Transport mechanism in lightly doped hydrogenated microcrystalline silicon thin films

A. Dussan[a)]
INTEC (UNL-CONICET), Güemes 3450, 3000 Santa Fe, Argentina

R. H. Buitrago
INTEC (UNL-CONICET), Güemes 3450, 3000 Santa Fe, Argentina and FIQ (UNL), Santiago del Estero 2829, 3000 Santa Fe, Argentina

(Received 22 April 2004; accepted 16 November 2004; published online 28 January 2005)

Boron-doped microcrystalline silicon films have been deposited in a plasma-enhanced chemical vapor deposition system using silane diluted in hydrogen, and diborane (B_2H_6) as a dopant gas. The temperature dependence of the dark conductivity has been measured from 120 to 420 K in all samples. In the high-temperature range above room temperature, the carrier transport is found to be thermally activated, with a single activation energy that changes with the B_2H_6 compensation degree. In the low-temperature range (300–120 K), variable range hopping (VRH) was established as a predominant electronic transport mechanism for all samples, with the exception of the sample with a diborane concentration of 12.5 ppm. A model for Mott's VRH, referred to as the "diffusional model," which yields a relation between the conductivity and the localized density of gap states, is presented. Using classical equations from the percolation theory and the diffusional model, the density of states near the Fermi level, as well as the hopping parameters, are calculated. A correlation between the hopping parameters for both models is deduced. A numerical factor that improves the value of each parameter is calculated. © *2005 American Institute of Physics*. [DOI: 10.1063/1.1848193]

I. INTRODUCTION

In recent years, hydrogenated microcrystalline silicon (μc-Si:H) has played an important role in the development of electronic devices such as solar cells, transistors and gas detectors.[1,2] The study and understanding of the transport mechanisms in this material has become a basic research topic. Numerous papers have investigated[3,4] correlations among electronic, optical, and micro structural properties with electronic transport models. However, no general theory providing an explanation for all the observed behaviors has been presented to date.

In the range of temperatures well below zero degrees centigrade, it has been reported[5] that μc-Si:H dark conductivity (σ_{dk}) does not follow a thermally activated model, which is the common case above room temperature. Different models have been proposed, but how charges respond to an electric field is still unclear.

In this paper, results on dark conductivity of microcrystalline silicon thin films lightly doped with Boron, μc-Si:H:(B), measured over a temperature range of 100–420 K are shown. Well-known theories for disordered materials, like variable range hopping (VRH),[6] were applied. It was found that the Golden Rule of fitting $\ln(\sigma_{dk})$ vs $T^{-1/4}$ to identify hopping mechanisms is a necessary but not a sufficient condition. In the case of μc-Si:H:(B), some corrections are required to find reasonable hopping parameters.

According to Mott's equation[6] for the three-dimensional case, if the density of states (DOS) is constant in a k_BT energy range around the Fermi level, the dark conductivity as a function of temperature is given by

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

where T is the absolute temperature, σ_0^* and T_0 are constants which depend on the material.

Many disordered or amorphous semiconductors and metal alloys follow this equation.[7,8] Recently, this behavior has been reported not only in the range of low temperatures and constant DOS, as it was originally predicted by Mott and David,[9] but also at high temperatures and for materials with a nonconstant DOS around the Fermi level.[10,11] Different kinds of functions can be proposed for the DOS in the gap and the band tails of these semiconductors. This point, however, will not be considered in this paper.

All the lightly doped microcrystalline silicon samples follow Mott's equation at low temperatures. Following the classical percolation theory, the characteristic hopping parameters, and the distance between states and energy differences were calculated. Results were in disagreement with the expected range of values. Therefore, we developed a "diffusional model" considering the Einstein relation, conductivity, diffusion coefficient, and hopping probability, which can be correlated with the percolation model equations to provide a method for the adoption of the correct numerical coefficients of both models.

a)Electronic mail: adussanc@intec.unl.edu.ar

II. FUNDAMENTAL THEORIES FOR VRH

A. Diffusional model

Considering a VRH regimen, it can be proposed that the carriers move in a diffusive way and have a diffusion coefficient D_{hop} given by[12]

$$D_{\text{hop}} = \tfrac{1}{6}R^2 p_{\text{hop}}, \tag{2}$$

where R is the range or average hopping distance and p_{hop} is the hopping transition probability between two states separated a distance R from each other. The transition probability can be written in general as[12]

$$p_{\text{hop}} = \nu_{\text{ph}} \exp(-2\alpha R - W/k_B T), \tag{3}$$

where ν_{ph} is the phonon frequency associated with the hopping processes; α^{-1} is the wavelength overlapping parameter; and k_B is the Boltzmann's constant. Therefore, $\exp(-2\alpha R)$ is the tunneling factor given by the overlapping of wave functions, and $\exp(-W/K_B T)$ is the Boltzmann's factor, which correlates with energy W between the initial and final hopping states.

If it is assumed that the density of states is constant in a range of some $k_B T$ around the Fermi energy, and the latter is within the localized states, then for the three-dimensional case, the number of states per unit volume and energy (N_F), separated by a hopping distance R, is related to the energy difference between hopping states by:

$$W = \frac{3}{4\pi R^3 N_F}. \tag{4}$$

Parameter W is also denominated as the "hopping activation energy," and is one of the most important parameters in identifying the hopping mechanism. This parameter will be used to compare different models.

Using Eq. (4) into (3), and evaluating the maximum of the function, we obtain the optimum distance R which allows us to get the higher rate of hopping[13]

$$R = \left[\frac{9}{8\pi\alpha N_F k_B T}\right]^{1/4}. \tag{5}$$

The Einstein relation allows the calculating of the dark conductivity, σ_{dk}, in terms of the diffusion coefficient and the density of states according to[13,14]

$$\sigma_{dk} = e^2 D_{\text{hop}} N_F, \tag{6}$$

where e is the electronic charge, D_{hop} is the diffusion coefficient, and N_F is the density of states near the Fermi level.

Combining Eqs. (2)–(6), the following equation for the dark conductivity was found:

$$\sigma = \frac{1}{6}e^2 R^2 N_F \nu_{\text{ph}} \exp\left[-\left(\frac{18.1\alpha^3/N_F k_B}{T}\right)^{1/4}\right], \tag{7}$$

which is similar to Mott's equation if we call

$$\sigma_0^* = \tfrac{1}{6}e^2 R^2 N_F \nu_{\text{ph}} \tag{7a}$$

and

$$T_0 = \frac{18.1\alpha^3}{N_F k_B}. \tag{7b}$$

As dark conductivity and temperature are easily measured in thin film materials, from a plot of $\ln(\sigma_{dk})$ vs $1/T^{1/4}$, the slope T_0 can be determined, and by choosing a reasonable value for α, the density of states at the Fermi level can be estimated. Subsequently, through Eqs. (4) and (5) the hopping parameters R and W can be calculated. Thus, the diffusional model gives us a method to calculate the hopping characteristic parameters, where only the very well-known α parameter have to be assumed.

B. Percolation theory

The percolation theory has been widely used to study transport phenomena in semiconductors, in particular to calculate the hopping parameters of Mott's equation for the case of VRH. The essence of such an approach lies in the fact that the spheres of radius R, on sites along a most favored path, must join up to form a percolation channel through the material. As a result, the spheres would overlap, offering problems to scientists in the estimation of R. There are a number of approaches being reported as having the same mathematical expression but a different multiplying coefficient, which ranges from 1.78 to 2.48.[9] On average, calculated values of R are smaller than the ones estimated by other methods. As a consequence, when used in Eq. (4), the resulting values for the hopping energies are higher than the expected ones. The proposed formulas[15,16] can be summarized as follows:

$$T_0 = \frac{C^4\alpha^3}{k_B N_F}, \tag{8}$$

where C is a number in the range of 1.84–2.28 predicted for a constant density of states around the Fermi level.[16] Comparing this to the value obtained for T_0 from the diffusional model, it was found that $C^4 = 18.1$, being $C = 2.06$, which is clearly within the range of percolation values. It is important to notice that the same value for Mott's temperature is obtained from two different models.

For the rest of the characteristic VRH parameters, the classical equations reported are[15,16]

$$W = k_B (T_0 T^3)^{1/4}, \tag{9}$$

$$R = \frac{3}{8}T_0^{1/4} T^{-1/4}\left(\frac{1}{\alpha}\right). \tag{10}$$

As both models allow us to calculate R and W, there should be a correlation between them. By including Eqs. (8) and (10) into (4), and Eq. (8) into (5), we obtain the following new expressions after some mathematical operations:

$$W^* = \frac{A}{C^4} k_B (T_0 T^3)^{1/4}, \tag{11}$$

$$R^* = \frac{B}{C} T_0^{1/4} T^{-1/4}\left(\frac{1}{\alpha}\right), \tag{12}$$

where $A = (128/9\pi)$ and $B = (9/8\pi)$.

It is interesting to notice that the new equations [Eqs. (11) and (12)] maintain the same structure of the ones predicted by the percolation theory, having a pre-factor which is a function of parameter C. Recently, Godet *et al.*[11] reported

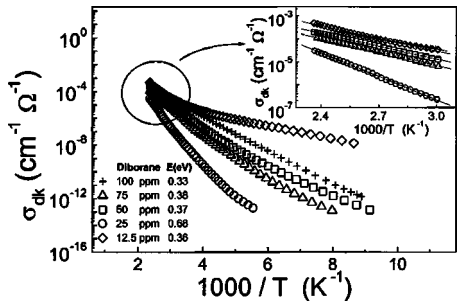

FIG. 1. Dark conductivity as a function of the inverse temperature for μc-Si:H samples with a diborane concentration between 12.5 and 100 ppm. The figure inset shows a lineal fitting for all samples in the high-temperature range. E is the activation energy.

that C^4 could reach the value of 310 for materials having an exponential density of states, instead of the maximum value of 16 admitted by Mott's theory for a constant density of states. Therefore, these results indicate that the correlation between different models and the shape of the density of states depend on the value of C.

III. EXPERIMENT

The μc-Si:H:(B) samples were prepared in a capacitively coupled HF-PECVD reactor working at a frequency of 50 MHz. A description of the characteristics and the operational conditions of the reactor were reported elsewhere.[10] Corning 7059 glass was used as a substrate, and the deposition temperature was 150 °C. The reaction gas was a mixture of 94% hydrogen and 6% silane, containing diborane in the range of 0–100 ppm. The total flux and pressure were kept constant at 20 sccm and 4.5×10^{-1} Torr, respectively.

Conductivity measurements were carried out in a cryostat using thermally evaporated aluminum coplanar electrodes. They were 25 cm in length, interdigited, and separated 0.01 cm from each other. The electrical current was measured with a Keithley electrometer 617 connected to a computer. The samples were annealed at 420 K and then cooled down to 120 K at a constant rate of 1.5 K/min. The applied field was 1000 V/cm.

Modulated photocurrent measurements (MPC) were performed with the same contact configuration. A He–Ne laser was partially modulated (12% of its total intensity) by using an electro-optical modulator at 4 kHz. The dc generation rate was 2.7×10^{17} cm^{-3} s^{-1} and the applied field was 4 $\times10^4$ V/cm. Phase lag and amplitude of the MPC signal were simultaneously detected with a lock-in amplifier.

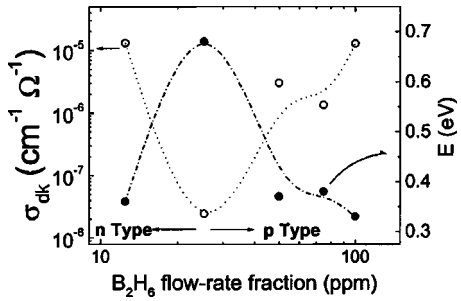

FIG. 2. Room temperature dark conductivity and activation energy for μc-Si:H samples with different boron doping degrees. The lines are drawn to guide the eye.

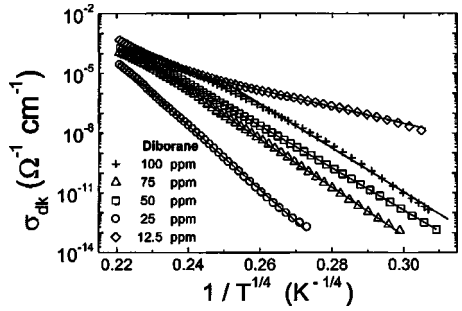

FIG. 3. Dark conductivity vs $T^{-1/4}$ for μc-Si:H samples lightly doped with B.

IV. RESULTS AND DISCUSSION

Figure 1 shows an Arrhenius plot of the dark conductivity of the lightly doped μc-Si:H:(B) samples. A linear behavior is only observed in the high-temperature region, as shown in the figure inset. In this temperature region (over 25 °C), the transport mechanism involves carriers activated directly from levels below the Fermi level to states at the bottom of the conduction (or valence) band. The activation energies (E) indicate that the samples change from a n-type to a p-type semiconductor passing through a compensated μc-Si:H:(B) sample (doping around 25 ppm), as it is shown in Fig. 2. The intrinsic microcrystalline hydrogenated silicon (μc-Si:H) is a n-type semiconductor. If a small amount of Boron is added, which acts as an impurity acceptor, it will push down the Fermi level from the conduction to the valence band, changing the microcrystalline material to p-type. Being the conductivity an exponential function of the activation energy, small changes in the Fermi level will result in large variations of σ_{dk}, as it can be seen in Fig. 2.

Since the Arrhenius plot does not fit at low temperatures, with the exception of the sample doped with 12.5 ppm of diborane, other possible transport mechanisms were sought. In Fig. 3, the variation of dark conductivity versus $1/T^{1/4}$ is shown. At low temperatures, the lineal fitting is very good, giving the expected correlation of Eq. (1). Using Mott's equation, the slopes T_0 were determined (Table II). Therefore, based on the diffusional model for T_0 and the density of states measured in our laboratory by the method of modu-

TABLE I. Wavelength overlapping (α^{-1}) calculated from the diffusional model. Values of N_F are experimental DOS data measured by the MPC method.

Sample (ppm B_2H_6)	N_F (cm^{-3} eV^{-1})	α^{-1} (Å)
12.5	1×10^{16}	61
25	7.8×10^{15}	11
50	1.01×10^{16}	18
75	6.80×10^{15}	17
100	5.04×10^{16}	10

TABLE II. DOS values and hopping parameters ($T=150$ K) from the diffusional and percolation models.

			T. Percolation		M. Diffusional	
Sample (ppm B_2H_6)	T_0 (K)	N_F ($eV^{-1}\,cm^{-3}$)	R (cm)	W (eV)	R (cm)	W (eV)
12.5	9.15×10^{7}	8.31×10^{17}	1.46×10^{-6}	0.36	1.46×10^{-6}	0.09
25	1.90×10^{10}	4×10^{15}	5.57×10^{-6}	1.37	5.57×10^{-6}	0.34
50	3.55×10^{9}	2.13×10^{16}	3.66×10^{-6}	0.9	3.66×10^{-6}	0.22
75	6.07×10^{9}	1.25×10^{16}	4.18×10^{-6}	1.03	4.19×10^{-6}	0.25
100	4.24×10^{9}	1.79×10^{16}	3.82×10^{-6}	0.94	3.83×10^{-6}	0.23

lated photocurrent (MPC),[17] the wave length overlapping parameter was determined. The results for α^{-1} and DOS are shown in Table I.

Table I shows that α^{-1} varies in the range of 10–18 Å, with the exception of the sample having a diborane concentration of 12.5 ppm, a fact that will be discussed later. The agreement between the α^{-1} values found here and the ones predicted by the percolation theory[18] is worth noticing. Taking this into consideration, the mean value of α^{-1} equal to 14 Å will be adopted for the next calculations.

Table II shows the results for the hopping parameters R and W, calculated from the diffusional model [Eqs. (4) and (5)] and the percolation theory [Eqs. (9) and (10)] at a temperature of 150 K. The density of states at the Fermi level, N_F, was calculated using Eq. (8) and the values of $C=2.06$ and $\alpha^{-1}=14$ Å. These results present a fair agreement with the experimental values obtained by the MPC method,[19] reported in Table I. The sample doped with 12.5 ppm shows a discrepancy of one order of magnitude between the measured and calculated N_F values. Besides, if it is taken into account that the α^{-1} values calculated in Table I are relatively high, it should be considered that the possibility that the transport mechanism for this sample is different from VRH, even when Mott's equation is satisfied. A nearest-neighbor hopping behavior was checked, since the results were negative. It is concluded that for this sample the mechanism may be a carrier transport controlled by thermoionic emission,[20] as a reasonable value of 101 meV was obtained for the potential barrier.

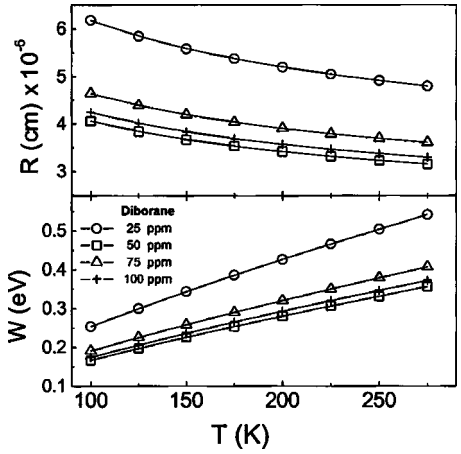

FIG. 4. Hopping parameters R and W as a function of temperature for μc-Si:H samples, according to the diffusional model equations.

Figure 4 shows the dependence of R and W on temperature. Both curves behave as expected by the VRH mechanism, i.e., when temperature decreases, R increases and W decreases.

The R values obtained either from the diffusional or the percolation models are the same, but the hopping energies W are quite different. The value predicted by the percolation method for W gives a value equivalent to the gap of the material. This value is in contradiction with the basic initial assumption that the density of states was constant around the Fermi level, and that the jump of the carriers from one state to the other were only of the order of some k_BT. On the other hand, the initial assumptions are satisfied for the value of W obtained from the diffusional model.

Recalculating R^* and W^* from Eqs. (11) and (12) using $C=2.06$, we again obtain the same values shown in Table II, corresponding to the diffusional model.

V. CONCLUSIONS

Dark conductivity measurements performed over a wide range of temperatures for lightly doped μc:Si:H:B samples are reported in this paper. It was found that for temperatures higher than 25 °C the dominant mechanism is the thermal activation of carriers. The different activation energies found are explained in terms of boron doping.

In the low-temperature ranges, the main transport mechanism for the μc-Si:H:B samples is the VRH, with the exception of the case doped with 12.5 ppm of diborane. From the diffusional model formulas, and using experimental data for the density of states, parameters C and α^{-1} were calculated. A good agreement was obtained with the predicted value from the percolation theory.

A correlation between diffusional and percolation model formulas for R and W was deduced. The resulting equations preserve the same mathematical structure of the percolation equations multiplied by a pre-factor, which is a function of parameter C. Introducing the C value obtained from the diffusional model, the values obtained from the new equations for R^* and W^* are reasonable for a VRH model with a constant density of states around the Fermi level. Higher value of C^4 would indicate that new basic assumptions are necessary in addition to Mott's condition.

ACKNOWLEDGMENTS

This work was supported by the Universidad Nacional del Litoral (CAI+D 2000, 6-1-84) and by ANPCyT (project PICT 12-06950).

[1]A. V. Shah, J. Meier, E. Vallet-Sauvain, N. Wyrsch, U. Kroll, C. Droz, and U. Graf, Sol. Energy Mater. Sol. Cells **78**, 469 (2003).
[2]M. Kondo, Y. Nasumo, H. Mase, T. Wada, and A. Matsuda, J. Non-Cryst. Solids **299**, 108 (2002).
[3]M. Goerlitzer, P. Torres, N. Beck, N. Wyrsch, H. Keppner, J. Pohl, and Shah, J. Non-Cryst. Solids **227**, 996 (1998).
[4]M. F. Cerqueira, J. A. Ferreira, and G. J. Adriaenssens, Thin Solid Films **370**, 128 (2000).
[5]P. Hapke, U. Backhausen, R. Carius, F. Figer, and S. Ray, Mater. Res. Soc. Symp. Proc. **420**, 789 (1996).
[6]N. F. Mott, Philos. Mag. **19**, 333 (1969).
[7]D. Adler and H. Fritzsche, *Tetrahedrally-Bonded Amorphous Semiconductors* (Plenum Press, New York and London, 1985).
[8]A. R. Long and L. Hansmann, *Hopping and Related Phenomena*, edited by H. Fritzsche and M. Pollak (Word Scientific, Singapore, 1990).
[9]N. F. Mott and R. A. Davis, *Electronic Processes in Non-Crystalline Materials*, 2nd ed. (Oxford University Press, Oxford, 1979).
[10]S. B. Concari, R. H. Buitrago, M. T. Gutierrez, and J. J. Gandia, J. Appl. Phys. **94**, 2417 (2003).
[11]C. Godet, J. Non-Cryst. Solids **299**, 333 (2002).
[12]R. A. Street, *Hydrogenated Amorphous Silicon* (Cambridge University Press, Cambridge, 1991).
[13]*Amorphous Semiconductors: Topics in Applied Physics*, edited by M. H. Brodsky (Springer, Berlin 1979), Vol. 36.
[14]G. Paasch, T. Lindner, and S. Scheinert, Synth. Met. **132**, 97 (2002).
[15]S. B. Concari and R. H. Buitrago, J. Non-Cryst. Solids **338–340**, 331 (2004).
[16]M. Thamilselvan, K. Premnazeer, D. Mangalaraj, and Sa. K. Narayandass, Physica B **337**, 404 (2003).
[17]C. Longeaud and J. P. Kleider, Phys. Rev. B **45**, 11672 (1992).
[18]R. M. Hill, Philos. Mag. **24**, 1307 (1971).
[19]A. Dussan, R. R. Koropecki, R. Arce, J. A. Schmidt, and R. Buitrago, J. Non-Cryst. Solids **338–340**, 430 (2004).
[20]A. Di Nocera, A. Mitiga, and A. Rubino, J. Appl. Phys. **78**, 3955 (1995).