A transient thermodynamic model for track formation in amorphous semi-conductors : a possible mechanism ?

C. Dufour [a], B. Lesellier De Chezelles[b], V. Delignon[b], M. Toulemonde[a], E. Paumier[a,c]

a CIRIL, rue Claude Bloch, BP 5133, 14040 Caen Cédex (France)

b Ecole Navale du Poulmic 29240 Brest Naval (France)

c LERMAT, ISMRa, Campus II, Bd du Maréchal Juin, 14050 Caen Cédex (France)

Abstract

Latent tracks have been observed in amorphous semi-conductors after heavy ion irradiation in the electronic stopping power regime. A transient thermodynamic model is developed including energy diffusion on the electron gas and on the atomic lattice and energy exchange between these two systems. A set of two non linear differential equations is solved numerically in cylindrical geometry in order to predict the radii of the latent tracks observed in amorphous germanium and silicon. A good agreement is obtained for the two materials using the same set of input parameters for the energy diffusion on the electronic system and the same coupling constant for the energy exchange between electron and lattice atoms despite the large differences in the macroscopic lattice thermodynamical parameters of the two materials

1. INTRODUCTION

Two models have been proposed in order to explain the appearance of latent tracks induced in matter by the slowing down process of incident ions in the electronic stopping power regime. The first one was the thermal spike proposed by Desauer [1] and reconsidered for metals by Seitz and Koehler [2]. The second one was the ionic spike proposed by Fleischer et al [3] in order to explain that metals are insensitive to the electronic excitation produced by fission fragments irradiation. In both models the key is the high mobility of the electrons in metals. In the ionic spike model the Coulomb repulsion was considered as too quickly screened by the return electrons which inhibits a Coulomb impulse. In the thermal spike model the electronic energy was considered as spread out in a too large volume to induce a significant increase of the lattice temperature. Since that time a systematic use of heavy ion accelerators has enlarged the number of materials (metals, semiconductors and insulators) [4-7] which present a defect creation induced by heavy ions in electronic stopping power (dE/dx) regime. Especially amorphous materials where the electron mobility is greatly reduced are more sensitive than the same materials in their crystalline phase [4 and 8, 4 and 9, 5 and 6]. Hence both models must be reconsidered. In the course of time the ionic spike arises in 10^{-14} - 10^{-13} s while the increase of temperature arises in 10^{-13} - 10^{-12} s As the thermal spike appears after the ionic spike, it can anneal all the previous displacements. Then it is necessary to know whether the observed latent

tracks are a consequence of the temperature rise. This latter hypothesis is supported by the experimental results following the electronic excitation induced by the high power femtosecond laser pulse irradiations of silicon [10] and As Ga [11]. These experiments have shown that melting arises anyway in a time of 2 10^{-13} s [10,11] i.e. in a phonon characteristic time, even if atomic motions could occur in a shorter time. The temperature increases after energy sharing between electrons by the electron-electron interaction [12,13] followed by transfer of the energy to the lattice atoms by electron-phonon interaction. In that case [13] the space and time evolution of the electron and lattice temperatures are governed by a set of coupled non linear differential equations which describes the energy diffusivity in the two systems respectively. This description was partially used in order to explain quantitatively the giant dimensional change in amorphous PdSi [14,15] and the radii of the latent tracks in a-Ge and a-Si [4,16] induced by heavy ion irradiations. In these two calculations the electronic system was supposed to be in a steady state contrarely to the atomic one and the electronic energy generation in the lattice is an analytical solution of the electron diffusivity equation in cylindrical geometry.

The goal of the present work is to determine the radii of latent tracks [4] in a transient thermodynamical model or thermal spike. The latent tracks correspond to a rapid quench of the liquid phase. The two coupled equations will be solved numerically in cylindrical geometry using realistic values of the parameters governing the electron energy diffusivity and electron-phonon coupling. The calculations will be limited to amorphous semi-conductors Si and Ge for which the macroscopic lattice thermodynamical parameters are well known.

2. PHYSICAL BASIS

Seitz and Koehler [2] established the theory of the temperature spike assuming that the electron gas and atomic lattice were both continuous media where they could write the classical equations of heat flow according to Fick's law. These equations are written in cylindrical geometry :

$$C_e(T_e)\frac{\partial T_e}{\partial t} = \frac{1}{r}\frac{\partial}{\partial r}\left[r\,K_e(T_e)\frac{\partial T_e}{\partial r}\right] - g\,(T_e - T_l) + A\,(r,t) \qquad (1)$$

$$C_l(T_l)\frac{\partial T_l}{\partial t} = \frac{1}{r}\frac{\partial}{\partial r}\left[r\,K_l(T_l)\frac{\partial T_l}{\partial r}\right] + g\,(T_e - T_l) \qquad (2)$$

C_i, K_i and T_i are the specific heat, the thermal conductivity and the temperature respectively. i is refering either to the electrons (e) or to the lattice atoms (l). g is the coupling constant related to the electron-phonon intaraction [12,13] and A(r,t) is the energy generation induced by the slowing down of the heavy ions in the electronic stopping power regime. r is the radius of the cylinder and t the time.
They are solved numerically because of the temperature dependance of all the coefficients. Moreover, numerical calcultations allow us to take the phase change (solid-liquid) into account. The thermodynamic characteristics of the lattice have been measured [17] .Those of the electron gas must be explained more precisely.

2.1. The electronic specific heat C_e

The classical theory for a free electron gas leads us to give the following relations.
For $T_e < T_0$: $C_e = \gamma T_e$ where γ is a constant which depends on Fermi level and electronic density of the material.

For Te $>T_0$: $C_e = 3\ k_B\ N/2L^3$ where k_B is the Boltzman constant and N/L^3 the electronic density. T_0 verifies the relation : $\gamma T_0 = 3k_BN/2L^3$.
The table below gives the calculated values for amorphous silicon and germanium.

	E_F (eV)	T_0 (K)	N/L^3 (cm^{-3})	γ ($Jcm^{-3}\ K^{-2}$)
a Si	12.5	88 000	2.10^{23}	$4.7\ 10^{-5}$
a Ge	11.5	81 000	$1.8\ 10^{23}$	$4.5\ 10^{-5}$

2.2. The electronic thermal conductivity K_e

Boltzman transport equation is applied to a system submitted to a temperature gradient [18]. The numerical solution gives the relation : $K_e = \alpha\tau\ T_e$. The constant α is determined by fitting the curve K_e / τ versus T_e : $\alpha = 6\ 10^{11}\ Jcm^{-1}\ K^{-2}\ s^{-2}$. The free parameter τ corresponds to the characteristic time of electron-electron interaction.

2.3. The electronic energy deposition A (r,t).

A (r,t) is the energy deposited by the incident particle to a cylindrical shell of the electron gas between r and r+Δr. We separate the space and time variables for simplification :
A (r,t) = F(r) G(t) dE/dx, dE/dx is the value of the electronic stopping power.

The spatial and time distribution of the deposited energy on the electrons has been discussed previously [19]. The spatial distribution F(r) was analytically derived by Waligorski et al [20] from Monte-Carlo calculations. In the present calculation it has been approximated by an exponential law, $F(r) = \exp(-r/r_0)/r_0$, where r_0 defines the initial spatial width for a specific energy of the incident ion (r_0 = 2.5 nm for an incident ion of 1 MeV/a.m.u). G(t) is the time dependent energy deposition. It has been taken as a gaussian law with its maximum at time t_0 which is of the order of 10^{-15} s. This time [19] corresponds to the time of flight of the delta electrons of average energy. The width of the gaussian is of the same order.

3. NUMERICAL RESOLUTION

We use an implicit method [21] which consists in replacing in discretisation of equation (1) the derivatives by the discrete expressions (i : space index, j : time index)

$r = (i - 0,5)\ \Delta r$ and $t = j\Delta t$

$C_e(T_e)\ \partial T_e/\partial t = C_e\ T_e(i,j+1) - T_e(i,j;r)/\Delta t$

$\partial T_e/\partial r = [T_e(i+1,j+1) - T_e(i-1,j;+1)] / 2\Delta r$

$\partial^2 T_e/\partial r^2 = [T_e(i+1,j+1) - 2T_e(i,j;+1) + T_e(i-1,j;+1)] / (\Delta r)^2$

$g(T_e - T_l) = g(T_e(i,j) - T_l(i,j))$.

We make the corresponding replacements in eq. (2), then both equations have the following form :

$$a_i\ T_e(i+1,j+1) + b\ T_e(i,j+1) + c_i\ T_e(i-1,j+1) = d_i T_e(i,j) + e_i \quad (3)$$
$$P_i\ T(i+1,j+1) + q_i\ T(i,j+1) + r_i\ T(i-1,j+1) = m_i\ T(i,j) + n_i = 0 \quad (4)$$

Using the matrical form, (3) and (4) result in :

$$\begin{bmatrix} b_1 c_1 0\ 0\ \ldots\ldots\ldots \\ a_2 b_2 c_2\ 0\ 0\ \ldots\ldots\ldots \\ \ldots\ldots\ldots\ldots\ldots\ldots\ldots \\ \ldots 0\ 0\ a_i b_i c_i\ 0\ 0\ \ldots \\ \ldots\ldots\ldots\ldots\ldots\ldots\ldots \\ 0\ 0\ \ldots\ldots\ldots 0\ 0\ a_n b_n \end{bmatrix} \begin{bmatrix} Y_1 \\ . \\ . \\ Y_i \\ . \\ Y_n \end{bmatrix} = \begin{bmatrix} X_1 \\ . \\ . \\ X_i \\ . \\ X_n \end{bmatrix}$$

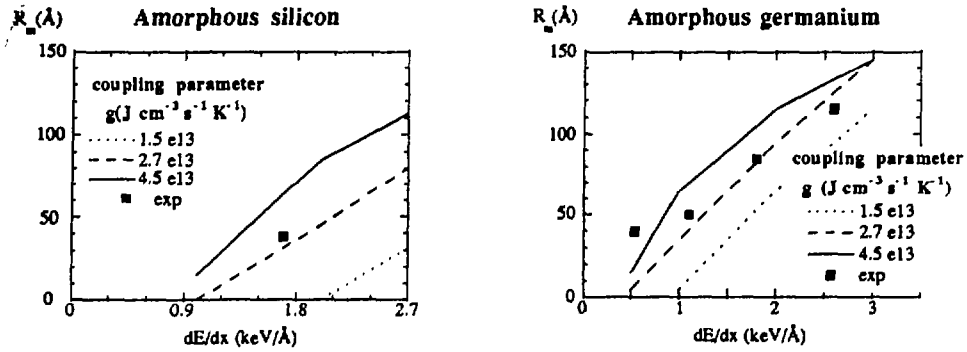
Where X_i are all known at the time j and Y_i (unknown) are functions of temperature at the time j + 1. Instead of inverting such a great matrix, we use Choleski's method [22] to deduce Y_i from X_i and the other parameters.
The calculations were made over a radius of 100 nm by steps of 1 nm and developed over a time of 10^{-12} s by step of 10^{-17}s. The space and time extensions are large enough to not influence the results.

4. RESULTS

The two main parameters in the calculation are g and τ. They are considered as free parameters to be determined after comparing the calculated diameter of the liquid phase to the observed diameter of the latent track. However fs laser experiments give limits to the values of these parameters. As the electron-phonon interaction is stronger in an amorphous material than in a crystal, the coupling constant g should be larger than the one measured in a crystal [12,13] which is of the order 10^{11} to 10^{12} Jcm^{-3} K^{-1} s^{-1}. The τ value can be extracted from the electronic energy diffusivity D_e. In the present formalism $D_e = K_e/C_e = \alpha\tau / \gamma$ if the electronic temperature is less than T_0 previously defined in the electronic specific heat. This approximation is valid since the electronic temperature is always less than T_0 for time larger than 2-3 10^{-15} s. In equilibrium state between electrons and atoms, experiments show that τ is in the range of 10^{-14} to 10^{-10}s for temperature varying from 300 K to 4 K respectively. In a non equilibrium regime between electrons and atoms the minimum electronic mean free path is of the order of one interatomic distance [23]. Moreover the electron velocity after the high electronic excitation is of the order of the Fermi velocity v_f ($\approx 10^8$ cm/s) [24]. As $\Lambda = v_f \tau$ the lower limit of τ is 10^{-16} s. So $\tau = 10^{-14}$ s is taken as the first value since in crystalline silicon. $D_e = 100$ cm^2/s [25]. Using this τ value for the calculation the g value was ajusted in order to fit the latent track radii in a-Si and a-Ge assuming that they correspond to a rapid quench of the liquid phase (fig. 1a and 1b). A unique value of g = 2.7 10^{13} Jcm^{-3}K^{-1}s^{-1} is extracted for both materials despite the large differences in their macroscopy lattice thermodynamical parameters. Moreover the calculated dE/dx threshold values agree with the experimental ones [4]. Several other sets of g and τ values have been tested. By fixing τ in a range of 10^{-15} to 10^{-14} s, it has been possible to reproduce the radii of the latent tracks by varying g between 2 10^{12} and 2.7 10^{13} Jcm^{-3} K^{-1} s^{-1}. But in these preliminary calculations the best fit seems to be obtained for $\tau = 10^{-14}$s.

The effects of the input parameters for the energy deposition have also been tested. The parameters r_0 and t_0 varied in the following ranges : $1 \leq r_0 \leq 5$ nm, 10^{-15} s $\leq t_0 \leq 10^{-14}$ s and the width of the gaussian distribution G(t) was taken equal to t_0. At dE/dx = 2 keV/Å for the amorphous germanium the calculated radii is the same than in figure 1 within 10 % for all the

different calculations. This weak sensitivity of the results to the input parameters of the deposited energy suggests that the electron-phonon interaction time is larger than the energy deposition time. In the present formalism the electron-phonon interaction time can be written as $\tau_{e\text{-}ph} = \rho C_l / g$ where ρ is the matrix density. The g value corresponding to the best fit is $\tau_{e\text{-}ph} = 2\ 10^{-13}$ s which is at least one order of magnitude higher than the deposition time. Hence energy diffusion in the lattice occurs a long time after the energy transfer between electrons and atoms.



a b

Figure 1. Molten cylinder radius versus dE/dx for different values of the coupling constant. The experimental errors are estimated to be ± 15 Å.

5. CONCLUSION

A transient thermodynamical model is applied to determine the latent track radii in amorphous semi-conductors Ge and Si. A numerical solution of the two coupled equations which characterize the energy diffusivity on the electrons and atoms and their coupling is performed. A good agreement is observed between the calculated and the observed latent track radii if it is assumed that they result from rapid quenching of the liquid phase. The two free parameters are the characteristic time τ of the electron-electron interaction and the coupling constant g between electrons and phonons. Realistic values of τ and g are extracted suggesting that the hot electron gas behaves as a free electron gas with respect to the energy diffusion, whereas g depends on the initial state of the cold matrix. This good agreement seems to support that the thermal spike which exists in a time of 10^{-13} s is the mechanism which governs the observed transformation at longer time. It could anneal all the previous atomic motions as it was observed in the fs laser experiments.

6. REFERENCES

1 F. Desauer, Z. Physik 38 (1923) 12.
2 F. Seitz and J.S. Koehler, Sol. St. Phys. 2 (1956) 305.

3 R.L. Fleisher, P.B. Price and R.M. Walker, Nuclear tracks in solids (1975) University of California Press.

4 K. Izui and K.S. Furuno, Proc. XIth int. cong. on electron microscopy (Kyoto 1986) 1299.

5 A. Audouard, E. Balanzat, G. Fuchs, J.C. Jousset, D. Lesueur and L. Thomé, Europhys. Lett. 3 (1987) 327.

6 A. Dunlop, D. Lesueur, J. Morillo, J. Dural, R. Spohr, J. Vetter, C.R. Acad. Sci. Paris 309 (1989) 1277.

7 F. Studer, C. Houpert, H. Pascard, J. Vetter, Jin Yun Fan and M. Toulemonde, Rad. Eff. and Def. Sol. 116 (1991) 59.

8 M. Toulemonde, J. Dural, G. Nouet, P. Mary, J.F. Hamet, M.F. Beaufort, J.C. Desoyer, C. Blanchard and J. Auleytner, Phys. Stat. Sol. 114 (1989) 467.

9 M. Levalois, P. Bogdanski and M. Toulemonde, to be published in Nucl. Instr. Meth. B.

10 H.W.K. Tom, G.D. Aumiller and C.H. Brito-Cruz, Phys. Rev. Lett. 60 (1988) 1438.

11 P. Saeta, J.K. Wang, Y. Siegal, N. Bloembergen and E. Mazur, Phys. Rev. Lett. 67 (1991) 1023.

12 P.B. Allen, Phys. Rev. Lett. 59 (1987) 1460.

13 S.D. Brorson, A. Kazeroonian, J.S. Moodera, D.W. Face, T.K. Cheng, E.P. Ippen, M.S. Dresselhaus and G. Dresselhaus, Phys. Rev. Lett. 64 (1990) 2172.

14 Ming-dong Hou, S. Klaumünzer and G. Schumacher, Phys. Rev. 41 (1990) 1144.

15 G. Szenes, private communication.

16 M. Toulemonde and E. Paumier, private communication.

17 E.P. Donovan, F. Spaepen, D. Turnbull, J.M. Poate and D.C. Jacobson, J. Appl. Phys. 57 (1985) 1795.
M.C. Webber, A.C. Cullis and N.G. Chew, J. Appl. Phys. 45 (1983) 669.

18 For example N.W. Ashcroft and N.D. Mermin (Solid state Physics (Holt, Rinehart and Winston New York 1976) chaps 2 and 17.

19 E. Balanzat, J.C. Jousset and M. Toulemonde, Nucl. Inst. Meth. B32 (1988) 368.

20 M.P.R. Waligorski, R.N. Hamm and R. Katz, Nucl. Tracks radiat. Meas. 11 (1986) 309.

21 M.S. Carslaw and J.C. Jaeger, conduction of heat in solids 2nd ed.(Clarendon press oxford 1959).

22 J.P. Nougier, Methodes de calcul numérique (Masson, Paris 1987) p.250.

23 H.M. Michlberg, R.R. Freeman and S.C. Davey, Phys. Rev. Lett. 61 (1988) 2364.

24 S.D. Brorson, J.G. Fujimoto and E.P. Ippen, Phys. Rev. Lett. 59 (1987) 1962.

25 E. Yoffa, Phys. Rev. B21 (1980) 2415.