Interstitial Cluster Evolution and Transient Phenomena in Si-crystal

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Abstract

The evolution of Interstitial (I) type defects in Si and its influence on out of equilibrium I super-saturation level is investigated. Two approaches complementary to Quantum Mechanics Calculations (QMC) are applied: the Kinetic Lattice Monte Carlo (KLMC) and the Non-Lattice Kinetic Monte Carlo (NKMC). Our simulations show that the behaviour of I-super-saturation during a far from equilibrium stage is strongly affected by the correspondent aggregate structural evolution. Therefore, even if KLMC and NKMC are based on the same energetics derived by QMC, they give a different prediction of the super-saturation behaviour.

1 Introduction

Transient phenomena occurring in Si, due to Interstitial (I) kinetic attracts a wide interest; and, nowadays, a large set of experimental data and theoretical results is available on this field [1-5]. In spite of this effort, a definitive interpretation of the experiments by means a reliable theory of the agglomeration kinetics is still lacking. Quantum Mechanics Calculations (QMC) evidenced a particular feature of stable I-clusters: i.e., in the small size regime, compact cluster formed by over coordinated atom are more stable that rod like defect [3-5]. One intriguing issue is the role of the structure-energetic relationship on the I kinetics evolution and, conversely, if a reliable description of such evolution can be obtained neglecting this relation.
In order to achieve such task, we compare the prediction of two kinetics approach based on the same energetics. In the first, the Non Lattice Kinetic Monte Carlo (NKMC) approach [6,7], one assumes that, in a capture (dissolution) event, a cluster of n defects instantaneously achieves the lowest energy configuration for a cluster with $n+1$ ($n-1$) members. In the second, the Kinetic Lattice Monte Carlo (KLMC) [7-8] approach, the relationship between energetic and cluster configuration is taken into account using an interaction model which matches the results of QMC. Thus, it can simulate structural transition of a given agglomerate between inherently different structures. These features allow to explore in detail the relationship between the structural evolution and the behavior free I density maintained by the clusters.

2 I cluster energetic and kinetic approaches

In the two stochastic approaches the kinetics is simulated by means a sequence of atomic transitions picked randomly according their own transition rate given by [6;7]

$$\nu(i => f) = \nu_\kappa \, x \, min\{1, exp[-(E(c_f) - E(c_i)/ k_B T]\} \qquad (1)$$

Here $E(c)$ is the total energy of the configuration c, T the reservoir temperature and ν_κ is the attempt frequency of the κ-th transition allowing the transition from c_i to c_f. In the NKMC method, the change of energy is $E(c_f) - E(c_i) = E_b(n)$ for a dissolution event (where $E_b(n)$ is the binding energy, i.e. the energy cost for the detachment of one I from the more stable n-sized cluster); whilst $E(c_f) - E(c_i) \leq 0$ for other processes (capture, monomer random jump).
In the KLMC approach, the energy is evaluated using a defect-defect potential formulated on the basis of the static calculated by QMC [7-8]. The configuration are mapped in a reference (super)lattice formed by N_{sites} of a Si diamond lattice and N_{sites} associated tetrahedral (Td) sites [10]. The number of Monte Carlo particles is $N_{atoms} = N_{sites} + N_I$, where N_I is the number of Is. Kinetics is driven by two kinds of elementary transitions: a) the displacement of an atom from a Td site to a nearest neighbor (n.n.) Td site ($\kappa \equiv I_T <=> I_T$), b) the displacement of a regular atom to an empty n.n Td site or vice-versa ($\kappa \equiv N <=> I_T\text{-}V$). The latter process leads to the formation or to the dissolution of an instable $I_T\text{-}V$ complex (with an energy cost $\pm E_{IV}$), if the remaining n.n Td sites are empty. Otherwise, if defective Si atoms fill these Td sites, the formation of the $I_T\text{-}V$ complex activates the possibility of binding (with binding energy E_b,) the I, belonging to the complex, to those atoms. In order to match the energetic of compact clusters calculated by the QMC, the cost of over coordination must also be taken into account [4]. Therefore we introduce two energy levels: E_5 for a five fold coordinated atom and E_6 for a six fold coordinated one ($E_6 > E_5 > 0$) [8]. Chainlike structures (structural unit of {311} defects) are mapped as correlated adjacent I_Ts lying in a <110> chain of the Td sub-lattice. Their energetics can be modeled by means of two different energy contribution E_{ex} or E_{in} ($E_{ex} > E_{in}$) for atom at the extreme and in the inner part of the chain respectively.
The energy difference in (1) can be evaluated in term of the variations Δn_α of the number of the single contributions $E(c_i) - E(c_f) = \Sigma_\alpha \Delta n_\alpha E_\alpha + \Delta_\kappa$, where $\Delta_\kappa = 0, E_{IV}, -E_{IV}$ when $\kappa = I_T => I_T$, $N => I_T\text{-}V$, $I_T\text{-}V => N$, respectively. We can use the formations energy (calculated by QMC) of six I-defect configurations in order to evaluate the six KLMC parameters. Using the Tight Binding Molecular Dynamics TBMD [3,4] or the Local Density Approximation DFT-LDA [5] calculations, we obtain the following set of KLMC parameters

$$E_{IV} = 4.0; E_b = 4.6; \; E_5 = 2.0; \; E_6 = 4.3; \; E_{ex} = 0.4 \; E_{in} = -2.7 \quad (TBMD) \qquad (2)$$
$$E_{IV} = 4.0, E_b = 4.5, \; E_5 = 2.2; \; E_6 = 4.2; \; E_{ex} = -0.9 \; E_{in} = -2.83 \quad (DFT\text{-}LDA). \qquad (3)$$

The agreement between KMLC and QMC energetics is not restricted to the six configurations considered, in order to extract parameters, but it occurs (irrespective to the cluster size) for all I-type defect belonging to the two structure classes.

3 I system kinetics and super-saturation behaviour

Snapshots of the I kinetics evolution are shown in Fig.1 for a system at T=650°C temperature (in this case KLMC model is set in order to recover energetic calculated by means TBMD) [3,4]) . The initial state is a homogeneous distribution of N_I =32 Td Is and N_{sites}=262144 Si atoms sitting in regular lattice sites.

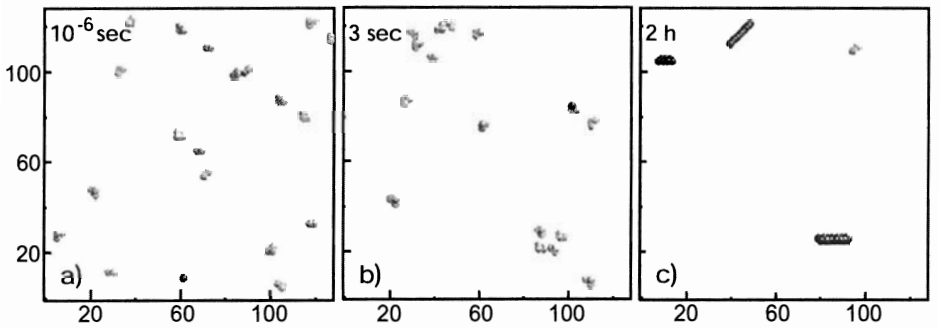

Fig.1 Snapshots of interstitial aggregates obtained by the simulated KLMC evolution for a closed system with N_{sites} = 262144, and N_I =32 at T=650°C at three different times. Bright spheres indicate atoms in compact cluster structures whilst dark spheres indicate atoms in chainlike structures.

Three stages characterize the kinetics: the nucleation of compact cluster initiated by Is diffusion along tetrahedral-dumbbell path (fig.1a); the formation of non correlated complexes formed by adjacent compact clusters (fig.1b), the structural transition from these complex to correlated chainlike structures, dominating the long time evolution (fig.1c). Structural transition to chainlike nucleus can occur only the system overcomes, by means thermal fluctuation, the kinetic barriers between the two configurations: this causes the metastable character of the stage dominated by compact cluster [8].

These kinetic features affect the behaviour of the super-saturation level S which the aggregates maintain in the space region where they are located. This is quantity correspond also to the diffusivity enhancement, during transient stages, for impurities which migrate by interstitials. By means of our simulation, we have calculated a parameter proportional to S: the rate $s(t) = \Delta t_{free}(t) / \Delta t_{sample}(t)$; here $\Delta t_{free}(t)$ is the time which the system spends to perform free I diffusive transitions during a suitable sampling time $\Delta t_{sample}(t)$. In Fig. 2 $s(t)$ is shown for a closed system (N_{sites}=262144, $N_I = 128$) with DFT-LDA energetics but with $E_{ex} = 0.1$ [5]. Compact clusters maintains the plateau of $s(t)$ between early stages (nucleation of compact clusters) and later stages (presence of chain structures). This behaviour $s(t)$ cannot be recovered by NKMC exploiting the same static (for the lowest energy states). Indeed it foresees a transition to the $s(t)$ level of rod-like defect just after $t > 10^{-5}$ sec. Anyway, the $s(t)$ dependences, calculated by KLMC, can be used to fit an $E^{Fit}{}_b(n)$ relation for a NKLC reproducing similar $s(t)$ behaviour (see fig. 2 dashed line and open circles). This fitting procedure gives the following value of the binding energy: $E^{Fit}{}_b(n) = 1.3, 1.0, 1.4, 1.0, 1.7, 1.1, 2.3, 1.3, 2.0 \ldots 2.2$ *for* $n=2,3,4,5,6,7,8,9,10,$

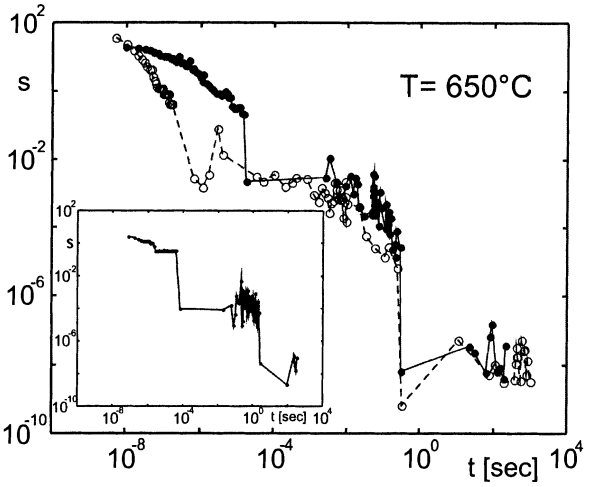

Fig 2 s(t) parameter for a closed system with N_{sites} =262144, N_I=128 and T = 650°C derived by a KLMC simulation (solid line and •) and by a NKMC simulation using with the binding energy dependence: $E_b^{Fit}(n)$ (dashed line and o). In the insert s(t) calculated by KLMC is for a system with N_{sites} = 262144, N_I=16.

...n≥11. Using the same $E^{Fit}{}_b(n)$ values a good agreement of the *s(t)* dependences derived by KLMC and NKMC is recovered for the same system at different *T*.
However, when a different density $\rho' \neq \rho$ of Is is considered, the NKMC model with the set of $E^{Fit}{}_b(n,\rho)$ values extracted gives an prediction of the *s(t)* behaviour which is in total disagreement with that foreseen by KLMC. Thus, in order to recover again a similar behaviour, a different $E^{Fit}{}_b(n,\rho')$ dependence on *n* should be imposed. For the same system but having a eight fold lower density of Is (see insert in fig.2) we have $E^{Fit}{}_b(n,\rho')$ = *1.3, 1.0, 1.8, 1.0, 2.3, 1.1, 2.8, 1.3, 2.0 ...2.2 for* $2 \leq n \leq 10$ *...n≥11* . These results make questionable the use of theories, which do not take into account the actual structural evolution of the cluster, to investigate non equilibrium I-kinetics: also the behaviour of average system properties (e.g. *s(t)*) is non predictable.

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