Interstitial oxygen in elemental and compound semiconductors: fundamental properties and trends

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Abstract. The equilibrium structure, electronic properties and potential energy surfaces of interstitial oxygen (O_i) in c-C, Si, BP, AlP, c-SiC and c-BN are calculated in small and large molecular clusters. The theoretical level ranges from the 'approximate *ab initio*' Hartree–Fock method of partial retention of diatomic differential overlap to large-basis-set *ab initio* Hartree–Fock followed by second-order corrections for electron correlation (MP2). The equilibrium site is a puckered bridged bond in all hosts. In compound semiconductors, O_i has a larger degree of bonding with the most electronegative of the two host atoms (P, C or N) than with the least electronegative one and puckers in a direction that maximizes the overlap with its second-nearest neighbour. The dipole moment of the defect and the barrier for reorientation of O_i around and through the (111) axis are calculated. In order to estimate the relative stability of O_i in the various hosts, we determine the energies involved in inserting molecular O_2 into the lattice and dissociating it into two isolated O_is. Finally, we calculate the barriers for migration of O_i between adjacent equilibrium sites. There are two such barriers in compound semiconductors. Whenever possible, we correlate the properties of O_i with various properties of the host, such as its bond length and its ionic character, in order to gain predictive insight into the fundamental properties of interstitial oxygen in semiconductors.

1. Introduction

Oxygen is one of the commonest impurities in many semiconductors. The vast majority of published studies about oxygen have been done in silicon [1–3]; the properties of oxygen in silicon have been studied for over forty years, and remain an active area of research. However, O and O-related complexes play important roles in other semiconductors as well, for example in GaAs [4, 5].

The presence of high concentrations of oxygen in Si was reported from optical absorption experiments [6] in the mid 1950s, and a puckered Si–O–Si equilibrium configuration of interstitial oxygen (O_i), with an Si–O bond length of about 1.6 Å was proposed. This geometry was soon confirmed [7–10] and a number of infrared (IR) frequencies for the various O isotopes were reported [11]. The barrier for rotation of O_i around the {111} axis was measured to be less than 0.09 eV. Corbett and co-workers [12] performed stress-induced dichroism experiments and found the diffusivity of O_i to be $0.23 \exp(-2.56\,\mathrm{eV}/kT)\,\mathrm{cm}^2\,\mathrm{s}^{-1}$. This number was later confirmed [13, 14].

A number of theoretical studies [15–21] have dealt with O_i in Si. There is general agreement among theorists regarding the Si–O bond length, which various groups predict to be between 1.59 Å [20] and 1.62 Å [17]. The Si–Si bond expands by about 0.8 Å to accommodate the interstitial, which is a slightly smaller expansion than in the case of bond-centred hydrogen [22]. Theorists predict a substantial charge transfer from the Si nearest

neighbours (NN) toward O_i (of the order of $0.8e^-$ to $1.2e^-$), which creates a large dipole moment. The calculated Si–O–Si bond angle varies between 152° [17] and 180° [18]. This discrepancy is due to the softness of the bending constant for this species.

There is a great diversity of predicted barriers for diffusion of O_i: the semiempirical method of MINDO/3 predicts [16] 2.49 eV, in close agreement with experimental data (see above). Much lower barriers are obtained using the density functional technique: 1.2 eV [17] and 1.8 eV [19]. In the latter paper, it is argued that dynamic effects raise the barrier by 0.5 eV to 0.9 eV, as the hopping of O_i occurs in a shorter time than the associated Si motion. Finally, the vibrational modes of O_i have been calculated [17, 18, 23].

Much of the interest in O_i in Si stems from its tendency to cluster or form complexes with other defects, thus altering the electrical and optical properties of the crystal. The most famous of these defects are the oxygen-related double donors [24–28] known as thermal donors (TD). TD formation correlates with the loss of O_i, but involves an activation energy of 1.8 eV, a number much lower than the measured barrier for diffusion of isolated O_i (2.56 eV). This has led to the search for oxygen dimers and other aggregates [16-19, 21, 29-31] which might diffuse more easily. Detailed calculations of possible structures for TD cores have recently been published, together with a review of TD-related theoretical work [31].

In this paper, we report studies of O_i in six group IV and group III–V diamond or zincblende semiconductors: c-C, Si, BP, AlP, c-SiC and c-BN. A discussion of the fundamental properties of these hosts and a comparison of experimental and theoretical bond lengths and valence bandwidths can be found in [32]. The present calculations deal with the following properties of O_i: equilibrium configurations, dipole moments, orientation, relative stability and barriers for migration from one site to the next (there are two such barriers in compounds). Whenever possible, we look for trends and correlate specific properties of O_i to the lattice constants, the ionic character or the bond strengths.

The paper is organized as follows. Section 2 contains a discussion of the methodologies used in this study. Section 3 deals with the equilibrium structures and the barriers for rotation. The stability of O_2 is discussed in section 4 and the barriers for diffusion are presented in section 5. A summary and a discussion of the results are given in section 6.

2. Methodology

The calculations were performed in molecular clusters containing 5–44 host atoms. The surface dangling bonds are saturated with H atoms as described in [33]. The host–host and host–saturator bond lengths were previously optimized [32]. The small clusters were used to obtain preliminary geometries which served as inputs for geometry optimizations in the larger clusters. All the geometries discussed below were obtained in the largest clusters. The effects of cluster size on the calculated properties of O_i have been monitored, but only small quantitative differences in the equilibrium geometries and bond orders were found. These effects are discussed in the text as appropriate.

All the geometry optimizations were done with the approximate *ab initio* Hartree–Fock (HF) method of the partial retention of diatomic differential overlap (PRDDO) [34]. True *ab initio* HF calculations require the calculation and storage of some N^4 two-electron integrals, where N is the total number of orbitals. In our largest clusters N is almost 500, which makes geometry optimizations computationally intractable at the *ab initio* level, even with minimal basis sets, especially since the symmetry is most often C_1. The method of PRDDO has been designed to reproduce *ab initio* HF calculations at a fraction of the cost without introducing adjustable parameters. The key is to orthogonalize the atomic orbitals using the Löwdin

procedure, which maintains the localized character of the orthogonalized atomic basis set. As a result, the two-electron integrals involving four different centres are exceedingly small and can be neglected. This reduces the dimension of the problem to a tractable N^3. The neglect of some integrals results in small and systematic errors (relative to minimal basis set *ab initio* HF calculations) which are corrected when constructing the Fock matrix (for details, see [34, 35]).

The method of PRDDO uses minimum basis sets of Slater orbitals, which are better suited than linear combinations of Gaussians since they have the correct cusp and tail. The geometries predicted by PRDDO are systematically very close to the ones predicted by *ab initio* HF (for example, bond lengths are within 0.01 Å). The PRDDO calculations reported below used the following Slater orbitals: one for H (1s); five for B, C, N and O (1s, 2s, 2p); nine for Al, Si and P (1s, 2s, 2p, 3s, 3p) except for the NN and second NN to O_i, which had an additional set of five orbitals (3d). We used PRDDO geometries as inputs for single-point *ab initio* HF calculations with split-valence basis sets with polarization functions.

The main weakness of PRDDO and *ab initio* HF methods is the neglect of electron correlation (electron exchange, however, is included exactly). For this reason, barriers for diffusion of an impurity such as O_i are overestimated: in a perturbation expansion, the first-order corrections are roughly proportional to the inverse of the energy difference between the occupied and unoccupied states. At the equilibrium configuration, this energy difference is large and the system is well described at the HF or PRDDO levels. At saddle points of the potential energy surface, however, the bonds are stretched, the energies of the bonding orbitals go up, the energies of the antibonding orbitals go down and the energy differences become smaller. As a result, the correlation corrections are more significant and their neglect results in too high energies.

In order to minimize these errors, we have used the PRDDO equilibrium and transition-point geometries and performed single-point large basis set *ab initio* HF calculations followed by second-order Møller–Plesset [36] electron correlation corrections (MP2). These calculations were done in five and eight host-atom clusters.

3. Equilibrium configurations and barriers for reorientation

Interstitial oxygen cannot remain at the tetrahedral interstitial (T) site because O_i is an orbital triplet in T_d symmetry and is therefore Jahn–Teller unstable. It moves off-centre toward a bond-centred (BC) site and strongly binds to the lattice. This is the only configuration for isolated O_i. Although the result is a puckered bridged bond, we will label it the 'BC' configuration for simplicity.

3.1. Equilibrium configurations

The equilibrium configurations were obtained by relaxing O_i both parallel and perpendicular to the $\langle 111 \rangle$ axis and allowing first and second NN to relax as well. The process was repeated with O_i oriented at various angles around the $\langle 111 \rangle$ direction. This not only produced the most stable configuration but also gave the barrier for rotation of oxygen around the $\langle 111 \rangle$ axis. The equilibrium configurations for O_i in the six hosts are shown in figure 1.

In all our hosts, the lowest-energy configuration has O_i in the {110} plane. However, it is only in group-IV hosts that O_i remains in the plane bisecting the original host–host bond and forms an equally strong bond with its two NN. In III–V hosts, O_i moves off the bisecting plane and forms a bond which has a larger degree of bonding [37] with the most electronegative (ME) of its two NN than with the least electronegative (LE) one.
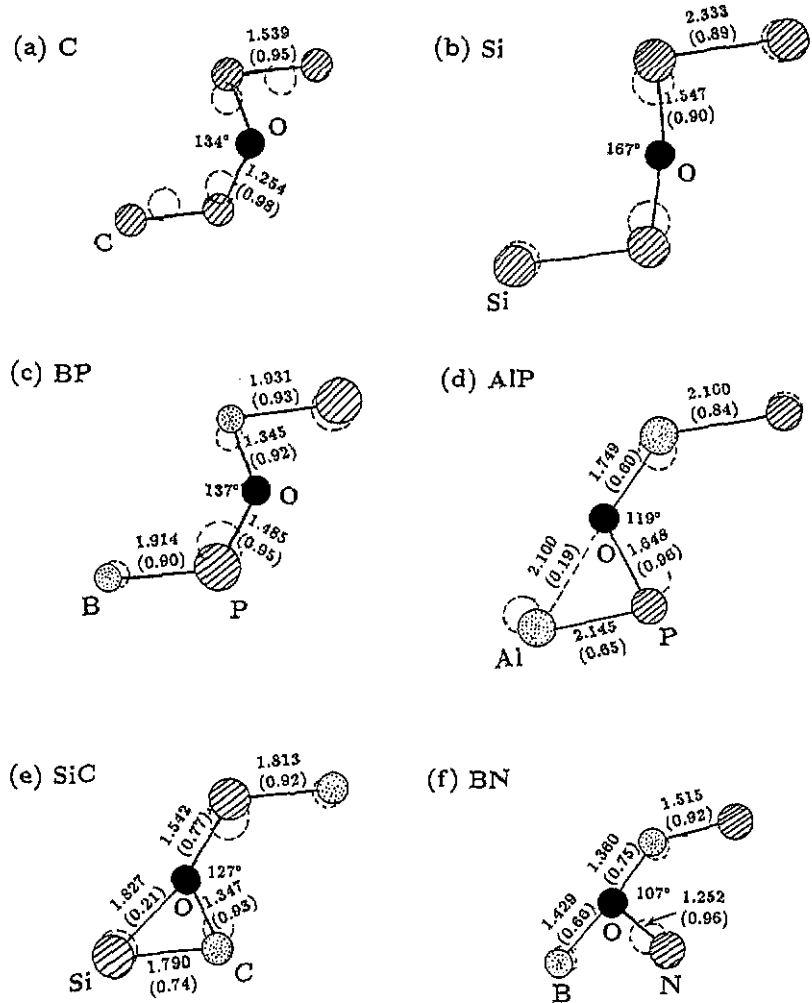
Figure 1. Calculated equilibrium configurations for O_i in c-C, Si, BP, AlP, c-SiC and c-BN. In elemental hosts, O_i has a symmetric configuration, while in compounds the degrees of bonding to the ME atom is larger. The figures give the bond lengths (in Å), the degrees of bonding (in parenthesis) and the bond angle (see text). The broken circles show the undisturbed locations of the host atoms.

Figure 1 shows that the equilibrium configuration of O_i is close to a 'true' BC configuration only in Si. This is due in part to the fact that Si has the largest lattice constant of the six hosts we studied and the insertion of O_i results in less distortion of the lattice. In the hosts with smaller lattice constants, O_i forms a much sharper angle. The most extreme case is BN, where the equilibrium configuration is actually very near the 'y-lid' conformation [16], which is the transition point between adjacent equilibrium sites. Several factors contribute to this unusual configuration. First, BN combines the smallest and the largest oxygen–host bond strengths [38]: O–N has 2.1 eV, O–B has 5.47 eV, while B–N is intermediate with 4.0 eV. This is the only occurrence where one of the O–host bonds is stronger than the host–host bond. As a result, in the lowest-energy configuration, O_i is

nearest to an N atom in a way that maximizes the overlap with *two* B atoms. Second, O_i is more massive than either B or N.

The most stable configuration has one of the second NN closest to O_i. In group-IV hosts, this produces six equivalent BC sites. In the compounds, there are two inequivalent configurations, one with an LE atom and one with an ME atom as the closest second NN. Figure 2 shows again the equilibrium configurations but the atoms are represented by circles with radius equal to the covalent radius [39] of that atom. Figure 2 shows that O_i always points towards the second NN with the largest covalent radius, in order to maximize the overlap with the lattice (the thick arrow in figure 2 shows the dipole moment, not the orientation of O_i). In general, the second NN with the largest covalent radius is the LE atom.
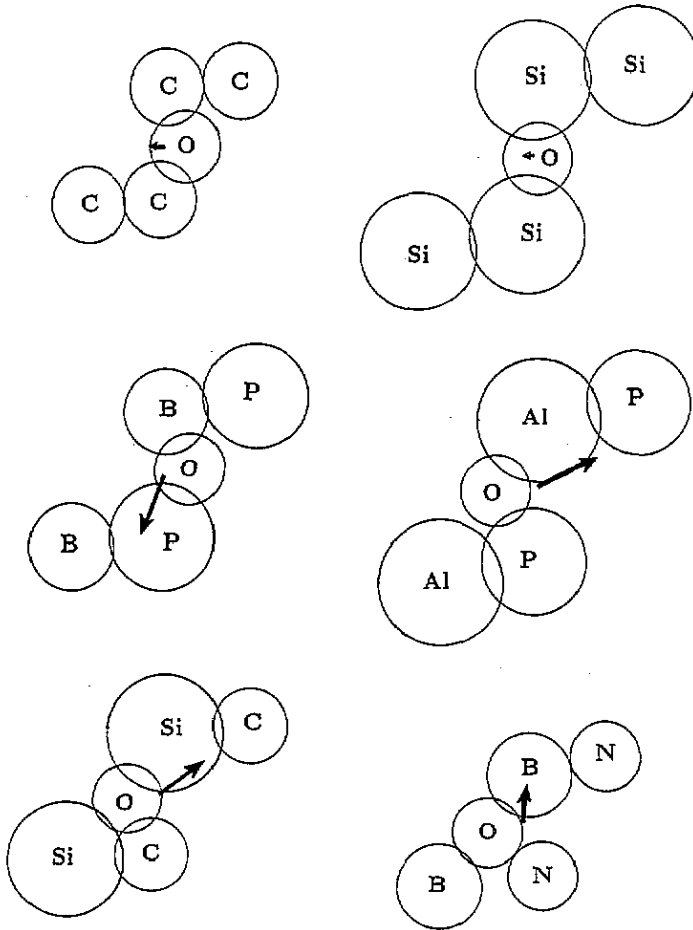

Figure 2. Lowest-energy configurations for O_i using covalent radii. O_i always points in the direction of the second NN which has the largest covalent radius (see table 1). The vectors show the strength and direction of the dipole moment (in Debye) induced by O_i (see text). Note that the dipole moment in elemental semiconductors is much smaller than in compounds.

Note that in BP, O_i points toward the ME atom. An examination of this case shows that the desire to maximize the overlap is not the only factor which determines the equilibrium

orientation of O_i in compound semiconductors. Oxygen has a large electron affinity and also wants to be as close as possible to the LE second NN atom in the lattice. In fact, in small clusters of BP, we find that O_i points toward the LE atom. In our largest cluster, in which second NN can be optimized, the configuration shown in figure 2 dominates, but only by 0.07 eV. This occurs because BP is the compound semiconductor with the smallest ionic character, i.e. B and P have almost the same electronegativity [40].

Finally, figure 2 also shows the dipole moments of O_i. They were calculated from the expectation value of the dipole moment operator rather than from the Mulliken charge distribution, which tends to be unreliable. We subtracted from the total dipole moment of O_i the calculated dipole moment of the perfect cluster. As expected, the dipole moment associated with O_i is much larger in compound than in elemental hosts. The origin of the dipole moment vector shown is at the BC site of the perfect lattice.

3.2. Barriers for reorientation

The barrier for rotation of O_i about the $\langle 111 \rangle$ axis does not involve breaking a covalent bond, except for the overlap with one of the second NN to O_i. We obtained this barrier by reoptimizing the geometry (first and second NN) for various orientations of O_i about the $\langle 111 \rangle$ axis. This procedure assumes that the lattice has enough time to fully relax as O_i rotates and therefore tends to underestimate the barrier. To some extent, this is balanced by the fact that PRDDO tends to overestimate barriers. The calculated barriers for rotation are shown in figure 3. The barrier heights show an almost perfect correlation with the Pauling ionic character [40] of the host. This suggests that one is mostly dealing with a dipole moment rotating in the electrostatic field of a partly ionic crystal.

Note that a rotation around the $\langle 111 \rangle$ axis which preserves a puckered-bond configuration is not the only way O_i can reorient between equivalent configurations. Oxygen can in principle also move *through* the centre of the bond (i.e. through the $\langle 111 \rangle$ axis) rather than around it. We took the value of this barrier to be the difference in energy between O_i at the stable equilibrium configuration and on the $\langle 111 \rangle$ axis (optimized with a bond angle of 180°), calculated at the PRDDO level. The two barriers are compared in table 1. Except for Si and AlP which have the largest lattice constants of the hosts considered here, this barrier is much higher than the barrier for rotation. The only hosts in which O_i could be expected to reorient *through* as easily as *around* the $\langle 111 \rangle$ axis are Si and AlP. In Si, both barriers are very low, showing that the bending force constant for this bond is very small.

Table 1. Pauling's ionic character and covalent radii (for compounds, the two covalent radii are in the same order as the atoms). E_{rot} is the barrier for rotation of O_i around the $\langle 111 \rangle$ axis. In compound semiconductors, this is also the difference in energy between the equilibrium configuration (figure 1) and the optimized configuration with O_i pointing in the opposite direction in the $\{1\overline{1}0\}$ plane. $E_{through}$ is the energy required for O_i to reorient through the $\langle 111 \rangle$ axis rather than rotate around it.

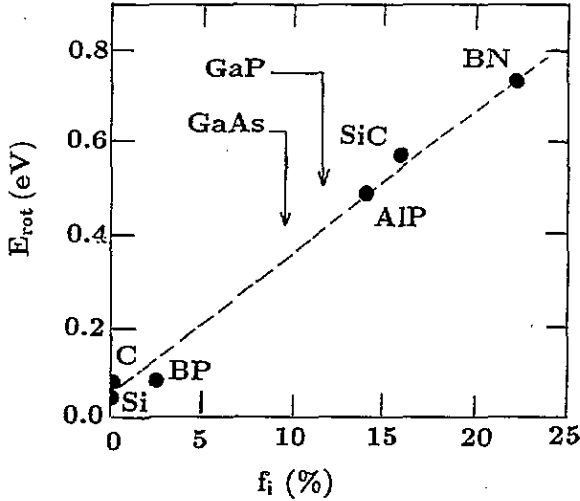| Host	f_i (%)	R_c (Å)	E_{rot} (eV)	$E_{through}$ (eV)
C	0	0.77	0.08	2.55
Si	0	1.18	0.04	0.03
BP	2.5	0.90/1.10	0.07	0.87
AlP	13.9	1.30/1.10	0.48	0.47
SiC	16.1	1.18/0.77	0.56	1.91
BN	22.1	0.90/0.75	0.73	1.32

Figure 3. Calculated barriers for rotations of O_i about the $\langle 111 \rangle$ axis as a function of the Pauling ionic character [40] f_i of the host. The arrows show where GaAs and GaP are located on this scale. The straight line is a fit through the calculated points.
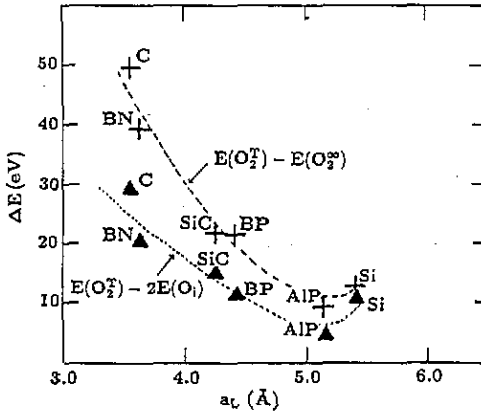

Figure 4. Upper curve (crosses): $E(O_2^T) - E(O_2^\infty)$ is the amount of energy required to insert a free O_2 molecule into the cluster near the T site as a function of the lattice constant a_L. Lower curve (triangles): $E(O_2^T) - 2E(O_i)$ is the energy gained by dissociating O_2^T into two isolated O_i. The broken curves are a guide to the eye.

4. Relative stability

In order to estimate the relative stability of O_i in the various hosts, we had to evaluate the energies of the equilibrium configurations relative to a common zero. In the case of interstitial H, we normally compare the energy of a defect in a cluster with atomic H outside the cluster to that of H bound to the defect. In the case of O, this cannot be done easily since the ground state of atomic O cannot be described with a single-determinant wavefunction. Instead, we defined the reference point as the free O_2 molecule far outside the undisturbed

cluster (labelled 'O_2^∞'). We then forced the molecule into the cluster and optimized its geometry near the T site (labeled 'O_2^T'). Finally, we compared this energy to that of two isolated O_is in the same host. For example, in the case of Si, we compared the following energies:

$$E(O_2^\infty) = 2E(Si_{44}H_{42}) + E(O_2)$$

$$E(O_2^T) = E(Si_{44}H_{42}) + E(Si_{44}H_{42} + O_2^T)$$

$$2E(O_i) = 2E(Si_{44}H_{42} + O_i).$$

Figure 4 shows these energy differences as functions of the lattice constant. For hosts with small lattice constants these energy differences clearly depend mostly on the volume available. When the lattice constant becomes large enough, other factors come into play, such as the strength of the host atom–O bond. Note that the free molecule (O_2^∞) has a double bond (a degree of bonding equal to 2.0) but once inserted into the semiconductor, O_2^T has only a single bond left (a degree of bonding equal to 1.0). In all hosts, O_2^T is unstable and spontaneously dissociates to form isolated O_is or other species. This result is consistent, for example, with the dissociation [41] of adsorbed O_2 between the first and second layers of c-SiC.

5. Barriers for diffusion

In compound semiconductors, there are two inequivalent ways for O_i to go from one BC configuration to another: the diffusion can be described as a rotation about the ME host atom or the LE host atom to which O_i is attached. Diffusion results only from overcoming the larger of the two barriers. In our notation, the 'LE barrier' refers to O_i moving from one BC site to the next while preserving the O–LE bond (see figure 5). Thus, overcoming the LE barrier requires breaking the O–ME bond at the initial BC site, then forming another O–ME bond at the neighbouring BC site. The reverse holds for the 'ME barrier'. In elemental semiconductors, only one barrier exists.

The optimized saddle-point configurations were obtained in clusters with 44 host atoms using PRDDO with relaxed first and second NN. Then, the barrier heights were calculated at the *ab initio* HF level with large basis sets followed by corrections for electron correlation (MP2: see section 2) in clusters containing five or eight host atoms. The difficulty in calculating these barriers is due to the fact that at the transition points the bonds are substantially stretched in some cases. This produces a highly unstable configuration that HF techniques (especially the ones that use minimal basis sets such as PRDDO) have difficulty describing correctly. These unstable configurations require the use of large basis sets and, if possible, the inclusion of excited states in order to add electron correlations into the calculation. For this reason, MP2 expansions were performed at both the equilibrium and the saddle-point geometries.

The influence of correlation corrections was the largest in situations where O_i must travel substantial distances to get to the saddle point. For example in Si, O_i must almost break a Si–O bond before reaching the saddle point. On the other hand, in hosts with a small lattice constant, O_i travels a much shorter distance and only needs to slightly stretch a bond before starting to form a new one. The extreme case is the LE barrier in BN, where O_i needs to move by only 0.1 Å from the equilibrium configuration to the saddle point. In this case, electron correlation minimally affects the energy difference between the two states. All
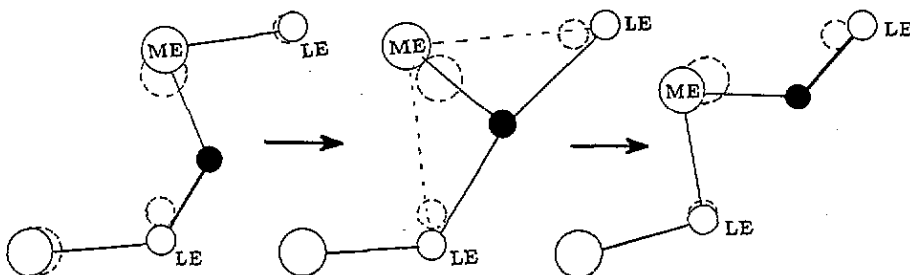
(a) LE barrier
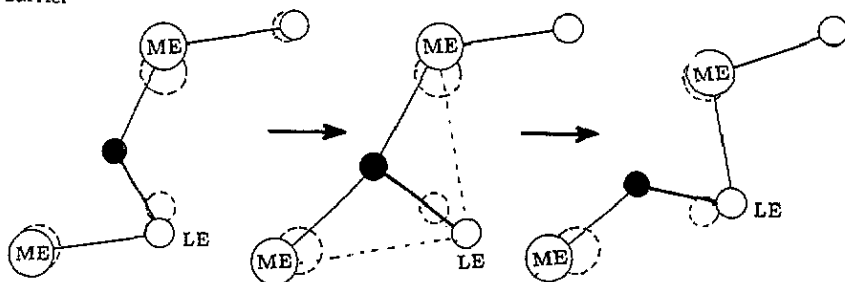
(b) ME barrier

Figure 5. Schematic comparison of the two possible diffusion paths of O_i in compound semiconductors. ME and LE refer to the most and least electronegative of the two host atoms, respectively, and O_i is the full circle. The 'LE barrier' has O_i rotating around the LE atom and involves the breaking of an ME–O bond. The 'ME barrier' is the reverse, but also involves the reorientation of O_i by a multiple of 60°.

Table 2. Barriers for diffusion of O_i calculated at the *ab initio* HF level with large basis set and second-order corrections in electron correlation using geometries optimized at the PRDDO level (see text). In compounds, the two barriers correspond to rotations about the least or most electronegative (LE or ME) of the host atoms, respectively. Thus, the 'LE barrier' is a migration of O_i that preserves the LE–O bond and breaks the ME–O bond.

	Barrier (eV)	
Host	ME barrier	LE barrier
C		3.2
Si		2.7
BP	2.1	3.6
AlP	0.1	2.0
SiC	1.0	4.4
BN	0.1	0.8

the barriers listed in table 2 are *ab initio* HF calculations with split-valence polarized basis sets followed by MP2 electron correlation expansions, except for the BN case which did not require an MP treatment. Note that these high-level calculations were done in geometries optimized at the PRDDO level.

In compound semiconductors, the ME barriers are consistently lower than the LE barriers. This is due in part to the preferential equilibrium orientation of O_i and in part to the ionicity of the host. The LE barrier corresponds to O_i rotating about the LE atom and breaking the

ME–O bond, i.e. overcoming the larger of the two barriers. The actual height of a specific barrier depends on three factors: the *bond strength* of the O–host bond which is being stretched, the *amount of stretching* needed to reach the transition point (this is related to the lattice constant) and, in compounds, the *difference in electronegativity* of the two host atoms.

6. Discussion

The equilibrium properties, relative stabilities, reorientation and diffusion barriers for O_i in c-C, Si, BP, AlP, c-SiC and c-BN have been calculated. The lowest-energy configuration is a puckered bridged bond in the {110} plane. O_i points toward the second NN which has the largest covalent radius. In Si, the bond angle is 167°. It is much smaller in the other hosts. In elemental hosts, O_i is symmetrically located between its two NN. In compound hosts, O_i has a larger degree of bonding with the ME host atom than with the LE one. The dipole moment of the defect is much larger in compound than in elemental hosts.

The barrier for rotation of O_i around the {111} axis increases linearly with the Pauling ionic character of the host. The barrier for migration *through* the {111} axis is much higher than the barrier for rotation in hosts that have a small lattice constant. In Si and AlP, the two barriers are comparable. In Si, the calculated barrier is in close agreement with the measured one.

It costs from 15–50 eV to insert an O_2 molecule into the various hosts. The largest amount of energy is required in semiconductors with the shortest lattice constants. Near the T site, the O–O bond is a single bond, not the double bond characteristic of an O_2 molecule. O_2 spontaneously dissociates in all semiconductors and forms two isolated O_i at a substantial gain in energy. We do not report here the possible configurations involving two O_i near each other.

Because O_i forms two unequal bonds with the host atoms in compound semiconductors, there are two ways for O_i to go from one BC site to the next. These calculations are tricky when the migration involves large distances (i.e. in hosts that have a large lattice constant). The more the bonds are stretched, the larger the influence of electron correlation. Our best barriers for the diffusion of O_i in Si is 2.7 eV, in close agreement with the measured value.

Some of the results obtained can be extended to the problem of O_i in GaAs and GaP. Because of the large lattice constants of these two hosts (approximately 5.7 Å and 5.5 Å for GaAs and GaP, respectively) the equilibrium configurations for O_i should be a slightly puckered bridged bond. The degrees of bonding for the O–Ga bond should be smaller than either the O–As or the O–P bond. This conflicts with recent density functional calculations [42] for O_i in GaAs. Oxygen should be out of the bisecting plane and slightly closer to As or P than to Ga. In GaP, the most stable configuration should be the one with O_i pointing toward a Ga second NN, whose covalent radius (1.20 Å) is slightly larger than that of P (1.10 Å). In GaAs, the covalent radii are almost identical (1.20 Å for Ga and 1.22 Å for As).

The barrier for rotation around the {111} axis should be approximately 0.4 eV for both hosts, with GaP having a slightly lower barrier than GaAs (see figure 3). Reorientation through the axis could occur more easily than rotation around it. Although GaP and GaAs are just outside the range in figure 4, O_2 molecules should be unstable against dissociation into isolated interstitials.

Since the barriers for diffusion do not correlate with any one property but depend on a combination of factors, our results do not allow a prediction of these barrier heights.

Acknowledgments

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