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Hopping mechanism of electric transport in intrinsic and p-doped nanocrystalline silicon thin films

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Abstract

The effect of temperature and applied electric field on transport properties of intrinsic nanocrystalline silicon thin films as well as p type doped with boron prepared by VH-PECVD have been studied. The conductivity of all samples, as a function of the exponential of $T^{-1/4}$ measured at intermediate fields, presented a linear behavior in all the temperature ranges studied (270–450 K). Following the method proposed by Godet [C. Godet, J. Non-Cryst. Solids 299–302 (2002) 333], a linear relationship between the conductivity prefactor (σ_{00}) and the characteristic temperature (T_0) of Mott's law was obtained for a group of quite different materials. From this, and using classical equations of Percolation Theory, the density of states near the Fermi level, the range of hopping, the activation energy for hopping, and the localization parameter were calculated. At low applied fields, dark conductivity becomes field dependent. The non-ohmic behavior of the conductivity observed is analyzed in terms of the hopping transport equations.

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1. Introduction

Recently, nanocrystalline semiconductor materials have reached great interest because of their potential application in optoelectronic devices [1]. Among them hydrogenated nanocrystalline silicon (nc-Si:H) has risen as a promising material in the developing of solar cells thin films technology [2,3].

The electronic transport depends in general on the density of states (DOS), the position of the Fermi level, the temperature and the applied field (F) [4,5]. The tunneling transition of electronic carriers from occupied to unoccupied states involves one or more phonons, and is called 'hopping'. When both the number of phonons and the energy decrease, the hopping between states that are closer in energy (even if they are wider spaced) becomes more preferable than that between the nearest neighbors whose energies differ substantially. This mechanism is known as variable range hopping (VRH) conductivity, or Mott's conductivity.

Mott [6] has established for the VRH of single phonon transitions a dependence of conductivity (σ_d) with temperature (T) as $T^{-1/(d+1)}$, d being the hopping space dimensionality. In the case of three dimensions, the conductivity may be stated as

$$\sigma_d = \sigma_{00} \exp[-(T_0/T)^{1/4}], \tag{1}$$

where σ_{00} and T_0 are material dependent constants. This behavior is observed in a large number of thin film materials and not only at low temperature and constant DOS, as was the original Mott and David's prediction [4], but up to 1000 K as occurs with some polymers. Furthermore, as Godet [7] has exposed, values of estimated Fermi level DOS from Mott's hypothesis have been much lower than calculated values from independent experiments. So, the hypothesis of a constant DOS (i.e., non-dependent of energy) near the Fermi level must be revised.

Different models have been proposed to understand the electronic transport in disorder semiconductors as well as for nc-Si:H. The differences are based on the set

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of variables considered by the authors, or the particular interest in studying the effect of the structural or electronic properties on the conductivity, like crystalline volume fraction or DOS respectively.

Hapke et al. [8] found evidence that transport in nanocrystalline silicon with low crystalline volume fraction ($X_c < 20\%$) is dominated by transport through crystalline percolation paths. They concluded that the grain boundary trapping-model alone could not explain the electronic properties of nc-Si:H, but tunneling processes through the barriers have to be considered. It was also states by the German group [9] that the percolation model is able to explain qualitatively the changes of conductivity as function of X_c and its temperature dependence in highly doped films. In that model, the transport takes place along percolation paths formed by crystalline regions. Kočka et al. [10] assume that a barrier formed at large grain boundaries limits band-like transport, and the dominant transport path is shifted down to hopping through tail states below the mobility edge (E_c).

All the models discussed above, and a lot more existing in the literature, do not state clearly when or why the electronic transport mechanism follows the Mott's model. Godet [7] showed that for a given range value of localization parameter (LP) (10^{-5}–1) and if monophonic VRH is the predominant transport mechanism, for an exponential DOS energy dependence, a linear correspondence between $\ln(\sigma_{00})$ and $T_0^{1/4}$ must exist. However, as Moustafa et al. [11] have pointed out, the apparent linear temperature dependence of $\ln(\sigma_{00})$ and $T_0^{1/4}$ does not relate to conduction by VRH of carriers in the band of localized states near de Fermi level.

The pre-exponential factor σ_{00} and the characteristic temperature T_0 are related to the density of localized states $N(E_F)$ and the wave function decay constant γ associated with these states. Using classical Percolation Theory [4], the characteristic Mott temperature in three dimensions can be estimated by

$$T_0 = \frac{c^4\gamma^3}{k_B N(E_F)}, \tag{2}$$

where c is a number in the range 1.84–2.28 [12] or may reach a maximum of $c^4 = 310$ [7]. Determining experimentally the T_0 value from Eq. (1), $N(E_F)$ may be calculated by adjusting the localization radius $(1/\gamma)$. This length typically varies in the range 3–30 Å [7].

The expression for the range of hopping and the activation energy for hopping in three dimensions are given by

$$\mathrm{Rhop}(T) = \frac{3}{8} T_0^{1/4} T^{-1/4} \left(\frac{1}{\gamma}\right) \tag{3}$$

and

$$\mathrm{Whop}(T) = k_B (T_0 T^3)^{1/4}. \tag{4}$$

In this paper we present results of dark conductivity measurements of intrinsic and Boron-doped nc-Si:H, in a broad range of applied field and temperature. The validity and limitations of the VRH formalism as a main transport mechanism is analyzed for this particular group of materials.

2. Experimental

The films were prepared on Corning 7059 glass through very high frequency plasma enhanced chemical vapor deposition (VH-PECVD) in a reactor and condition deposition described elsewhere [13]. The reactant gas used for intrinsic films was SiH_4, highly diluted with H_2. Diborane gas was added to prepare the p-doped films. Silane flow related to the total gas flow was varied between 2% and 6% for intrinsic films, and 6% was used for the p-doped ones. Diborane flow related to the total gas flow was in the range of $1.5\times10^{-4}\%$ to $6.0\times10^{-2}\%$ for the p-doped films. Intrinsic samples are indicated as 'IN' being $N = 2$, 3, 4, 5 and 6, corresponding to the value of silane flow (%) used in the deposition, and p-doped samples as 'PM' being $M = 15$, 30, 60, 100, 180, 750, 3000, 4500 and 6000, according to the value of 10^5 times the diborane flow (%).

Deposition rate of the films of both sets of samples was in the range 0.5–1.0 Å s^{-1}, and the thickness varied from 400 to 670 nm.

Lateral dark conductivity (σ_d) of the films has been calculated from current–voltage measurements made in a cryostat in the range of 270–450 K. A coplanar configuration of two graphite paint electrodes 0.1 cm apart was used for obtain I–V curves at a varying applied field in the range 0.1–10^3 V/cm.

3. Results and discussion

At room temperature the intrinsic nc-Si:H films show great variation of σ_d with silane flow with the maximum conductivity at room temperature for sample I2 (1.5×10^{-3} $\Omega^{-1}\,\mathrm{cm}^{-1}$) and dropping to negligible values for sample I6 (4.7×10^{-10} $\Omega^{-1}\,\mathrm{cm}^{-1}$) which behavior is similar to that of an amorphous material. σ_d of doped films also presents a great variation with diborane flow: 5.5×10^{-9}–1.1 $\Omega^{-1}\,\mathrm{cm}^{-1}$. Both sets of samples also present very different crystalline volume fraction (see Table 2) and grain size (see Ref. [13]).

Fig. 1 shows the obtained values of σ_d for an applied field of 10 V/cm for intrinsic (Fig. 1(a)) and doped (Fig. 1(b)) films. The data can be fitted by Eq. (1). Values of σ_{00} and T_0 are obtained from those figures. Following Godet's model [4,7], which states that if predominant

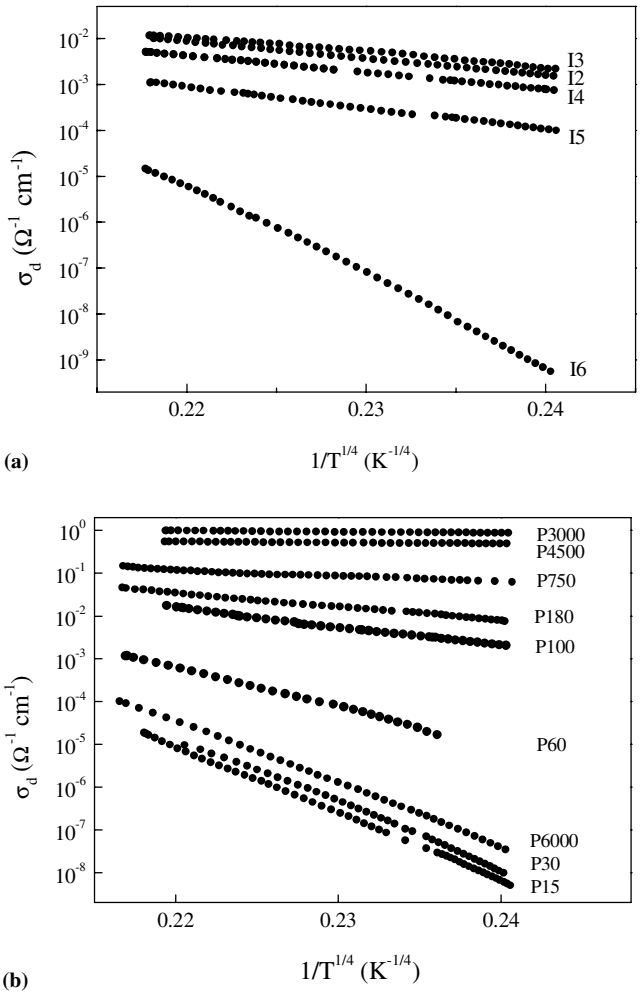

Fig. 1. Dark conductivity versus $T^{-1/4}$ for (a) intrinsic and (b) p-doped nc-Si:H films for an applied field of 10 V/cm in the range 270–430 K.

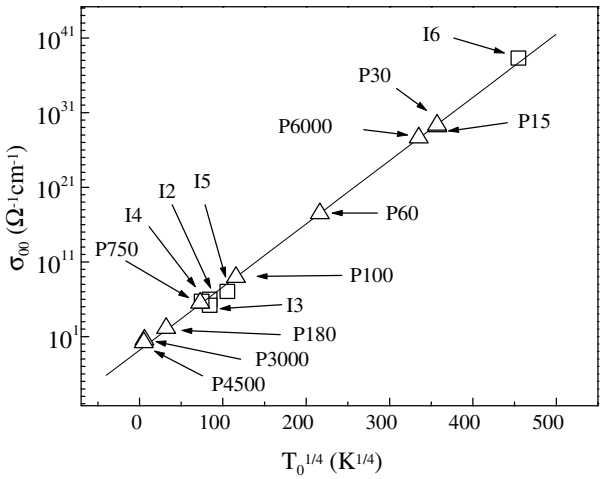

Fig. 2. Parameters σ_{00} versus $T_0^{1/4}$ for intrinsic (□) and p-doped (△) nc-Si:H films. Straight line is a linear fitting.

electric transport mechanism is a VRH and DOS near the Fermi level is an exponential function of energy, then there should be a linear relation between $\ln(\sigma_{00})$ and T_0. Values of $\ln(\sigma_{00})$ versus T_0 for intrinsic and p-doped c-Si:H films are plotted in Fig. 2. There is a unique linear relation for all the films of both sets of samples even when structural, optical and transport properties of the films are quite different and for values of σ_{00} and T_0 varying more than 38 and 9 orders of magnitude respectively. The values of σ_{00} and T_0 as well as those of $N(E_F)$, Rhop and Whop calculated with a mean value $c = 2$ and $(1/\gamma) = 10$ Å are listed in Tables 1 and 2 for intrinsic and p-doped samples respectively.

From Table 1 we can see that sample I6 has a LP value out of the range 10^{-5}–1, and very high values of

Table 1
Values of DOS and hopping parameters calculated from Eqs. (2)–(4) for intrinsic nc-Si:H films

Sample	σ_{00} (Ω^{-1} cm^{-1})	T_0 (K)	$N(E_F)$ (eV^{-1} cm^{-3})	Rhop (cm) at 273 K	Whop (eV) at 273 K	LP (eV^{-1})
I2	1.0×10^{6}	5.1×10^{7}	4.6×10^{18}	7.8×10^{-7}	0.49	4.4×10^{-3}
I3	1.5×10^{5}	5.1×10^{7}	4.6×10^{18}	7.8×10^{-7}	0.49	4.6×10^{-3}
I4	5.1×10^{5}	3.1×10^{7}	7.4×10^{18}	6.9×10^{-7}	0.43	7.4×10^{-3}
I5	1.1×10^{7}	1.2×10^{8}	1.9×10^{18}	9.7×10^{-7}	0.61	1.9×10^{-3}
I6	2.0×10^{38}	4.3×10^{10}	5.4×10^{15}	4.2×10^{-6}	2.6	5.4×10^{-6}

Table 2
Values of DOS and hopping parameters calculated from Eqs. (2)–(4) for p-doped nc-Si:H films

Sample	X_c (%)	σ_{00} (Ω^{-1} cm^{-1})	T_0 (K)	$N(E_F)$ (eV^{-1} cm^{-3})	Rhop (cm) at 273 K	Whop (eV) at 273 K	LP (eV^{-1})
P15	52	1.3×10^{29}	1.6×10^{10}	1.4×10^{16}	3.3×10^{-6}	2.1	1.4×10^{-5}
P30	40	2.2×10^{29}	1.6×10^{10}	1.4×10^{16}	3.3×10^{-6}	2.1	1.4×10^{-5}
P60	37	3.2×10^{17}	2.2×10^{9}	1.1×10^{17}	2.0×10^{-6}	1.3	1.1×10^{-4}
P100	38	9.2×10^{8}	1.8×10^{8}	1.1×10^{18}	1.1×10^{-6}	0.67	1.1×10^{-3}
P180	40	3.2×10^{5}	2.8×10^{7}	8.2×10^{18}	2.9×10^{-6}	0.42	8.2×10^{-3}
P750	56	1.4×10^{2}	1.0×10^{6}	2.2×10^{20}	6.7×10^{-7}	0.19	2.2×10^{-1}
P3000	82	3.8	1.4×10^{3}	1.7×10^{23}	2.9×10^{-7}	0.035	1.7×10^{2}
P4500	70	1.7	6.8×10^{2}	3.4×10^{23}	4.7×10^{-8}	0.030	3.4×10^{2}
P6000	12	4.2×10^{27}	1.3×10^{10}	1.8×10^{16}	3.1×10^{-6}	1.9	1.8×10^{-5}

Whop and Rhop. Comparing this sample with the rest of the intrinsic ones, it is clear that I6 has not a VRH as the main transport mechanism.

In Table 2, the hopping parameters of a group of nine p-doped nanocrystalline thin films are shown. As the intrinsic case, P15, P30 and P6000 have unreasonable high values of the hopping energy and length, besides their LP is within the expected range. On the other hand, samples P3000 and P4500 have LP out of range and present non-acceptable values of Rhop and Whop.

For the rest of the samples the value of T_0/T, which represents the degree of disorder [12] is directly related to the value of X_c of the doped samples as was expected (Table 2). Also value of $N(E_F)$ calculated from T_0 for sample P60 ($\sim 10^{17}$ $eV^{-1}\,cm^{-1}$) is in good agreement with values of DOS obtained by modulated photoconductivity technique (MPC) for this sample, being about 8×10^{16} $eV^{-1}\,cm^{-1}$ [14], within the experimental errors and in addition, P60 has an exponential DOS.

Dark conductivity of p-doped films was also measured for an applied field varying in the range 0.1–10^3 V/cm at different temperatures. As field dependence of σ_d is quite similar for all the samples, only the results for sample P60 are presented in Fig. 3. Two different dependence regions appear. For very low fields ($F < 1$ V/cm) a non-ohmic behavior is present, while for intermediate fields up to $\sim 10^3$ V/cm, non F dependence of σ_d is detected.

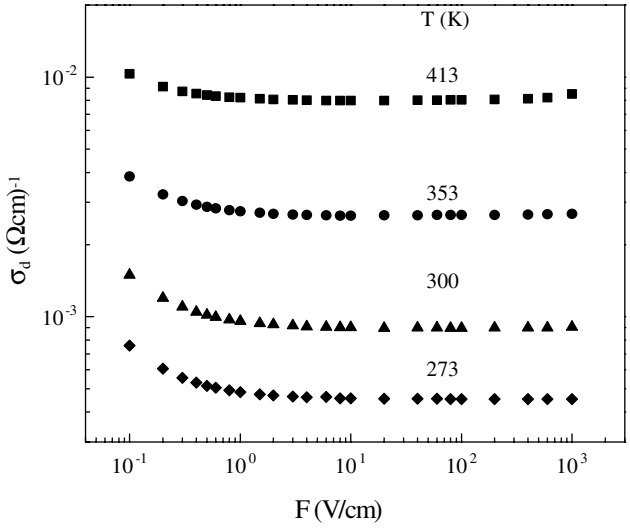

Fig. 3. Dark conductivity versus electric field measured at different temperatures for sample P100.

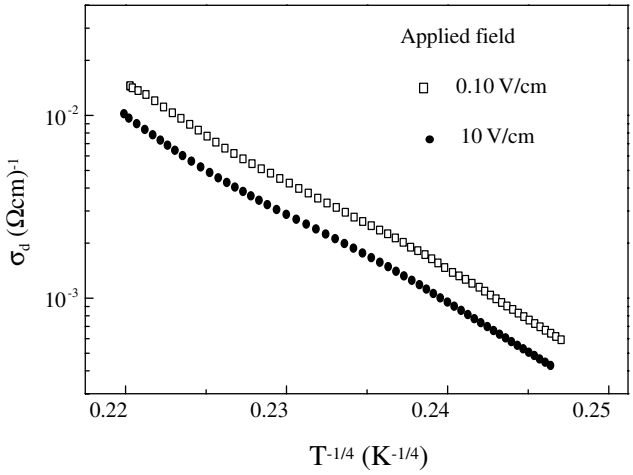

Fig. 4. Parameters σ_{00} versus $T_0^{1/4}$ for the sample P100 for a low (□) and an intermediate (●) value of the applied field F.

Curves of $\ln(\sigma_d)$ versus $T^{-1/4}$ for 0.1 and 10 V/cm are shown in Fig. 4. By a linear fitting, values of prefactor and characteristic temperature were obtained, as well as the hopping parameters presented in Table 3. T_0 value calculated for $F = 0.1$ V/cm is the same within the experimental error as the one calculated before. It follows that the main hopping parameters are the same for low and intermediate fields.

The difference observed in the value of dark conductivity within the field range of 0.1–1 V/cm (Fig. 4) is due to the different values of the prefactor (Table 3). This weak dependence of σ_{00} with the temperature and the field is in agreement with the results of Apsley et al. [15] and Godet et al. [16], who pointed out that σ_{00} may vary within a factor of 2 for low and intermediate fields.

Summarizing from the data contained in Tables 1–3, we interpret that samples I1 to I5 and P60, P100, P180 and P750 could have a VRH as the main transport mechanism.

4. Conclusions

The σ_d measurements of nanocrystalline silicon thin films reveal that beside they have a wide range of structural, morphological, optical, and electric properties, all of them follow the Mott's equation and the Godet's relationship [$\ln(\sigma_{00})$ linear with $T_0^{1/4}$], but it is not possible to assure that in the range of temperature and field studied, the VRH represents the main trans-

Table 3
Values of DOS and hopping parameters calculated from Eqs. (2)–(4) for the sample P100 for two values of the applied field E

E (V/cm)	σ_{00} ($\Omega^{-1}\,cm^{-1}$)	T_0 (K)	$N(E_F)$ ($eV^{-1}\,cm^{-3}$)	Rhop (cm) at 273 K	Whop (eV) at 273 K	LP (eV^{-1})
10	9.2×10^{8}	1.75×10^{8}	1.1×10^{18}	1.1×10^{-6}	0.67	1.1×10^{-3}
0.1	1.9×10^{9}	1.82×10^{8}	1.1×10^{18}	1.1×10^{-6}	0.67	1.1×10^{-3}

port mechanism. These two relationships arise as a necessary but not sufficient condition. Only calculation of the whole set of hopping parameters allows us to determine in witch case the VRH holds.

Moving from low to intermediate applied fields, conductivity changes from a non-ohmic to an ohmic regime, but it seems that the hopping parameters remain constant.

Acknowledgements

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