Quantum chemical models of defects in thin silicon films

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Cluster models and quantum chemical methods were used to investigate electronic structure and properties of defects in silicon, including extended defects of crystals, such as surface and interphases dislocations, which create regions of compression and strain. Pressure effect was simulated by reduction of the lattice constant. This approach is adequate for investigation of thin films. Reduced influence of chemical bonding and enhanced use of free volume during O migration under high pressure have been shown. The Si and O interstitial migration activation energies were estimated as 4.21 eV and 2.73 eV, respectively, the former being indifferent to pressure.

Keywords: silicon, oxygen, point defect, quantum chemistry, cluster model.

1. Introduction

Compression or strain arise in thin film-substrate border region due to differences in thermophysical properties. Extended defects in crystals, such as dislocations and inclusions of amorphous phase, also create regions of compression and strain. Precipitation of O_i in Czochralski grown silicon crystal (Cz-Si) can create internal pressure up to several GPa. Cluster models are useful in studying creation and properties of point and extended defects in solid state. As putting a smaller value for the bond length can easily simulate pressure effect, this approach allows to investigate properties of thin films and technologies for their creation and use. We applied this model to analysis of some point defects in Si films. Quantum chemical methods and cluster models were used to investigate properties of O and Si interstitials (O_i, Si_i) as well as their changes under compression.

2. Techniques

The *ab initio* self-consistent field method and the code Gaussian-92 were used to calculate the electronic and spatial structure of defects. The embedded molecular cluster model, consisting of several (5 to 41) Si atoms with H pseudoatoms modelling the rest of crystal were used. Pressure effect was simulated by reduction of the lattice constant (0.23514 nm for perfect crystal).

Models for Si_i in silicon were built using ideal crystal fragments. Si_i in tetrahedral and hexagonal positions was studied using a 9- and a 10-site fragment. The latter contains both the high symmetry positions and a four-Si- coordinated Si atom. Two dumbbell structures (with Si replaced with a dumbbell oriented in <100> or <110> direction) were studied. In case of O_i and other O defects the Chadi model [1] was used, with the cluster of C_{2v} symmetry for $V\text{-}O_2$ and $V\text{-}O_4$ defects.

To model an amorphous phase domain in a solid, cluster models were used containing two groups of atoms in fixed positions representing the host matrix, and the third group, representing the amorphous phase and placed between the two first groups. We investigated the electronic and geometrical structure of small "quasi free" groups of (1 or 2) atoms belonging to the amorphous phase to study features of the amorphous phase domain and of arising distortion. Interaction in covalent solid is short range, hence only nearest neighbours are important for simple model calculations. Therefore, we used clusters of several Si or C atoms. Only atoms from the crystalline-amorphous phase frontier region were included directly in the model. The rest of solid was simulated by H pseudoatoms at dangling bonds.

3. Results

The model of O_i is given in Fig. 1. O_i defect was shown to be linked with two Si atoms standing a bit apart from the middle of Si-Si bond. The nearest neighbours of O_i are shifted from their positions in ideal lattice outside by 0.05 nm. We investigated the transition state between two neighbouring equilibrium configurations (the geometry is shown in Fig. 1, and its resulting optimised parameters are given in Table 1 for different pressures). The total-energy variation during O migration is a very complex hypersurface in a multidimensional space [2]. The path of the O atom during diffusion is asymmetric. As the ridge for the transition in the multidimensional space has roughly a constant height over a considerable range, the symmetric tran-

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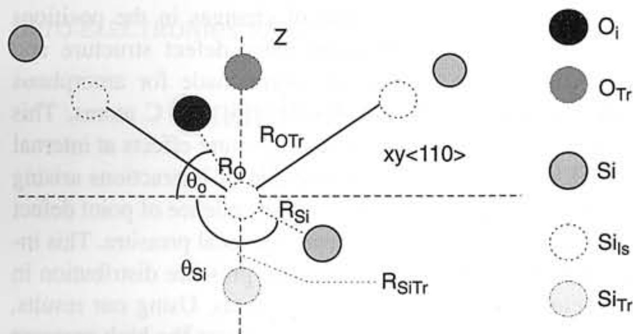

Fig. 1. Oxygen interstitial defect model in silicon. O_i is the interstitial oxygen atom, Si is the silicon atom in plane (110), Si_{ls} is the silicon atom position in perfect crystal; O_{Tr} and Si_{Tr} are O and Si atom positions in a transition states.

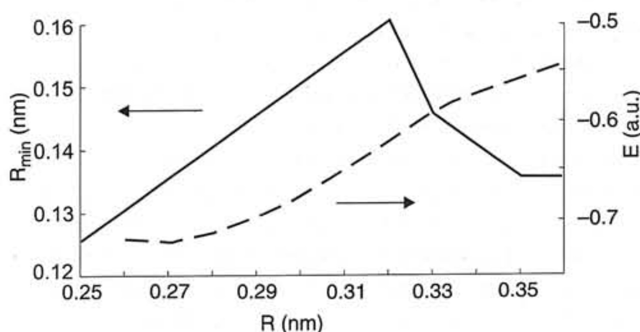

Fig. 2. Modelling of strain effect onto cluster H_2C-C-CH_2. The middle C atom separation R_{min} (solid line) from the nearest C atom and the total energy E (dashed line) as functions of the distance R between the outer C atoms in the cluster model H_2C-C-CH_2.

sition state represents well the transition activation energy. The energy difference between the symmetric transition state and the equilibrium configurations can be assumed to be a good estimate for the diffusion activation energy. This estimate was made for symmetric transition state. We assume the changes in the estimate for the diffusion activation energy to be independent from the real diffusion path. As is can be seen from Table 1, under a uniform compression causing 0.25, 0.37, or 5.0% reduction of the lattice constant, the angle O-Si-Si in O_i defect equilibrium state grows from 30 to 40 degrees, and in diffusion transition states O atom moves away from the nearest Si atom, but the Si atom approaches its ideal lattice position. The general tendency for higher pressure seems to be lower influence of chemical bonding and more efficient use of free volume during the O transition. The migration activation energy for O_i defect was estimated as 2.73 eV at the atmospheric pressure, and 2.70, 2.68, and 1.92 eV for the lattice compressed by 0.25, 0.37, or 5.0%, respectively.

The cluster used for V-O_2 defect was found to have slight deviation from D_{2d} symmetry for all studied pressure values. The distance between the O atoms is 0.25 nm, each of them being chemically bound with the two nearest Si, saturating their dangling bonds. The cluster used for V-O_4 defect shows slight deviation from D_{2d} at atmospheric pressure, a strong deviation at 5.0% lattice compression, and two energetically near (by 0.15 eV) configurations at 0.37% compression.

Tetrahedral and hexagonal positions and two dumbbell structures oriented in <100> or <110> directions were used to calculate Si_i defect. In all cases, the nearest neighbours of the interstitial are shifted from their positions in ideal lattice outside by approximately 0.05 nm, which demonstrates the repulsive interaction of Si_i with environment. The Si_i migration activation energy estimated as energy difference in tetrahedral and hexagonal sites is 4.21 eV and does not change with pressure. We performed an analysis of the electronic structure of defects. In case of Si_2 <100> defect simulated by the cluster of Si_{12+6} (Si_{x+y} means that x Si atoms were held at their fixed positions while the positions of y atoms were optimised), the dumbbell silicon atoms are strongly bonded only with one another, having the bond order 0.36. The bond is formed with strong participation of π type orbitals. The bonds are σ type with bond order 0.24 in the crystal. The total energy of Si_2 <110> defect simulated by Si_{12+6} cluster is a bit lower, but the structure is significantly different. One atom of the Si_2 dumbbell is placed near the regular lattice site, forming bonds close to ones in the regular lattice. Another Si atom is pushed out in nearly tetrahedral position with weak links with nearest atoms. This result demonstrates validity of the model calculations where Si atom in tetrahedral site is used as a model for the Si interstitial and energy difference in tetrahedral and hexagonal positions is used as an estimate of migration activation energy.

Table 1. Oxygen defect model in silicon: interstitial geometry and transition state geometry (cf. Fig. 1) and diffusion activation energy (E_a) at different pressures.

Compression (%)	Pressure (GPa)	E_a (eV)	θ_o (deg)	θ_{Si} (deg)	R_{OTr} (nm)	R_O (nm)	R_{Si} (nm)	R_{SiTr} (nm)
0.00	0.00	2.73	58.8	148.3	0.1623	0.1226	0.0465	0.0250
0.25	0.75	2.70	59.3	148.5	0.1629	0.1229	0.0464	0.0244
0.37	1.10	2.68	59.7	148.5	0.1631	0.1231	0.0463	0.0241
5.00	~15	1.92	68.3	149.4	0.1694	0.1276	0.0452	0.0155

Main results concerning energy dependence on the structure of the amorphous phase are shown in Fig. 2 for the cluster H_2C-C-CH_2 as an example. As it can be seen in the figure, the middle C atom is at the middle of the straight line connecting two other C atoms in case of moderate lengths of the molecule. When the distance R between the outer atoms exceeds approximately 0.33 nm, the symmetry breaks so that the middle atom is displaced to one side, that manifests appearance of disorder in the structure and justifies its interpretation as an inclusion of amorphous phase. Respectively, at the same distance, changes were observed in the behaviour of the total energy of the system (see Fig. 2), that takes there a value of -115.589 a.u. The model H_2C-C-C-CH_2 (chain of two carbon atoms between CH_2 groups) demonstrates the lowest energy for axial position, symmetrical regarding the central point of the central C-C group.

4. Conclusions

Point defects in bulk and on surface can be used as elements of electronic devices. Nanostructures in thin films, formed from point defects and their clusters are especially perspective in molecular electronics. We have used quantum chemical calculations to study oxygen defects in silicon, silicon interstitials, as well as Si and C nanostructure formation and properties. Scanning probe microscopy (SPM) may be used very effectively for creation and investigation of nanostructures. During SPM studies, local compression and strain arise, and individual chemical bonds can be rearranged significantly. We have simulated influence of the compression and of changes in the positions and chemical bonds of atoms onto defect structure and properties. Some calculations were made for amorphous phase simulations with 2, 3, and 4 Si and C atoms. This model could serve to investigate pressure effects at internal interfaces, as well as for description of interactions arising in SPM. We have calculated the dependence of point defect diffusion activation energy from the local pressure. This information may be used to measure pressure distribution in the neighbourhood of extended defects. Using our results, we have analysed the experiments where the high pressure was created specially.

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