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Modeling of Annealing of High Concentration Arsenic Profiles

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ABSTRACT

Understanding the diffusion and activation of arsenic is critical for the formation of low resistance ultra-shallow junctions as required for nanoscale MOS devices. In this work, we use results of *ab-initio* calculations in order to gain insight into the fundamental processes involved in arsenic activation/deactivation. Utilizing continuum modeling, we find it is possible to account for both the very rapid initial deactivation of arsenic as well as the strongly superlinear dependence of interstitial supersaturation on doping level which accompanies deactivation. The critical process is the rearrangement of As atoms via interstitial mediated diffusion leading to ejection of silicon atoms from arsenic complexes and formation of arsenic-vacancy clusters.

INTRODUCTION

There is a strong attractive interaction between arsenic and vacancies due to the combination of strain compensation and valence [1]. As a result, under most conditions deactivation of arsenic occurs primarily via the formation of arsenic vacancy complexes. *Ab-initio* calculations [2,1] find that As_4V complexes (4 substitutional As atoms surrounding an empty lattice site) are the most energetically favorable, which seems reasonable given that this configuration allows each valence 5 As to have 3 nearest neighbors. It has been observed experimentally for high active arsenic concentrations, initial deactivation is very rapid (within 15 seconds at 750°C) [3]. Arsenic also shows strong deactivation for temperatures as low as 400°C [4].

It has been observed that deactivation of high concentration arsenic layer injects interstitials into the substrate [5]. It was proposed, based on XSW (X-ray standing waves) [6] and positron annihilation spectroscopy (PAS) experiments [7] that several second nearest neighbor As atoms (two or more) may kick-out adjacent Si atom, forming an arsenic-vacancy cluster and a self-interstitial. *Ab-initio* calculations suggest [8] that energetically the most favorable reaction of this kind is: $As_4Si \rightarrow As_4V + I$. The strong binding energy between arsenic atoms and a vacancies dramatically reduces the energy associated with Frenkel pair formation at sites surrounded by arsenic.

We have investigated these processes via *ab-initio* and continuum simulations. By including both interstitial and vacancy-mediated diffusion processes, we find it is possible to account for both the very rapid initial deactivation of arsenic as well as the strongly superlinear dependence of interstitial supersaturation on doping level. The critical process is the rearrangement of As atoms via AsI pair diffusion leading to formation of arsenic clusters which are favorable for vacancy incorporation and interstitial ejection.

MODELING

Ab-initio calculations

The energy barriers for ejection of a silicon atom from an As_4Si tetrahedral cluster was calculated via density functional theory (DFT). The initial state for the process consisted of a 64 atom silicon lattice in which four silicon atoms were replaced with arsenic atoms. The As_4Si cluster forms a tetrahedron with a silicon atom at the center of the cluster. The arsenic atoms are thought to be electronically active in this configuration [2]. During the deactivation process the central silicon atom is ejected from the cluster, becoming an interstitial (I) and leaving behind a vacancy (V). A final state was chosen with the interstitial silicon atom as far from the deactivated As_4V cluster as possible in a hexagonal interstitial site. The minimum energy path for the process was calculated with the nudged elastic band (NEB) [9] method in which 8 images were used to connect the initial and final states. The DFT calculations were done with the VASP [10] code using the PW91 functional [11] and ultrasoft pseudopotentials [12]. Plane waves up to a 200 eV energy cutoff were used to represent the wavefunction in the unit cell. The calculations were done with eight points in the k-point mesh.

The results of the NEB calculation are shown in Fig. 1. There is a small initial barrier of 0.2 eV in which the silicon atom moves from the center of the As_4Si tetrahedron (a) to a stable site at the center of one of the tetrahedron faces (b) (e.g. in the center of the triangle formed by 3 of the 4 As atoms, which have relaxed apart). The dimer method [13] was used to search for low energy saddle points leading from the initial state. Five independent dimer searches found the process to (b) to have the lowest barrier. From (b) to (c) the mobile silicon atom continues in the same direction away from the cluster through a tetrahedral site to a hexagonal interstitial site over a barrier of 1.4 eV. At this point the arsenic cluster is thought to be inactive as the interstitial silicon atom is removed from the cluster. This is supported by the final process in which the interstitial silicon atom diffuses to another slightly lower energy hexagonal site (d) because the barrier of 0.3 eV is nearly the same as the bulk hexagonal-tetrahedral-hexagonal diffusion barrier. The overall process is particularly interesting because the presence of the arsenic atoms allow for the creation of an interstitial vacancy pair with a barrier of 1.4 eV which is much less than the Frenkel pair formation DFT barrier of more than 7 eV. Because there does not appear to be any barrier higher than the normal interstitial diffusion barrier, we consider the reverse process to be diffusion limited in the continuum simulations described below.

Continuum simulations

To simulate arsenic deactivation we used four discrete arsenic-vacancy clusters, assumed to be neutral: $(As_2V)^0$, $(As_3V)^0$, and $(As_4V)^0$. Since clustering involves reactions of point defects and defect-dopant pairs of different charge, we include charge transfer reactions, and simulate all possible pathways of clustering reaction. The binding energies for these reactions were fitted to equilibrium activation levels from experimental data [14 ,15]. The comparison of simulation data to experiments is plotted in Fig. 2.

To model interstitial ejection during As deactivation, we include arsenic-assisted Frenkel pair generation in addition to bulk generation/recombination. Since *ab-initio* calculations described above find no additional barrier beyond that required for the I to diffuse away, for I ejection reactions we simply reduce the normal Frenkel pair energy by

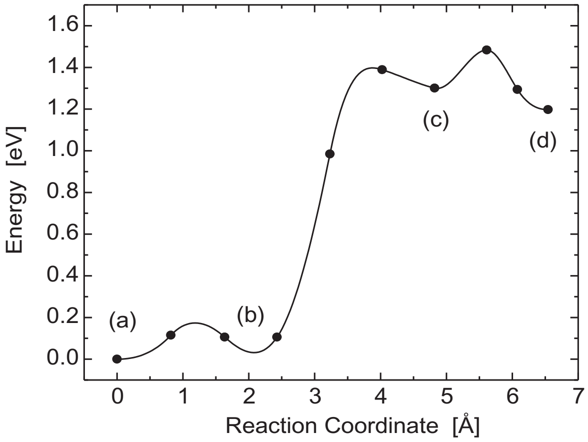

Figure 1. Energy versus distance for kick-out of a silicon atom from between 4 substitutional As atoms.

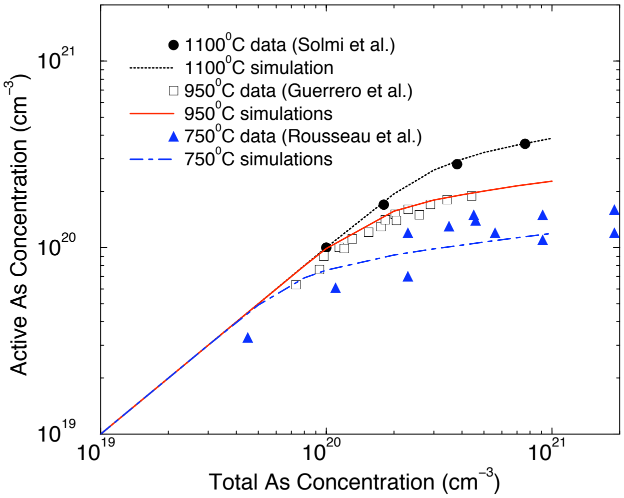

Figure 2. Comparison of arsenic-vacancy clustering model to experimental measurements of active versus total arsenic concentration at long times. The model was fitted to data from Solmi *et al.* [14] at 1100°C and Guerrero *et al.* [15] at 950°C and extrapolated to lower temperature. Extrapolation to 750°C temperature is compared to data from Rousseau *et al.* [16]

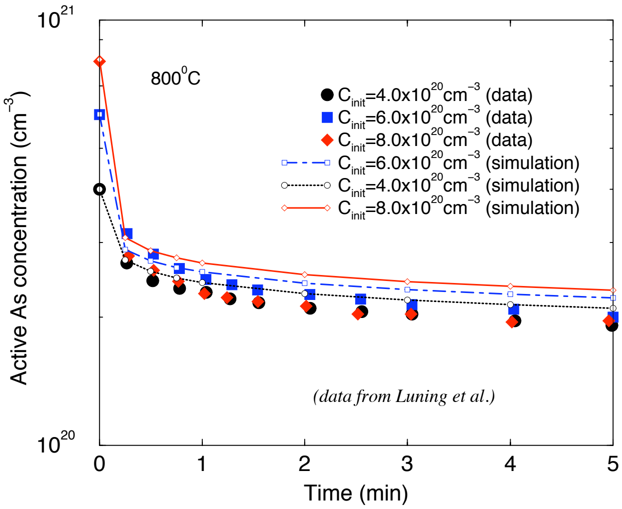

Figure 3. Comparison of simulation results to experimental observations of deactivation kinetics at 800°C for laser annealed As layers [3]. Note that initial deactivation is very rapid and different initial arsenic concentrations quickly reach similar activation levels. Initially As layer was fully activated by laser melt.

the same binding energies that were found from comparison to equilibrium activation. Our analysis shows that dominant reaction for high concentration As deactivation is:

$$(\mathrm{As_4Si})^{4+} + 4\mathrm{e}^- \rightarrow (\mathrm{As_4V})^0 + \mathrm{I}^0. \tag{1}$$

The initial number of $\mathrm{As_4Si}$ complexes after ion implantation and regrowth is estimated based on random distribution of dopants and the corresponding occupational probabilities,

$$C_{\mathrm{As_4Si}} = C_{\mathrm{Si}}\left(C_{\mathrm{As}}/C_{\mathrm{Si}}\right)^4\left(1 - C_{\mathrm{As}}/C_{\mathrm{Si}}\right). \tag{2}$$

During deactivation anneal $\mathrm{As_4Si}$ complexes are assumed to be formed by AsI pair migration, again based on random reconfiguration. The strong super-linear dependence of deactivation reaction on As concentration gives a sharp onset of deactivation as a function of As concentration. Since a large number of interstitials are released during As deactivation, a corresponding large interstitial supersaturation is present throughout the process. We used a moment-based {311}/loop model to account for extended defect formation [17]. High interstitial supersaturation significantly increases As diffusivity via AsI pairs which helps maintain sufficient concentration of $\mathrm{As_4Si}$ complexes during the deactivation process.

COMPARISON TO EXPERIMENTS

It has been observed in isothermal anneal experiments [3], that for high arsenic active concentration, initial deactivation is very rapid (within 15 seconds). After this initial deactivation, activation level is similar for all doses. After initial deactivation (15 seconds), deactivation continues but on much slower time scale. At lower temperature the deactivation kinetics are substantially slower but show same basic behavior. Fig. 3 and Fig 4 shows comparison of our model to experimental data. It has also been observed via buried B marker layers that deactivation of high concentration arsenic layers injects

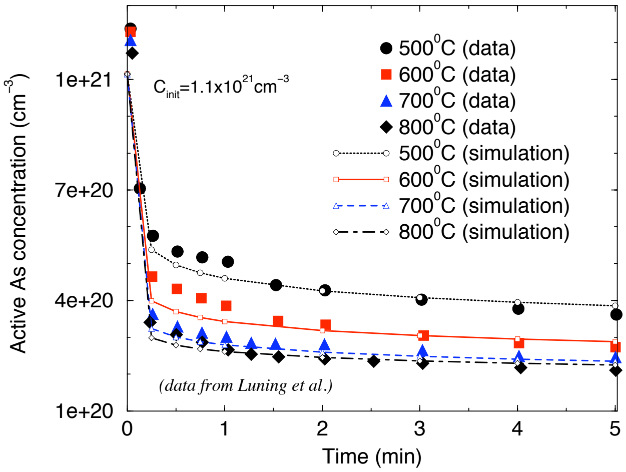

Figure 4. Deactivation kinetics for laser annealed As layers, with comparison of simulations to experimental data from Luning [3]. Even though equilibrium solubility is higher for higher T, initial deactivation is limited by kinetics, so the lower T anneals give higher active concentrations.

interstitials into the substrate [5]. Initial rapid deactivation is due to interstitial ejection from As clusters which form due to random dopant motions. Figure 5 shows comparison of simulation results to experimental data of Rousseau for arsenic layers which were initially fully-activated via laser anneal.

CONCLUSIONS

We utilized a combination of *ab-initio* calculations (DFT) and continuum modeling in order to gain understanding of arsenic diffusion and activation/deactivation. The results highlighted the importance of ejection of silicon atoms from arsenic clusters. The barrier for Frenkel pair generation is reduced by the strong binding of V to As clusters. These As clusters form via random interstitial-mediated diffusion. We find it is possible to account for both the very rapid initial deactivation of arsenic as well as the strongly superlinear dependence of interstitial supersaturation on doping level which accompanies deactivation.

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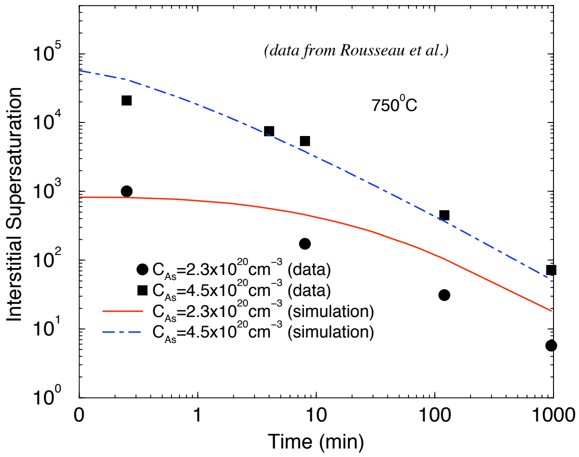

Figure 5. Comparison of simulation results to experimental observations of interstitial supersaturation versus time for different arsenic concentrations, measured via buried marker layer [16]. Note order of magnitude difference in supersaturation with factor of 2 change in initial As concentration.

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