Dopant dynamics and defects evolution in implanted silicon under laser irradiations: a coupled continuum and Kinetic Monte Carlo approach

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***Abstract*—Defect evolution and dopant dynamics in boron implanted silicon under excimer laser irradiation is investigated by means of continuous model and kinetic Monte Carlo (KMC) simulations. Both approaches rule the post-implant kinetics of the defects-dopant system in the extremely far from-the equilibrium conditions caused by the laser irradiation. The thermal problem has been solved within the phase-field methodology. Our model, based on the interaction between defects and the active/inactive impurities, elucidates the dopant activation as well as the observed defect aggregation. Concurrently to the solid-phase problem for the dopant activation, Boron evolution mechanism in silicon melting phase induced by the laser heating have been investigated in details. The analysis suggests an anomalous impurity redistribution in the molten regions induced by the melting laser irradiation related to the mixed (metal+covalent) bonding character of the liquid state. This microscopic mechanism explains the anomalous B segregation whereas accurate comparisons between experimental chemical profiles and simulation results validate the two state diffusion model.**

I. Introduction

The investigation of the dopant evolution in semiconductor substrates during annealing processes turned out to play a central role in the dopant activation mechanism. Nowadays several thermal process methods are used for ultra-shallow junction fabrication in micro- and nano- devices. From this point of view sub-μs Laser Thermal Annealing (LTA) annealing, supplying localized annealing at the sub-μm scale, can satisfy new requirements for junction engineering. In the case of sub-μs annealing treatment the localized thermal budget can lead to activation without diffusion in the solid phase irrespectively if melting takes place or not [1], [2]. In the molten region dopant activation is the consequence of impurity's trapping [3], whilst in solid phase should be the result of the less known kinetics in the highly damaged crystalline matrix where dopant-defect interactions play a central role [4]–[6].

Concerning the solid-phase dopant activation, the Kinetic Monte Carlo (KMC) method is the key formalism for the accurate computational study of this thermally ruled kinetics [7] in suitably large systems. Anyhow conventional KMC algorithms cannot be applied for the simulation of the laser annealing process since it induces a highly non uniform fast varying T field. We investigate by means of an original Phase-Field KMC (PF-KMC) code the post-implant kinetics of the boron atoms, implantation damage and boron-interstitial complexes (BICs) in the extremely far-from-equilibrium conditions caused by the sequence of dopant implantation and laser irradiation in the non-melting, partial melting and melting regimes. A key feature of our method is the coupling of the KMC code with a phase field model which properly simulates the thermal field evolution in irradiated sample also when liquid-solid phase transition takes place.

In this last case, several issues remain unresolved as the peculiar impurity evolution in quasi-covalent liquid Si (l-Si). Liquid Si is a metal with electrical and optical properties comparable to other Lennard-Jones metals (e.g l-Al) but with a coordination number $\sim$ 6 much lower than that $\sim$ 12 predicted by (dynamic) close packing arguments. It is now well understood that the low coordination number of l-Si is related to the persistence of covalent bonds in the liquid phase, predicted by atomistic simulations [8], and recently evaluted by Compton scattering measurements [9]. The emerging scenario for the atomic structure of l-Si is the coexistence between the conventional liquid metal states with locally covalently bounded regions which are continuously formed and dissolved in short time scales. The question arises whether local bonding fluctuations also affect mass transport in l-Si such as self-diffusion and/or impurity diffusion. A continuum two state diffusion model will be presented explaining the anomalous Boron redistribution in molten Silicon.

II. KMC for the dopant-defects system

Solid-phase dopant activation dynamics has been investigated by means of a non-lattice PF-KMC code. The code allows particles to be free to move inside the simulation box without lattice restrictions, simulating the evolution of interstitial- and vacancy-type defects as well as impurity atoms. The PF-KMC code has been coupled with a phase-field model

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[2], [10] which properly simulates the fast-varying nonuniform thermal field T (**r**,t) evolution in the irradiated samples, also when the liquid-solid phase transition takes place. The thermal field rules the evolution of the dopant-defect system in the KMC scheme. The implementation details for the pure defect system can be found in Ref. [11]. Dopant atoms can reside in a substitutional position B_s or form a complex with interstitial defects, i.e. a Boron Interstitial Clusters (BICs) [12, and references therein]. Without loss of generality, we assumed that I and V point defects as well as the BX complex (one dopant atom bounded to one point defect) are the only mobile species and defect clusters X_m (X = I *or* V) as well as the dopant-defect cluster B_nX_m (a cluster formed by n dopant atoms and m point defects) can only absorb or emit point defects. We also assume that boron atoms can only interact with interstitial-type defects [12], hence forming the mobile complex BI or an immobile aggregate B_nI_m. Therefore, in order to reproduce the defect system evolution as a function of the time, diffusion events for point defects and dissolution events for clusters has been considered with Arrhenius-like probabilities.

Periodic and boundary conditions have been setting as done in Ref. [11]. The projected range of the boron ions (30 keV) is 120 nm and the maximum melt depth corresponding to the highest laser fluence employed (2.6 cm^{-2}) is 140 nm, so the choice of a simulation box ($X_b \times Y_b \times Z_b$) with a depth of Z_b = 600 nm (in the direction of laser laser irradiation) ensures the validity of the real bulk approximation. On the other hand, the choice of the remaining dimensions X_b and Y_b of the simulation box is determined by the total number of particles to simulate in a KMC run. This number, which plays a central role in CPU time, can be determined by the initial defect density, strictly related to the implantation process characteristics and to the concentration resolution. In our case, we choose a simulation box with X_b = Y_b = 90 nm. KMC parameters (i.e. exponential prefactors, migration and binding energies) have been taken from literature [11]–[13].

In order to deeply investigate the boron activation dynamics as well as its diffusion in *l*-Si under LTA treatments in implanted Si, we have experimentally realized and studied the B redistribution and its activation in Si considering two distinct implant conditions: B 30 keV energy, 1×10^{15} cm^{-2} dose with a projected range R_p of $\sim$ 120 nm and B 3 keV energy, 5×10^{14} cm^{-2} dose with a R_p of $\sim$ 15 nm. The samples have been annealed using the EXCICO LTA system (λ = 308 nm) at room temperature, with a pulse duration of 160 ns and a frequency of 1 Hz for multi-shots annealing. Laser energy densities of 1.5, 2.0, 2.3 and 2.6 J/cm^2 have been considered in order to achieve different thermal budgets and maximum melt depth R_{melt}).

All these process have been simulated applying the PF-KMC code for the solid-phase B activation investigation. The defect system was initialized by coupling binary collision approximation (BCA) and atomistic KMC simulations of the defect evolution at room temperature after the implant. Simulation results suggest a reduction of 60% of the BCA-estimated total implantation damage. Boron atoms during their evolution promoted by the laser thermal budget can reach substitutional lattice sites or form immobile aggregates with interstitial defects (BICs). The first component will increase

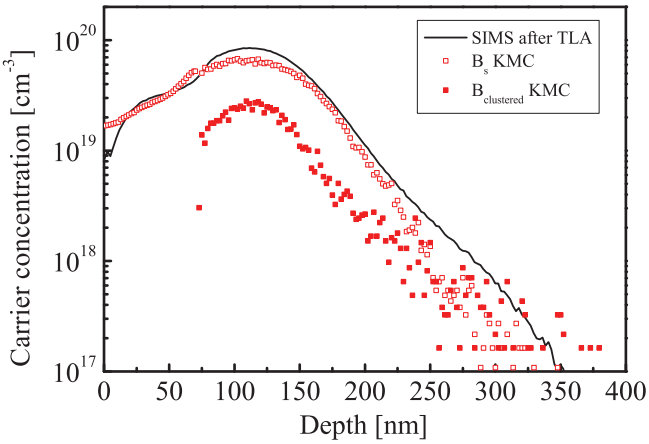

Fig. 1: Profiles of substitutional Boron atoms (empty squares) and trapped in BICs complexes (filled squares) for 2.3 J/cm^2 laser process. The SIMS profile (dark line) after LTA is also reported.

the carrier density whilst the second will need furthermore thermal budget to dissolve and increase the local activation level. In Figure 1 it has been reported the active Boron concentration B_s (empty squares) as well as the component stored in the B_nI_m clusters (filled squares) for the 2.3 J/cm^2 case. As reference the SIMS profiles (dark line) has been also reported. KMC simulation reproduces a full dopant activation in the molten region as well as the activation efficiency in solid phase. The total boron activation efficiency pass from 78 % (1.5 J/cm^2), to 92 % (2.3 J/cm^2) and 94 % (2.6 J/cm^2). In these conditions a fraction of boron atoms is partially trapped in B_nI_m aggregates. The activation process induced by a such thermal treatment is the results of competitive events, namely dissolution events of the mobile BI from a B_nI_m complex and its diffusion in the highly damaged crystalline matrix before to be promoted in a substitutional site. From this point of view the simulation of the complete dopant-defects system without furthermore approximation during LTA is crucial in order to predict the correct dopant activation level.

III. Two State-Diffusion Model

Solid-phase dopant activation is the result of the impurity-defect kinetics in the highly damaged crystalline matrix. In the liquid state defects entirely dissolve and dopant atoms are positioned in a substitutional state B_s during the recrystallization process. In this case the focus resides on the impurity redistribution in the molten region where anomalies have been commonly observed both in Si and Ge substrates. We have experimentally studied the B redistribution in Si due LTA processes in the specimens implanted with Boron 3 keV and a dose of 5×10^{14} cm^{-2}.

Figure 2 reports an example of anomalous impurity redistribution after LTA for three different laser processes. The anomaly refers to the apparent against-gradient diffusion process which cannot be modeled by means of a simplified Fickian schema or a conventional segregation-based model ($k \leq 1$ at *l-s* interface). In a first attempt we simulate the B transport

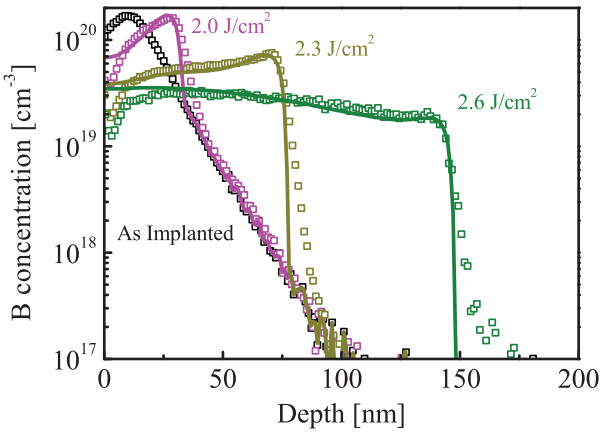

Fig. 2: SIMS (squares) and simulated (two-state model Eqs. (1) and (2), solid lines) B profiles obtained after single pulse laser irradiations at 2.0 (magenta), 2.3 (dark yellow), and 2.6 (green) J/cm^2 energy densities.

during laser irradiation coupling the Fickian diffusion equation for the B concentration with a model [14] for the Stephan problem. This model predicts the time evolution of the thermal field T and liquid-solid boundary. The latter can be evaluated within the phase-field approach by means of a phase function Φ which takes different values in the liquid and solid regions [2], [10], [15]. A significant discrepancy between the simulated and the measured density profile has been found (not shown).

Although the anomalous segregation can be qualitatively described by a position dependent $k(x)$ segregation coefficient model, the microscopic mechanism causing this anomalous segregation kinetics of B and other impurities is not known. We hypothesize that the waterlike anomalies of the bonding in *l*-Si make unreliable the Fick-law scenario for the impurity diffusion in *l*-Si. In particular, we speculate that the balance between the covalent and metallic local bond states as a function of T in liquid phase is responsible for the adsorption behavior of the *l-s* boundary, which practically acts as an impurity sink. In order to bring stronger supporting argument on this hypothesis we propose a modified B diffusion model which is consistent with the *l*-Si atomic structure.

We assume, in analogy with the twofold coordination number of *l*-Si, that B atoms can coexist in two different states, one highly mobile and the other slowly diffusing [3]. The mobile state is virtually bounded to the metallic zones while the low diffusivity state is trapped by those Si atoms forming covalent bonds. The temperature affects the corresponding concentrations as the persistence of covalent bonding depends on T and becomes more relevant in under-cooled *l*-Si. As a consequence, we model the balance between the two states by means of rate equations where rate parameters are T-dependent [3]. The model reads

$$\frac{\partial C_B^{HD}}{\partial t} = \nabla \left[D_B^{HD} \nabla C_B^{HD} \right] + k^{\tau} \left(C_B^{LD} - \bar{R} \cdot C_B^{HD} \right) \quad (1)$$

$$\frac{\partial C_B^{LD}}{\partial t} = \nabla \left[D_B^{LD} \nabla C_B^{LD} \right] - k^{\tau} \left(C_B^{LD} - \bar{R} \cdot C_B^{HD} \right) \quad (2)$$

where D_B^{HD} and D_B^{LD} are the diffusivity of boron atoms in the higher and lower diffusivity state in liquid phase. C_B^{HD} and C_B^{LD} are the corresponding concentrations. k^{τ} is a rate coefficient ruling the transition between the two B states which should be also related to the rapidity of the bonding order fluctuations in *l*-Si. Its value was fixes as a constant (not null in the melting phase). $\bar{R}$(T) is the average (equilibrium) ratio between low and high diffusivity states at constant T. When dopant atoms in the lower diffusivity state are strongly favored (i.e. undercooled regions), $\bar{R}(T) > 1$, whilst $\bar{R}(T) < 1$ when atoms in the higher diffusivity state characterize the impurity kinetics (i.e. stable liquid regions).

The designed experiment allows us to follow the dopant evolution in the wide range of conditions, from shallower melting processes to deeper ones, necessary for getting a reliable calibration of k^{τ} and $\bar{R}$(T). Solid lines in Figure 2 represent the simulated B dopant re-distribution after one pulse laser irradiations for all the processed samples. A satisfying agreement can be found for the against-gradient, pile-up and no-pile-up regime. The calibration procedure gives the value of k^{τ}= 1.0×10^7[s^{-1}] for the reaction rate. The limit values of $\bar{R}$(T) in the deep under-cooled and over-heated regimes are 50.0 and 0.4, respectively. $\bar{R}$(T) switches from 50.0 to 0.4 in a $\sim$ 10K wide region close to the melting point.

Temperature-dependent bulk diffusivity is one direct consequence of the two-state model. However, the anomalous segregation behavior cannot be explained only by means of this dependence for the dopant average diffusivity in the liquid phase being the impurity pile-up mechanism inherently related to the local un-balance between states with high and low mobility. In order to clarify this issue, snapshots of the dopant evolution have been reported in Figure 3 for the 2.3 J/cm^2 laser fluence case. The temperature dependence on the position (Figure 3 blue solid line) helps to follow the different evolution stages in undercooled and non-undercooled *l*-Si.

During a melting laser annealing process, boron atoms are in two different states with different mobilities. In particular, dopant atoms in the lower diffusivity state are strongly favored in regions of low temperature (i.e. undercooled regions), whilst atoms in the higher diffusivity state characterize the impurity kinetics in the stable liquid regions. For a laser irradiation with a maximum melt depth greater than the dopant region, during the melting stage (upper panels of Figure 3) the majority of the dopant atoms (71 %) resides in their high diffusivity state as the temperature is significantly above the Silicon melting point. After the maximun melt depth is reached, during re-growth the dopant atoms are shifted towards the solid/liquid interface (lower panels of Figure 3, green lines), due to the presence of the undercooled phase which favors the B state with low diffusivity and a large density gradient of the high diffusivity component (red lines). As a consequence a net migration of impurity atoms from left to right (in the panel) is the combined result of the two-component evolution.

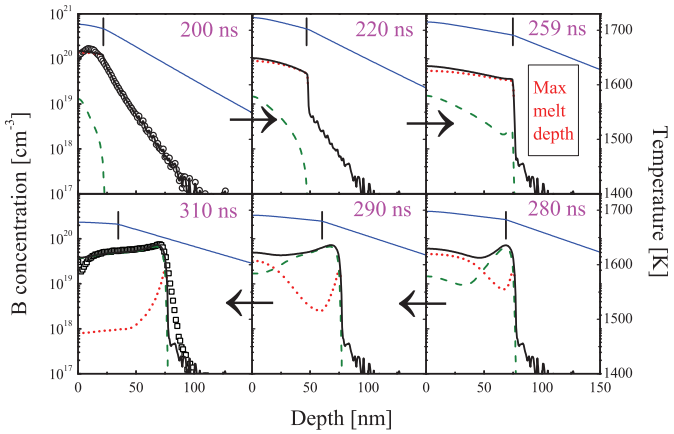

Fig. 3: Dopant evolution during the laser irradiation process (2.3 J/cm^2). Melting (re-growth) stage is indicated by the forward (backward) arrow. We plot he total (black), the HD (red) and the LD (green) boron concentrations. The as-implanted (empty circles) and the final (empty squares) SIMS profiles are also shown, as well as the local temperature (blue line) and the *l-s* interface (bar).

IV. Conclusion

In conclusion our PF-KMC simulations of the boron-damage evolution during a sub-μs LTA process suggest that initial defective system, i.e. interstitial and vacancy cluster as well as BICs complexes, play a key role on the boron activation process. A component of the implanted impurity ions remains trapped in the BICs aggregates also when the number of shots, i.e. the thermal budget, was increased. In addition our results demonstrated that the calibration of the *I* and *V* defects in Silicon as well as BICs complex, extracted from fitting procedures for constant temperature processes, correctly predicts the activation dynamics in an highly damaged matrix during a sub-μs laser annealing treatment. In *l*-Si the anomalous impurity redistribution during a LTA process has been also investigated. The developed model is consistent with the peculiar properties of *l*-Si, i.e the coexistence between the covalent and metallic bonds, and reproduces the experimental data for all the studied regimes by varying laser fluence.

Acknowledgment

The research leading to these results has received funding from the European Seventh Framework Programme (FP7/2007-2013) under the grant agreement n 258547 ATEMOX (Advanced Technology Modeling for Extra-Functionality Devices).

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