An electrical field <50 V cm^{-1} was used to obtain the results represented in Figs. 1, 2, and 3.

B. Conductivity in He ambient

First, we address the He-gas ambient results. As may be seen clearly from Figs. 1, 2, and 3 (filled circles) all samples, both as-deposited and annealed, strictly follow the $T^{-1/4}$ law at low T. The σ_0 and T_0 values obtained with least-square fitting are given in Table II, together with the spin density N_s deduced by ESR from the DB signal. A remarkable aspect is the annealing behavior of the conductivity. As may be seen from Fig. 1, T_0 of film *S*1 (i.e., *a*-Si) remains roughly constant upon annealing at 340 °C, whereas the overall conductivity drops to a lower level. On the contrary, as shown in Figs. 2 and 3, T_0 of film *S*2 and *S*3 *decreases* sharply with annealing at 340 °C attendant with an overall *upward* shift of the conductivity. This is surprising [see relation (2)], all the more be-

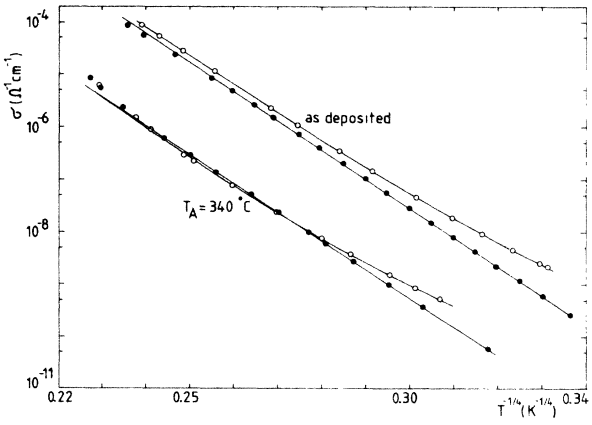

FIG. 1. Conductivity of slowly sputtered *a*-Si (cf. film *S*1, Table I) plotted in logarithmic scale vs $T^{-1/4}$, measured both in helium (filled circles) and in vacuum (open circles) ambient. The solid lines are fittings as described in the text. Typical error bars do not exceed the symbol size.

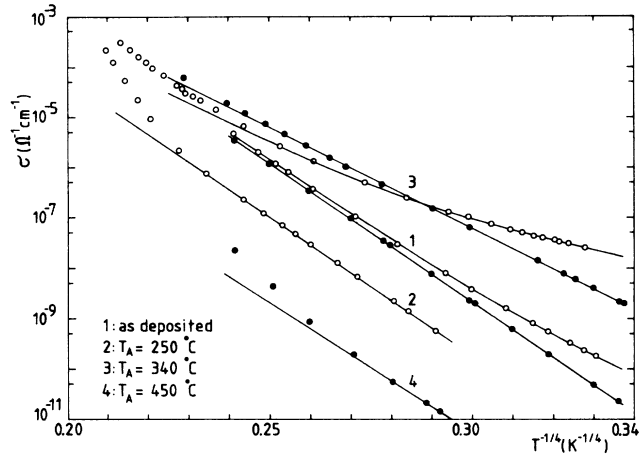

FIG. 2. Conductivity of weakly-hydrogenated, slowly-sputtered *a*-Si:H (cf. film *S*2, Table I) plotted in logarithmic scale vs $T^{-1/4}$, measured both in helium (filled circles) and in vacuum (open circles) ambient. The solid lines are fittings as described in the text. Typical error bars are below the symbol's size.

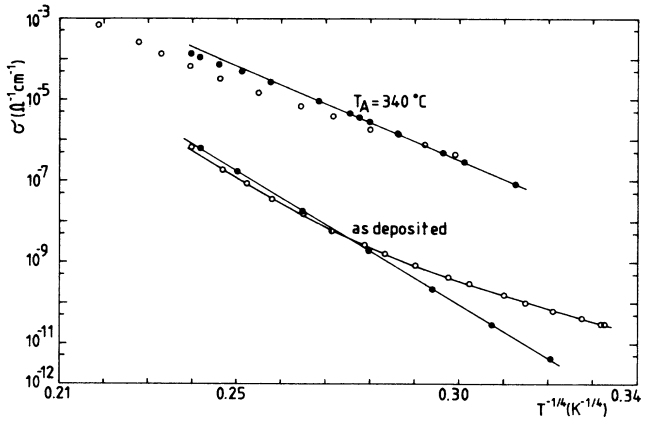

FIG. 3. Conductivity of weakly-hydrogenated, slowly-deposited *a*-Si:H (cf. film *S*3, Table I) plotted in logarithmic scale vs $T^{-1/4}$, measured both in helium (filled circles) and in vacuum (open circles) ambient. The solid lines are fittings as described in the text.

cause $N(E_F)$ is expected to decrease upon annealing as indicated by the *decrease of* N_s (cf. Table II). However, this peculiar behavior is not observed after annealing at lower temperature (247 °C). As may be clearly seen from Fig. 2 and Table II, annealing of film *S*2 at 247 °C reduces σ_0 but has no influence on T_0; this is similar to the annealing behavior of film *S*1 ($T_A = 340$ °C). This result indicates that the increase of σ and the decrease of T_0 induced in films *S*2 and *S*3 by annealing at 340 °C are due to a substantial change of film structure—not due to the creation of DB's since N_s decreases monotonically with annealing (cf. Table II). Annealing at 450 °C of film *S*2 causes T_0 to increase again while the overall σ drops to a much lower level.

C. Conductivity in vacuum

Surprisingly, in contrast with the results obtained in He-gas ambient where the $T^{-1/4}$ law is strictly followed at low *T*, *significant deviations from this are found in vacuum ambient.* In the logσ versus $T^{-1/4}$ plot, the curves bend up gradually as *T* decreases (cf. Figs. 1, 2, and 3). For the as-deposited samples *S*1 and *S*2, σ increases at all temperatures above the He-gas ambient values. For all other cases σ in vacuum is smaller than σ in He ambient at high *T* (i.e., $T \geq 160$ K) and is larger at low *T*. It is important to mention that various evacuations of the sample space alternated by gas admittances led reproducibly to identical data. We shall refer to this later as the "ambient effect."

D. Gas diffusion

To get more insight, gas diffusion experiments have been carried out—firstly with He. The system at RT was shortly evacuated and filled with He ($p_a = 1$ atm) without any preceding degassing process, upon which it was cooled at 77 K and subsequently evacuated down to $p_a \approx 10^{-4}$ Torr. About two hours later the conductivity reached the same value as given in Fig. 1, i.e., σ in vacu-

TABLE II. Summary of conductivity data and ESR spin densities of rf-sputtered *a*-Si and *a*-Si:H films.

Sample	He-ambient data		Fitting results to vacuum-ambient data				
	T_0 (K)	σ_0 (Ω^{-1}cm^{-1})	$T_0(1)$ (K)	$\sigma_0(1)$ (Ω^{-1}cm^{-1})	$T_0(2)$ (K)	$\sigma_0(2)$ (Ω^{-1}cm^{-1})	N_S (cm^{-3})[c]
*S*1 AD[a]	2.70×10^{8}	1.4×10^{9}	2.67×10^{8}	1.6×10^{9}	4.4×10^{7}	7.4×10^{2}	1.0×10^{20}
340 °C[b]	2.55×10^{8}	1.6×10^{7}	3.46×10^{8}	1.5×10^{8}	4.2×10^{7}	2.45×10^{1}	2.5×10^{19}
*S*2 AD	2.55×10^{8}	6.1×10^{7}	2.59×10^{8}	8.0×10^{7}	3.7×10^{7}	2.01×10^{1}	2.5×10^{19}
250 °C	2.52×10^{8}	4.8×10^{6}					4.9×10^{18}
340 °C	7.25×10^{7}	6.6×10^{4}	7.94×10^{7}	4.9×10^{4}	2.5×10^{6}	1.0×10^{-2}	4.5×10^{18}
450 °C	1.87×10^{8}	8.6×10^{3}					2.2×10^{18}
*S*3 AD	5.28×10^{8}	5.0×10^{9}	5.83×10^{8}	8.0×10^{9}	2.66×10^{7}	6.7×10^{-1}	$(1.4\pm0.2)\times10^{18}$
340 °C	1.31×10^{8}	2.8×10^{7}					$\sim5\times10^{17}$

[a]AD denotes as-deposited film.
[b]Annealing temperature.
[c]Estimated absolute error $\approx 20\%$, relative error $\approx 5\%$.

um. From this it was realized that the degassing process at RT or higher T is not necessary. The influencing gas molecules can easily be pumped away at any T at least down to 77 K. Subsequently, pure He gas (purity $>99.999\%$) was quickly admitted to a pressure $p_a \approx 5\times 10^{-2}$ Torr into the vacuum chamber through a leakage valve. This will be termed the "gas-indiffusion" experiment. 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 an indiffusion experiment. After the gas indiffusion experiment, the system was pumped again and the change of σ with T was registered again. This is called the "gas-outdiffusion" experiment. These diffusion results are presented in Fig. 4. No significant temperature change occurs during the whole process. The same experiments were repeated with pure Ar (99.9999%), N_2 ($>99.9999\%$), and CH_4 ($>99.99\%$) gases. He, Ar, and N_2 ambients all lead to essentially the same σ versus T behavior which demonstrates that *the influence of the gas molecules simply cannot be their adsorption at the film's free or internal surfaces.* It is not known to what extent the adsorption of these gases on a-Si surfaces really happens; but, presumably, if it would happen, the adsorption energies of the He atoms and Ar atoms are quite different.[15]

The inset in Fig. 4 gives the gas-indiffusion curve for CH_4 at 85 K and $p_a \approx 0.1$ Torr. After the initial decrease, σ increases again and stabilizes at a value between the σ in vacuum and σ in He ambient. This is the consequence of the adsorption of CH_4 molecules on the cold chamber walls, thus reducing the effective pressure in the measuring chamber. This experiment at once also excludes the

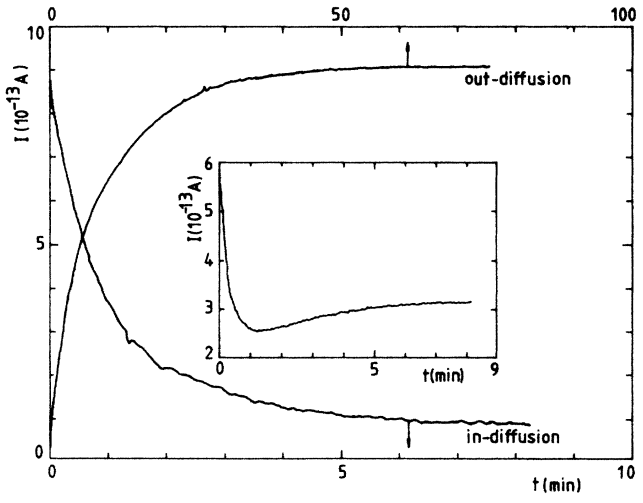

FIG. 4. Change of conductivity at 77 K represented by the current (I) plotted vs time (t) during the outdiffusion and indiffusion experiments using He gas for the as-deposited film $S3$ (cf. Table I). The origin of the time scale corresponds to the moment at which gas atoms (pressure $\approx 5\times 10^{-2}$ Torr) were admitted in the measuring chamber during the indiffusion experiment or the onset of pumping for the outdiffusion experiment. The inset presents the change in σ ($T=85$ K) by admitting 0.1 Torr CH_4 gas into the measuring chamber.

impurities, eventually present in the system and gases used, as the major origin of the observed ambient effect. Indeed, if these were important, such as, e.g., H_2 molecules, why then should they behave differently in CH_4 and He? This also demonstrates that it is not gas molecules adsorbed on the film's free surface that reduced σ significantly. If they did, while CH_4 molecules get more and more adsorbed on the film's free surface, σ would keep decreasing instead of increasing again after some time (see Fig. 4). Thus, there does not exist something like a surface defect (spin) system governing the main part of the film conductivity, which conclusion was arrived at previously.[16] Also, the fact that the ambient effect is reversible at 77 K excludes water molecules as a possible influential impurity. It is almost impossible to pump out H_2O molecules at 77 K. Moreover, all gases were sent through a liquid nitrogen trap before entering the system. Hence, we must conclude that it is the presence of inert gas molecules in the microvoids—whose presence will be shown immediately—which causes the ambient effect. Finally, it is worth mentioning that ESR experiments carried out in either vacuum or He ambient do not lead to any noticeable difference in N_s; thus, at least, DB's are not created by pumping.

E. Structure analysis

More detailed knowledge of the film structure is required to answer questions such as: How can gas molecules influence σ and how can they penetrate into the *bulk* of the film? Transmission electron microscopy (TEM) experiments were carried out on the same film as used for σ measurements. They were chemically separated from the quartz substrate, and etching in HF (10 vol%) for 10 min was carried out just before mounting the sample in the TEM vacuum chamber. Figure 5(a) shows the TEM picture of the as-deposited sample $S3$. The morphology shown is a nonuniform columnar structure. Regions of dark areas about 400 Å in diameter are surrounded by a network of density-deficient regions or voids (light areas). The voids are rodlike and aligned perpendicular to the film surface with ellipsoidal cross-sectional dimensions which vary significantly from $\approx 20\times 200$ Å^2 to $\approx 200\times 1000$ Å^2. The dark and light areas are separated quite clearly from each other. Figure 5(b) presents the electron micrograph of the film $S3$ annealed at 340 °C. Now, the separation between dark and light areas is much less clear. Large voids disappeared by means of atomic diffusion from the dense areas into the void regions. In this sense, the film has become more homogeneous.

IV. DISCUSSION

A. Annealing effects; nature of the hopping centers

It is generally accepted that the DB center is the major defect in a-Si and a-Si:H with an energy level in the band gap. Naturally, this defect is also considered to be directly involved in hopping conduction.[13] However, it is not quite clear yet whether other types of defects also con-

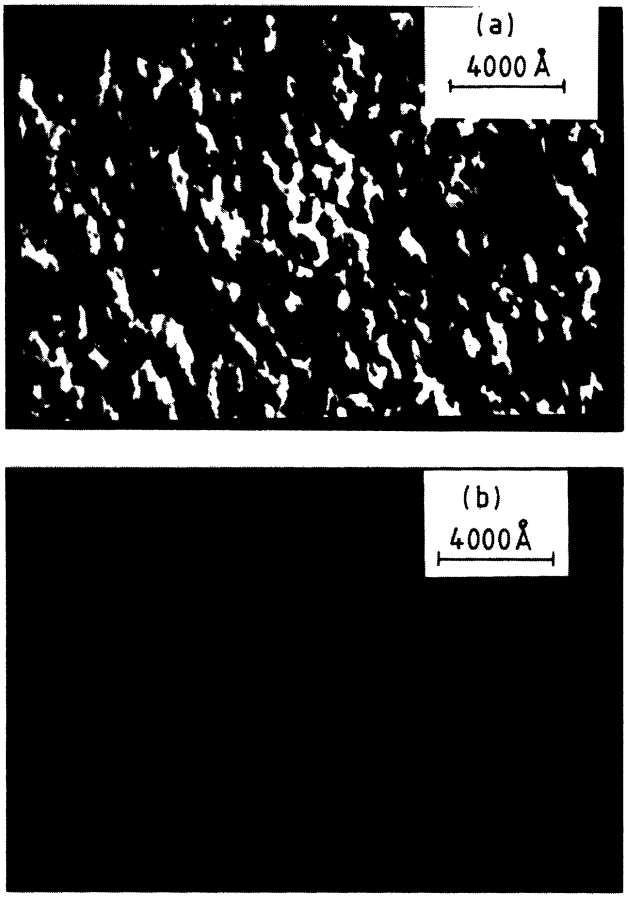

FIG. 5. Bright-field electron micrograph of (a) the as-deposited film *S*3 (cf. Table I) and (b) film *S*3 annealed at 340 °C. Notice the remarkable difference in structural inhomogeneity.

tribute to hopping conduction. It is known[6,7,8] for pure *a*-Si or *a*-Ge that T_0 increases with annealing or remains constant. Attendant herewith, the DB density decreases with annealing. Our pure *a*-Si film *S*1 exhibits such behavior (for simplicity, we will only refer to He-ambient data). On the contrary, films *S*2 and *S*3, when annealed at 340 °C, exhibit a strong overall increase of σ while T_0 decreases by about a factor of 3. At first sight, this increase would indicate that defects are created with annealing at 340 °C. However, ESR measurements show that the DB density decreases with annealing and no other ESR signals were observed. Regarding this, it is known that the H atoms present in *a*-Si:H deposited at RT are distributed quite inhomogeneously.[17] Upon annealing, a first peak in the hydrogen-evolution rate occurs at $T_A \approx 320$ °C, corresponding to the release of H_2 from polysilane $(SiH_2)_n$, which exists predominantly in the intercolumnar regions. At $T_A \approx 600$ °C, a second peak emerges corresponding to the release of atomic H from isolated $=SiH_2$ sites.[17] It is quite likely that the drastic change of σ at $T_A \approx 340$ °C corresponds to the release of H_2 from $(SiH_2)_n$ regions concurrent with the reconstruction of the amorphous matrix (cf. Fig. 5) since film *S*2, when annealed at 247 °C, does not show such changes. Two possible explanations may be offered. Firstly, the increase of σ and the decrease of T_0 are solely ascribed to structural changes—from inhomogeneous to more homogeneous—of the film, and no new defects (certainly not usual DB's) are created; hopping conduction is facilitated by the homogeneous structure. Annealing then at higher temperatures, e.g., 450 °C, may now again lower σ and increase T_0 as a result of the overall decrease of N_s. Indeed, annealing film *S*2 at 450 °C increases T_0 from 7.25×10^7 to 1.87×10^8 K which, according to Eq. (2), agrees perfectly with the decrease of N_s from 4.5×10^{18} cm^{-3} at $T_A = 340$ °C to 2.2×10^{18} cm^{-3} at $T_A = 450$ °C. The second possibility is that the only effect of H_2 outdiffusion is that it leaves new defects which contribute to hopping conduction. Upon annealing at 450 °C, these new defects are eliminated and T_0 is dominated again by DB's (cf. Table II, film *S*2). However, as exemplified by Fig. 5, annealing at 340 °C does not simply release H_2 from $(SiH_2)_n$ chains but causes a total reconstruction of the film. We do expect the defect density to decrease with such a reconstruction process as N_s indeed indicates. Therefore, we believe that no new kind of defect—ESR active or not—is created at $T_A = 340$ °C, certainly when considering that it has to be totally annealed out already at 450 °C.

Obviously, in the first explanation, *structural inhomogeneity does not only influence* σ_0, *but also* T_0, which is revealed by the decrease of T_0 at $T_A = 340$ °C. This shows that a small uncertainty in T_0 (e.g., factor of 2) caused by structural changes may result in a significant deviation in σ_0 which makes σ_0 unreliable for theoretical prediction within the "homogeneous" hopping model. The simultaneous increase of σ and decrease in N_s may be well understood. ESR measures all spins no matter whether they prevail isolated or not, whereas σ (and T_0) is only sensitive to those DB defects in the tightly connected regions. Thus, only N_s of a *homogeneous* film reflects the quantity $N(E_F)$ occurring in (2). Isolation of certain regions could arise from structural inhomogeneity, but also from chemical inhomogeneity. For example, the prevailing $(SiH_2)_n$ chains might function as good "insulations." Hence, upon annealing at 340 °C, while σ increases because the effective defect concentration increases (i.e., isolated domains get connected and contribute to conductivity), the total spin concentration (N_s) may decrease. We believe that the presence of H atoms helps homogenizing the film upon annealing because they can release strain.

We thus find that our results are consistent with associating the DB centers with the major hopping centers. However, they also indicate that it is not only the total number of prevailing defect centers which determines the conductivity behavior; the influence of homogeneity on both σ_0 and T_0 cannot be ignored. Since the usual $T^{-1/4}$ hopping mechanism has been derived only for a homogeneous system, it is not surprising that no direct parameter influenced by the samples's inhomogeneity can be traced back in the σ_0 and T_0 expressions.

B. The ambient effect

1. *Measurement-induced artifacts*

Before addressing the physical aspects of the ambient effect, it should be carefully checked on possible artifacts. Firstly, the quality of the contacts applied was checked. Two kinds of electrical contacts, i.e., silver paint and evaporated Al layers, were employed which were several times removed and replaced. No differences in the ambient effect were ever observed. Experiments were repeated both in vacuum and He ambient using different electric field strengths, up to 100 V cm^{-1}. The contacts are ohmic over the whole T range covered, which means that the contacts form good electron reservoirs. The ambient effect is thus not due to any field effect, such as, e.g., the Poole-Frenkel effect. Besides, there is no reason for any change in the contact quality with ambient condition. The Al contacts function as good protective layers which prevent gas penetration towards the metal-semiconductor interfaces. Mechanical change of the system with pumping is totally irrelevant since a change in vacuum from 10^{-2} Torr to 5×10^{-2} Torr can almost totally destroy the extra conductivity observed in vacuum at 77 K. Such a tiny pressure change can hardly be conceived as a source of mechanical distortion.

Possible temperature gradients between the thermocouple and the film were also found irrelevant. Both the thermocouple and film are situated on the same copper block enclosed with a copper capsule. Thermal transport is mainly by means of radiation and direct contact with the copper block. The temperature gradient, if any, is thus expected to be the same in vacuum and gas ambient. If insinuating the existence of a larger temperature gradient in vacuum than in He ambient as a possible explanation for the σ deviation, a temperature difference between the thermocouple and the film as large as 30 K would be needed in vacuum, which is quite unrealistic. Besides, the temperature gradients needed to bring the curved logσ versus $T^{-1/4}$ plot in vacuum back to a straight line are quite different from sample to sample. This is impossible for a quite reproducible result obtained on one film remounted several times in the same setup.

2. *The origin of the ambient effect*

Apparently, since the presence of gas atoms in the voids can alter the bulk conductivity, as concluded previously, this change must be related with conduction via internal surfaces. Various possibilities have been considered. Firstly, one could consider a change in the (local) phonon spectrum induced by gas atoms. This, however, is easily excluded as any strong coupling between void surfaces and He atoms is hardly conceivable. Moreover, as has already been evidenced, the influencing gas atoms are not adsorbed on the void surface. Scattering of gas atoms does not introduce new modes of vibration. Secondly, there is the possibility of a phonon-bottleneck situation. Supposing that phonons cannot lose their energy obtained via the charge carriers from the electric field efficiently to the thermal bath without the presence of gas atoms, then σ in vacuum at low temperature would depend on the electric field strength employed. As mentioned before, this is not the case. Finally, band bending effects also seem quite unlikely, mainly because the high N_s value would not allow any significant Fermi level shift. Furthermore, it is hard to see how inert gas atoms such as He could induce band bending.

Instead, we suggest that the usual hopping conduction mechanism via defect states located in the bulk of the *a*-Si(:H) (i.e., the dense film regions) is paralleled by a second (hopping) conduction path,[16] such as tunneling across the microvoids. Supposing that the conductivity in vacuum σ_v is given as

$$\begin{aligned}\sigma_v &= \sigma_{\text{bulk}} + \sigma_a \\ &= \sigma_0(1)\exp\{-[T_0(1)/T]^{1/4}\} \\ &\quad + \sigma_0(2)\exp\{-[T_0(2)/T]^{1/4}\}\ ,\end{aligned} \tag{4}$$

where $\sigma_{\text{bulk}}[\sigma_0(1),T_0(1)]$ and $\sigma_a[\sigma_0(2),T_0(2)]$ pertain to the ordinary hopping and second conduction path, respectively, curve fittings were performed with $\sigma_0(1)$, $T_0(1)$, $\sigma_0(2)$, and $T_0(2)$ as parameters for both the as-deposited and annealed samples. The best fits, represented by the solid lines in Figs. 1, 2, and 3, were obtained with the values given in Table II. Although the best fit was looked for with all possible values of the four fitting parameters, all $\sigma_0(1)$ and $T_0(1)$ came out nearly equal to the σ_0 and T_0 values measured in He gas ambient except for annealed film *S*1, most likely due to the very small region at high temperatures where the $T^{-1/4}$ law is followed in vacuum which causes uncertainty in fitting. This fitting result supports the two paths conduction model and suggests that the second conduction mechanism obeys the $T^{-1/4}$ law too, which is consistent with the tunneling process across microvoids.[18–20] Also, the magnitudes of the $T_0(2)$ values are in agreement with the tunneling model.[18–20] Clearly then, the effect of gas atoms (ambient) is to diminish the second hopping mechanism; the mechanism via which this occurs, however, is not yet fully understood. Presumably, the inelastic scattering of electrons at gas atoms plays an important role. The tunneling electron might exert its electric field on the gas atoms since all these have a finite atomic polarizability. By losing energy to gas atoms, tunneling through the voids becomes impossible since the Fermi levels are equal on "opposite" sides of the void surfaces.

V. CONCLUSION

It has been found that in agreement with previous work, the $T^{-1/4}$ law is generally obeyed in defective *a*-Si and *a*-Si:H. The bulk hopping conductivity mechanism accounts extremely well for the observed σ behavior over many temperature decades; perfectly straight lines are found on the logσ versus $T^{-1/4}$ plot when measured in He ambient. However, in inhomogeneous films—as studied in the present work—electron tunneling through voids may occur when measured in vacuum, in addition to the bulk hopping conduction. At low temperatures ($T<160$ K), this void-tunneling conduction results in an "upward" deviation of the logσ versus $T^{-1/4}$ plot measured in vacuum compared to the He-ambient situation.

This offers an explanation for the similar upward bendings observed on various occasions previously.

It has been demonstrated that the T_0 value in the $T^{-1/4}$ law does not only depend on $N(E_F)$, but also on film structure. This is revealed by the behavior of T_0 with annealing. It was observed that T_0 decreases with a factor of 3 after annealing at 340 °C, whereas N_s decreases. This is in contradiction with theories supposing a homogeneous structure. It was pointed out that although the structural influence on T_0 itself is not dramatic, it has a pronounced influence on σ_0 through its influence on T_0; this makes σ_0 unreliable for theoretical predictions if structural influence is not included in the theory.

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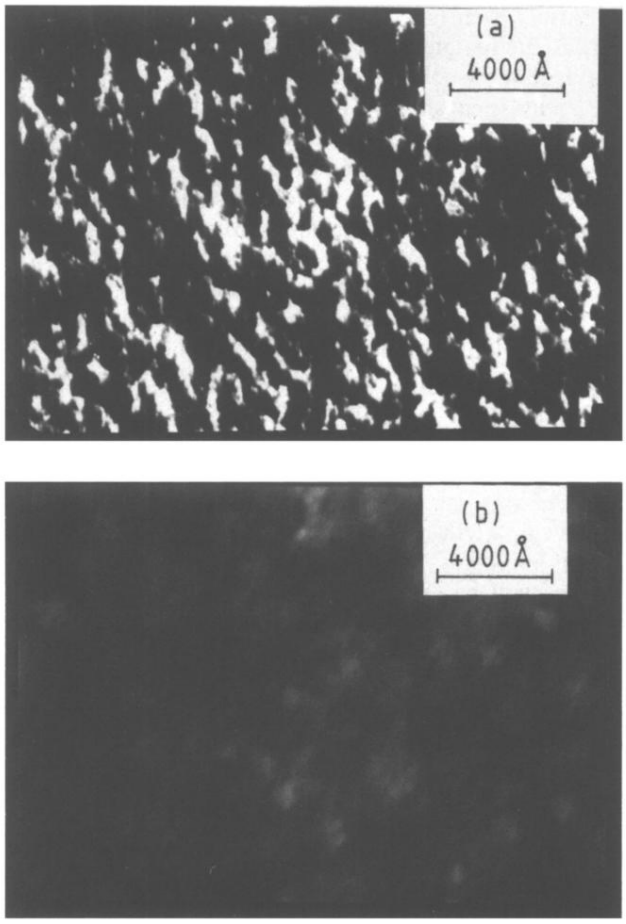

FIG. 5. Bright-field electron micrograph of (a) the as-deposited film *S*3 (cf. Table I) and (b) film *S*3 annealed at 340 °C. Notice the remarkable difference in structural inhomogeneity.