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COMPLEX DIFFUSIVE PROCESSES IN SILICON

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Diffusion is often viewed as a simple process of atoms in an equilibrium configuration making a jump along some path overcoming an energy barrier. First-principles calculations have revealed that even seemingly simple processes can hide enormous complexity. This paper reviews several such cases that have been recently investigated by the authors.

1. Introduction

The simplest case of atomic diffusion in a solid is that of an interstitial impurity. One can imagine that the impurity can jump from one interstitial site to another equivalent interstitial site by overcoming a simple barrier of height E . The diffusion coefficient in such a case is of the form

$$D = D_0 e^{-E/kT}.$$

Many other cases of diffusion (e.g. self-diffusion mediated by vacancies, diffusion of a complex consisting of a vacancy bound to an impurity, etc.) lend themselves to a similar description.

Recent advances in first-principles calculations have made it possible in recent years to investigate the details of complex atomic configurations and complex migration modes. This article presents a review of a number of such cases that have been studied by the authors. In one such case, namely the segregation of As impurities in Si grain boundaries, the theoretical predictions have been complemented and confirmed by high-resolution microscopy.

2. Theoretical method for atomic-scale calculations

All the atomic-scale theoretical results described in this article were obtained with state-of-the-art techniques based on density functional theory, first-principles pseudopotentials, and the local-density approximation for the exchange-correlation potential. Supercells and plane-wave basis sets were used. This methodology has been

pseudopotentials, and the local-density approximation for the exchange-correlation potential. Supercells and plane-wave basis sets were used. This methodology has been tested in a wide range of solid-state systems by many researchers and has been established as accurate and reliable for total-energy-based properties such as those discussed here. Details of the calculations can be found in the original references given below.

3. Oxygen in Silicon: A Very Complex Simple Jump

This is a case that on the face appears very simple, yet turns out to hide enormous complexity. The work has been reported by Ramamoorthy and Pantelides in Ref. 1, where references to the original literature can be found.

Oxygen has long been known to occupy a bridge site between neighboring Si atoms, forming a buckled Si-O-Si chain virtually identical to the Si-O-Si chains in SiO₂. Its migration has been measured over a range of more than 1000 degrees and has been found to have a simple Arrhenius behavior with a 2.5-eV activation energy. The migration ought to be a simple process: the O atom jumps from one bridge site to the next. The saddle point should be at the midpoint of the O path.

Theory over the years had difficulty accounting for the observed activation energy. Calculated values for the O atom at the midpoint of its migration path ranged from 1.2 eV to 4.1 eV. Some authors found ~2.5 eV, but those calculations were not the most definitive. Then, a paper by Jiang and Brown[2] in 1995 reported more extensive calculations using classical interatomic potentials. These authors stepped the O atom along its entire path, relaxing the Si atoms at each step. They found that the maximum energy was at a point after the O atom passed the midpoint of its path. This maximum energy was ~2.5 eV, in apparent agreement with the observed value. However, Jiang and Brown did not notice that the total-energy profile they computed along the path did not satisfy a basic symmetry requirement, namely time reversal, which requires that the energy profile be symmetric about the midpoint of the path.

Ramamoorthy and Pantelides[1] performed systematic first-principles calculations and unveiled an enormous amount of complexity while accounting for both the experimental data and the earlier theoretical work. It was found that the motion of the O atom is intimately coupled to the motion of the "central Si atom" – the one that participates in both the initial and the final Si-O-Si chain (see Fig. 1). Both these atoms face barriers. Figure 2 shows the barrier faced by the central Si atom when the O atom is at the midpoint of its path. Note that it is not a simple barrier but rather the intersection of two different curves. This result signals even more complexity. In fact, it was found that one needs a total-energy hypersurface in at least four dimensions (the angular and radial positions of the O

atom and the central Si atom in the (110) plane) to properly describe oxygen migration. Fig. 3 shows a cut of this hypersurface in two dimensions. The surface exhibits a "saddle ridge" and a multiplicity of paths crossing the ridge. The height of the ridge is ~ 2.5 eV except at the point where the O and central Si atoms cross the vertical symmetry axis at the same time. Around that point the ridge has a small dip to about 2.2 eV. The Jiang and Brown path corresponds to just one path over the ridge (the solid line in Fig. 3), namely a path where the O atom crosses the ridge first while the central Si atoms moves very little until the O atom almost reaches the end of its path.

More recent work to be published elsewhere[3] examined the effect of H on O diffusion. It was found that H also occupies a buckled bridge position next to the O. Migration of the O atom now proceeds as follows: the O atom heads toward the bridge site occupied by H; the latter moves toward the next bridge site in front of it. This synergism leads to a lowering of the activation by about 1 eV, in agreement with observations. A similar lowering of the activation energy occurs when a second oxygen atom instead of an H atom participates in the process. Again the second O atom occupies a buckled bridge position next to the first O atom. The two O atoms move in tandem.

3. Complex Diffusive Phenomena in Heavily Arsenic Doped Silicon

In the dilute limit, As impurities occupy substitutional sites and act as donors. It has been possible by non-equilibrium techniques to incorporate As impurities as substitutional donors at very high concentrations, as high as 10^{21} cm^{-3} . However, moderate heating ($\sim 300\text{--}400^\circ\text{C}$) leads to rapid deactivation. Partial reactivation is possible by heating to higher temperatures ($>800^\circ\text{C}$). Early work attributed the deactivation to the formation of As_nV_m clusters (where V stands for a vacancy), but there has been no consensus about the values of m and n for the dominant defect. Another major puzzle has been the fact that, in the dilute limit, there is no observable diffusion in the $300\text{--}400^\circ\text{C}$ temperature range. Thus, some other diffusion mechanism must be operating in the heavily-doped limit to enable the As atoms to migrate and form clusters. Early diffusion measurements in heavily-doped samples, however, found that the diffusion constant increases gradually with increasing As concentration, but then begins to drop for As concentrations above $\sim 3 \times 10^{20} \text{ cm}^{-3}$. More recent experiments using rapid thermal annealing techniques, found a sharp increase in the value of the diffusion constant beginning at the same concentration. References to all the relevant experimental work can be found in Ref. 4. Though explanations for some of the observations have been proposed by earlier workers, no comprehensive account of all the data has been possible.

A set of comprehensive calculations by Ramamoorthy and Pantelides reported in Ref. 4 have provided a systematic account of all the perplexing observations and made additional predictions. In particular, it was found that:

- i) Complexes of the form As_nV_m have a negative formation energy for $n>2$. For all such complexes, the binding energy of each As atom (relative to an isolated substitutional site in the bulk crystal) is ~ 1.5 eV. These results mean that As-doped Si is a metastable system at all As concentrations. If it were not for kinetic constraints, all As atoms would decorate vacancies and multivacancies. The result is a consequence of the chemical valency of As which makes threefold-coordinated As energetically favored.
- ii) It has long been known that, in the dilute limit, As diffusion is mediated by AsV pairs. The pair migrates as follows: The vacancy loops around a six-member ring and positions itself "in front" of the As; the As atom jumps into the vacant site; the vacancy again loops around another six-member ring and again positions itself "in front" of the As atom. The activation energy for diffusion by this mechanism (formation plus migration energy of the pair) was computed in Ref. 4 to be 3.9 eV, in excellent agreement with experimental data.
- iii) In the heavily doped limit, Mathiot and Pfister[5] proposed that the same mechanism operates, but the activation energy is lowered by the presence of nearby As atoms. In particular, during migration, as the vacancy loops around a six-member ring, it is likely to pass by another As atom. Mathiot and Pfister recognized, however, that such proximity with another As atom would require extremely high concentrations. They resolved this quandary by invoking percolation theory, according to which an infinite percolation network with very high As concentrations forms when the total concentration exceeds $\sim 3 \times 10^{20} \text{ cm}^{-3}$. The activation energy for the mechanism proposed by Mathiot and Pfister was computed in Ref. 4 to be ~ 1 eV lower than the simple AsV pair mechanism. It would appear, therefore, that the percolation model can account for the mobility of As atoms leading to clustering at moderate temperatures and the observed enhanced diffusion at high concentrations. The model, however, does have a problem in that enhanced diffusion within the percolation network would quickly lead to the formation of As_nV_m clusters that would break up the continuity of the network. In contrast, the experiments show that the clustering process persists for long times.
- iv) Calculations reported in Ref. 4 demonstrated that As_2V complexes are mobile and can, therefore, mediate As diffusion. The net activation energy was computed to be 2.8 eV, i.e. essentially the same as in the mechanism advocated by Mathiot and Pfister. The key difference is that diffusion mediated by As_2V complexes does

not need a continuous percolation network but only high-concentration regions. Such regions may exist, for example, when the average concentration is just below the percolation threshold (pre-percolation patches) or after an initial rapid diffusion for average concentrations that exceed the percolation threshold (post-percolation patches). In the latter case, the initial diffusion leads to clustering that breaks up the percolation network, but As_2V complexes continue to mediate diffusion by traveling both through and between patches.

- v) Mobile As_2V complexes account for all the observed phenomena in a systematic way (see Ref. 4 for more details). In addition, they lead to predictions on the nature of the dominant complexes in deactivated samples. The complexes AsV , As_2V and As_3V are the only one which can break up into an isolated substitutional As and a mobile complex. In each case, the energy to "peel off" an As atom is ~ 1.5 eV, which is the same as the value of the reactivation activation energy Schwenker et al.[6] extracted from their experimental data. Since EXAFS data established that in deactivated samples virtually all As atoms are second neighbors to each other,[7] we conclude that the dominant complexes in deactivated samples are As_2V and As_3V . Higher-order complexes also exist and are the ones that persist during reactivation at 1000°C because the energy needed to break them up is much larger than 1.5 eV.

4. Segregation of As atoms in Si grain boundaries

This is worked carried out by Maiti, Chisholm, Pennycook and Pantelides and is reported in detail in Ref. 8, where references to original literature can be found. The issue is that virtually 99% of As in polycrystalline Si segregates in grain boundaries. This is undesirable because As in grain boundaries is electrically inactive and one normally would like to dope polycrystalline Si very heavily to be used as contact.

The segregation energy (defined to be the energy difference per As atom between As atoms in the grain boundary and the bulk crystal) is measured to be ~ 0.5 eV and is responsible for the observed behavior. It is worthwhile to determine if this large segregation energy is an intrinsic property of grain boundaries in Si or it is a consequence of defects or steps where As atoms bind preferentially. This question became particularly relevant when it was determined by both theory and experiment that tilt grain boundaries in Si without steps or impurities relax to configurations where all Si atoms are fourfold-coordinated.

Recent theoretical work by Arias and Joannopoulos[9] found that As atoms placed at fourfold-coordinated sites in a fully relaxed $\Sigma=5$ grain boundary in Ge remain fourfold and

lower their energy by a minimal amount over bulk sites (~ 0.1 eV). They suggested that the observed large segregation energy is likely to be caused by defects or steps.

The main objective of Ref. 8 was to explore the possibility that As atoms can be incorporated in threefold coordination in otherwise perfect grain boundaries. It was found that threefold coordination is possible if As atoms are incorporated in pairs. The phenomenon is quite intriguing. Two nearest-neighbor substitutional As atoms repel each other trying to achieve threefold coordination (their preferred chemical valence) at a cost of elastic energy in the distorted back bonds. The calculations show that in the bulk crystal and energy gain and cost roughly balance out. In the grain boundary, however, the cost is a bit less. The net result is that a dimer binds in the grain boundary through repulsion! The segregation energy of such dimers was found to be in the range 0.1-0.2 eV. For chains of dimers, however, the segregation energy increased to 0.35 eV (for a case where one actually perfectly ordered As atoms with equal As-As distances) and to 0.5 eV.

The dimer calculations were done for two distinct $\Sigma=5$ boundary structures, both of which have all Si atoms fourfold coordinated, with total energies that are very close (one is higher by 0.15 eV/atom). The As chains with the highest segregation energy are in fact in the grain boundary structure with the slightly higher energy. This result leads to the intriguing suggestion that As atoms segregating in a grain boundary may actually induce a structural transformation of the entire grain boundary.

In addition to theoretical investigations of As impurities in Si grain boundaries, an experimental search was undertaken for evidence of As segregation. Arsenic was implanted and annealed for a prolonged period of time. Micrographs obtained with high-resolution transmission microscopy using the Z-contrast technique ^{Fig. 1} reveal evidence of chains of As atoms. A detailed report of this work will be published elsewhere.[10]

Finally, calculations have been performed to investigate whether the ordering of As impurities in grain boundaries occurs also in isolated dislocations. The results indicate that chains of As dimers again form along the dislocation pipe with very large segregation energies (~ 1 eV).[11]

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FIG. 1. The geometry of O migration in a (110) plane. The solid dots are the nominal positions of Si atoms in the perfect crystal. The open circles show the positions of the Si and O atoms in the equilibrium configuration.

FIG. 2. The total-energy variation of the system, as a function of θ_{Si} when the O atom is at $\theta_o = 90^\circ$. The zero of the energy in this and in subsequent plots is taken as that of the equilibrium configuration.

FIG. 3. The total-energy variation as a function of θ_o and θ_{Si} . The central dot and the hand-drawn path (in the direction of the arrowhead) are discussed in the text.

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