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On the Variation of Hopping Transport in Amorphous Silicon with Preparation Conditions

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The *dc* conductivity of amorphous silicon prepared by two successive ion bombardments at different temperatures has been measured as a function of temperature. The results may be expressed in terms of a generalized hopping formula $\sigma=\sigma_0 \exp[-(T_0/T)^n]$ where the parameter set $\{n, T_0, \sigma_0\}$ varies with the irradiation conditions. In particular, the hopping exponent has been found to assume the limiting values of $n\sim 1/4$ at irradiation temperatures of $T_i \lesssim 100\,\mathrm{K}$ and of $n\approx 1/2$ at $T_i \gtrsim 500\,\mathrm{K}$, whereas intermediate values of n have been observed for temperatures inbetween. It is concluded that thermally activated redistribution processes of radiation defects control the final state of disorder in the irradiated samples, which in turn determines the particular hopping characteristics. Within the framework of existing theories the two limiting cases can be explained to be due to a disordered solid of homogeneous and granular structure, respectively.

Introduction

There have been two different approaches to the controlled variation of hopping conductivity in amorphous silicon (*a*-Si):
1. conventionally prepared amorphous films are subjected to a postdeposition bombardment with energetic ions [1, 2];
2. crystalline silicon (*c*-Si) is first bombarded with Si ions beyond the amorphisation threshold dose and then reirradiated for modification of the amorphous structure [3-6].
While samples obtained by the first approach have usually exhibited hopping conductivities obeying a $n\sim 1/4$ law in both the as-deposited and postbombarded state, the second procedure has yielded $n\sim 1/2$ characteristics for all cases studied so far. The concomitant two other parameters T_0 and σ_0 differ by orders of magnitude.
This controversial situation may have the simple reason in that the amorphous films as obtained by the two different processes are not in the same state of structural disorder, i.e. the idea of a uniquely defined amorphous phase only differing in the concentration of certain structural defects cannot be maintained. Recently we have shown that reirradiation of ion bombarded amorphous silicon at elevated temperatures gives rise to a very strong modification of the *dc* conductivity [4]. So the obvious question to ask is what the result of a low temperature reirradiation will be.
It is the purpose of this paper to show that silicon films prepared under different temperature conditions exhibit widely varying transport properties including those previously thought to be typical for evaporated or sputtered specimens only.

Experimental

Since the experimental procedures have remained the same as reported previously [3-6], a rather short description of the basic points is in order:
material: 0.6 μm *c*-Si (silicon on sapphire);

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amorphisation: a total dose of about 4×10^{15} Ne/cm^2 at selected energies to amorphize the entire sample;
modification: $0.3-3 \times 10^{15}$ Ne/cm^2 into a depth of about up to 0.1 μm at temperatures between 15–700 K;
contacts: evaporated Al strips with a 2 mm gap in-between;
measurements: *dc* conductivity in the temperature range from 14 to 300 K.
Irradiations with Ne ions, obtained at the required specifications more easily, were found to lead to the same results as obtained with Si ions.
The *dc* conductivity data have been analyzed by following the procedure introduced by Hill [7] which has been used in our previous work also [4, 6]. The important point of this method is that no a-priori assumptions on physical quantities such as the gap state density distribution have to be made which would fix the hopping exponent n of the relation

$$\sigma = \sigma_0 \exp[-(T_0/T)^n]. \quad (1)$$

Instead, by calculating the local activation energies ΔE at each temperature point T from

$$\Delta E = -d(\ln \sigma)/d(1/kT), \quad (2)$$

and by plotting $\log(\Delta E)$ vs. $\log(1/kT)$ the correct exponent n is determined first and the other characteristic parameters T_0 and σ_0 thereafter. It is very important to keep the errors involved in the extraction of n as small as possible, since the further evaluation of T_0 and σ_0 depends on this quantity sensitively. The precision of the n values reported here is about $\delta \sim \pm 0.03$ on average.

Results

Figure 1 summarizes our results in terms of five physical quantities as a function of the irradiation temperature T_i at which the modification of the amorphized samples was performed. In addition to the characteristic hopping parameter set $\{n, T_0, \sigma_0\}$ the values of the conductivity and local activation energy at the reference temperature of 100 K are given by σ_{100K} and ΔE_{100K}. The dashed line at $T_i = T_c$ separates two regimes of different qualitative behavior of the *a*-Si films towards a modification bombardment. Below T_c a reirradiation leads to a new saturation value in conductivity after a certain threshold dose has been exceeded. The data shown in Fig. 1 for $T_i < T_c$ refer to samples in the saturation state of disorder. In the temperature regime of $T_i > T_c$ this saturation effect is not observed. Instead, the

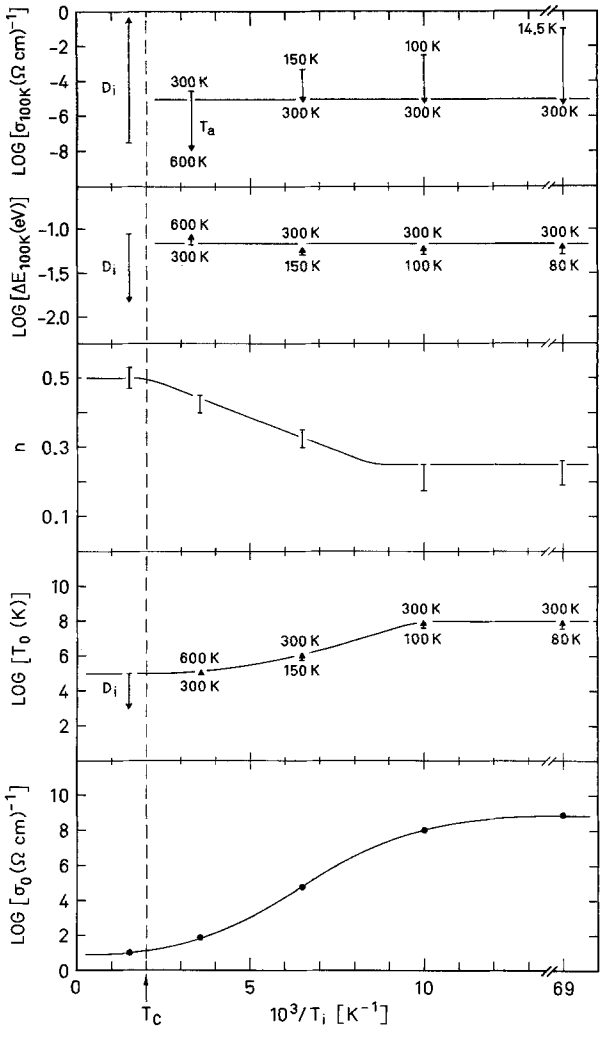

Fig. 1a–e. The sections from top to bottom, labelled (a)–(e) in the text, display the dependence of the following five quantities on the temperature T_i of a modification irradiation of *a*-Si:
a σ_{100K} = conductivity at 100 K; **b** ΔE_{100K} = activation energy at 100 K; **c** n = hopping exponent in a T^{-n} relation; **d** T_0 = characteristic activation temperature; **e** σ_0 = conductivity prefactor. T_c denotes a temperature critical for the modification behavior of the *a*-Si film; D_i indicates the dependence on dose at $T_i > T_c$, and T_a the effect of annealing in the regime $T_i < T_c$

conductivity continues to change with the level of the applied ion dose D_i in a complex pattern which has been discussed in two papers recently published [5, 6]. These latter results have been included for the purpose of a discussion within a larger context.
Turning to the low temperature reirradiation first we note from Fig. 1(a) that σ_{100K} depends on T_i significantly. Annealing to $T_a = 300$ K, however, removes these individual differences and results in very nearly the same conductivity level for all specimens, as the arrows and the horizontal line indicate. This fact is quite remarkable in view of the conductivity changes by several orders of magnitude.

Comparatively little dependence on T_i is seen with the local activation energies which remain to be about the same at a slightly increased common level, as indicated in Fig. 1(b) by the full line, at about $\Delta E = 60\,\text{meV}$.

This situation changes with approaching the hot modification regime at $T_i \gtrsim T_c$. Here, depending on dose D_i, ΔE can very considerably, and the same is true for σ.

Whereas the data displayed in Sect. (a) and (b) of Fig. 1 are "direct" in the sense that no model assumptions have had to be made, this is different for the rest of the data of Fig. 1 which display the hopping parameter set $\{n, T_0, \sigma_0\}$ as derived on the basis of the generalized hopping formula of (1) and the definition of the activation energy given by (2).

The hopping exponent n is seen to assume the asymptotic limits of 1/2 and 1/4 in the high and low temperature limits, respectively. In the relatively broad transition region between about 100–500 K intermediate values of n are observed. The concomitant changes in T_0 and σ_0 amount to many orders of magnitude. It is quite remarkable that n and σ_0 remain unaffected by annealing treatments, whereas T_0 changes by up to about a factor of 2. Very strong decreases in T_0 are observed in the hot modification regime at $T_i > T_c$, where σ_0 remains nearly constant and also n, as reported before [6]. In total, the observed hopping parameters strongly depend on the preparation conditions and it is natural to ask what the corresponding microscopic changes in the amorphous structure might be.

Discussion

It is relevant to stress that two limiting forms of hopping transport have been observed at high and low reirradiation temperatures in *a*-Si prepared by ion bombardment. Using the generalized method of analysis as given by (1) and (2), we find that they can be characterized by hopping exponents of $n \sim 1/4$ and $n \sim 1/2$, respectively.

The theory of Mott [8], derived on the assumption of an amorphous body with a gap state distribution homogeneous in space and energy, predicts $n = 1/4$. This behavior has frequently been observed for evaporated and sputtered films. So far, however, no satisfactory explanation has been given as regards the experimental prefactor σ_0 which usually exceeds the theoretical value by many orders of magnitude. We like to emphasize that our low temperature modification process yields material which very much resembles conventionally prepared material and gives an independent additional corroboration of this fact.

The electrical transport parameters of the high temperature modificaton of our *a*-Si have been interpreted [6] within the framework of the theory by Abeles and Sheng [9] which describes the conduction characteristics in a granular disordered system consisting of conductive islands in an insulating matrix. We have proposed that voids in the disordered network of *a*-Si play a similar role as the metallic grains in the cermet systems do.

This state of affairs leads to the question, what the basic processes are which control the formation of different states of structural disorder. In case of ion bombardment radiation defects are introduced. The situation is complex, since these primary defects can interact with each other and form secondary defect species. This process is known to be temperature dependent in general, as different defects have individual activation energies as regards diffusion and dissociation processes.

Turning back to the data of Fig. 1, we note that at $T_i \sim 100$–$150\,\text{K}$ a correlated change in the characteristic hopping parameters takes place. Since it is known that the monovacancy in its neutral charge state becomes mobile at about 150 K [10], it appears quite natural to invoke this mechanism for these effects also. Within this picture, vacancy agglomerates of higher degree can be formed as a result of the monovacancy diffusion; at higher modification temperatures other simple point defects, e.g. divacancies etc., dissociate and the resulting monovacancies may be captured by defect clusters of sufficient thermal stability [11]. At the point where $n = 1/2$ is observed, only large clusters, "microvoids", would remain.

Conclusions

Ion bombardment techniques can be used to modify the defect structure of *a*-Si in a controllable way. Vacancy motion is inferred to play an important role in determining the type of defect structure. By low temperature modificaton treatments a homogeneously disordered solid is obtained, whereas high temperature reirradiation produce films of granular structure. Some, but not all features of this interpretation are supported by theories of Mott [8] and of Abeles and Sheng [9], respectively, while previously existing discrepancies, e.g. the σ_0 problem for the case of $n = 1/4$ hopping, still persist.

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