PHYSICAL REVIEW B **68**, 153201 (2003)

# Modified neglect of diatomic overlap parametrization of oxygen: A cluster study of oxygen defects in silicon

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(Received 21 March 2003; revised manuscript received 8 July 2003; published 9 October 2003)

We present a parametrization of oxygen within the framework of the modified neglect of diatomic overlap (MNDO) technique. The atomic structure and formation energy of a oxygen defect in silicon are studied as a test of the reparametrized MNDO technique. We find that the geometry and the associated formation energy are in good agreement with experiment as well as with results of *ab initio* calculations. Even the calculations based on the MNDO technique are by 2 or 3 orders of magnitude less expensive than *ab initio* calculations.

DOI: 10.1103/PhysRevB.68.153201 PACS number(s): 71.55.Cn, 31.15.Ct

With the advent of highly powerful computers, calculations at the atomic level offer a chance to shed light on the obscure properties of silicon. Historically, the electronic structure problem has been solved using the translational symmetry of the system.[1] This appeared to be more than a good idea. However, there are some good reasons for considering alternatives. In particular, defects can break the periodic symmetry and then it is difficult to use the idea of crystalline periodicity. If the defect is charged, the situation is even more complicated, and a spurious neutralizing medium has to be inserted to remove the divergent Coulombic repulsion energy. The cluster approach with a hydrogen-saturated surface coupled with the Hartree-Fock (HF) techniques[2] developed mostly for quantum chemistry avoids some of these problems and could have advantages over the periodic systems. One of the strongest ones is that calculations based on the cluster approach, with well-tuned parameters, give results by 2 or 3 orders of magnitude faster than simulations based on the local density approximation (LDA) technique. All HF techniques are self-consistent field methods taking into account electrostatic repulsion and exchange stabilization. In semiempirical HF methods, all calculated integrals are evaluated by approximate means. However, the implementation of a semiempirical HF technique could be limited by the choice of physically plausible model parameters. Generally, this can be done by fitting the model to either experimental data or accurate *ab initio* calculations.

Oxygen as the most common impurity in silicon can be introduced in many different ways. If a silicon crystal is grown by the Czochradski method, then it is contaminated from the surrounding quartz crucible[3] and can contain approximately $10^{18}$ oxygen atoms in one cubic centimeter.[4] The ubiquitous presence of oxygen in silicon has led to an extensive study of this defect by a multitude of experimental[5–7] and theoretical[8–10] techniques for more than 30 years. The equibrium structure of the oxygen defect in silicon has been extensively studied, including computation of vibration modes,[11] and diffusion,[12] or reorientation energy.[13] The generally accepted model shows the oxygen atom ‘‘squeezed’’ between two neigboring lattice atoms. It is believed that oxygen breaks the silicon-silicon bond and forms a Si-O-Si bridge.[14] Two lattice silicon atoms dilate the Si-Si bond by around 36%.[15,16] The interaction between the neighbors forms a virtual Si-O-Si molecule with $C_{2v}$ symmetry.[13] The defect is electrically neutral and induces a shallow acceptor level at $E_c-0.07$ eV (Ref. 17). Irradiation of oxygen-rich silicon at room temperature produces mobile vacancies and interstitials. In case a vacancy meets an interstitial oxygen, a $VO$ complex ($A$-center) is formed. The defect is associated with an acceptor level at $E_c-0.17$ eV (Ref. 17) due to the weak bond between the pair of silicon atoms bordering the vacancy. Another pair of silicon atoms forms an Si-O-Si bridge and moves the oxygen from the substitutional site to the [100] direction. Although the basic structure for the oxygen defect is generally accepted, it still hides many secrets and its properties remain poorly understood.

In this paper, we present a parametrization for oxygen in the framework of the modified neglect of diatomic overlap (MNDO) technique. This method neglects the repulsive ortogonalization corrections and the attractive penetration integrals of the one-center core Hamiltonian matrix elements. These two terms, in general, compensate each other but the compensation is not perfect. For this Dewar and Thiel[18] added a new term with the aim to adjust the balance between the attractive and repulsive terms. This correction is outside the quantum-mechanical framework and is given as a summation of spherical Gaussian functions,

$$E(A,B)=\frac{Z_A Z_B}{R_{AB}}\sum_{i=1}^{n} a_i e^{b_i(R_{AB}-c_i)^2}, \qquad (1)$$

where $E(A,B)$ is the correction function, $R_{AB}$ is the pair distance, and $a_i, b_i, c_i$ are adjustable parameters. This approach was used in AM1 (Austin method) (Ref. 19) and later in PM3 (parametric method Ref. 20).

In our study, we used two different in size silicon clusters. In particular, we used $Si_{75}H_{64}$ and $Si_{102}H_{82}$ (this we will refer to as large) clusters. The lattice constant was set to the ex-

TABLE I. Oxygen defect geometry computed on $Si_{102}H_{82}$ cluster using various MNDO parametrizations.

| | | $O_i$ | | |
|---|---|---|---|---|
| Method | AM1 | PM3 | NOP | LDA [a] |
| Si-O-Si (deg) | 155.9 | 144.3 | 152.3 | 154 |
| Si-O (Å) | 1.72 | 1.64 | 1.65 | 1.65 |
| | | OV | | |
| Si-O-Si (deg) | 112.5 | 109.5 | 138.9 | 148 |
| Si-O (Å) | 1.88 | 1.78 | 1.69 | 1.69 |

[a] Reference 22.

perimental value of 5.43 Å (Ref. 21). The dangling bonds on the cluster surface were saturated by hydrogen in such a way that the new bonds become equivalent with the original bonds of the crystal. The quality of surface silicon bonds approximation depends mainly on the distance between the surface silicon and the related hydrogen atom. The optimized distance corresponding to the minimum total energy was found to be 1.48 Å. The geometry and size of the clusters used guarantees that all silicon atoms are equivalent to each other as well as all hydrogen atoms are equivalent to each other.

To treat the oxygen defect, we use large cluster. The interstitial oxygen we positioned at the Si-Si bond center in the center of the cluster. For the oxygen-vacancy defect (*A* center) we alternate one silicon by oxygen. In both cases, relaxation underwent by the second shell of atoms around the defect. We found that original AM1 as well as PM3 parametrization for oxygen, as used in MOPAC, gave misleading results both in geometry and formation energy. To solve this problem we change adjustable parameters for oxygen in the MNDO parametrization by fitting the geometrical data to the *ab initio* values. In particular, for interstitial oxygen we employ an Si-O-Si angle of 154° and Si-O distance of 1.63 Å (Ref. 22), and for *A* center we employ an Si-O-Si angle of 148° and Si-O distance of 1.69 Å (Ref. 22). Geometrical data of the oxygen defect complex computed on large clusters within the framework of the MNDO technique for various parametrizations are listed in Table I. Note that both parametrizations AM1 and PM3 give in the case of the *A* center misleading $T_d$ symmetry instead of generally accepted $C_{2v}$ symmetry. Comparing the original AM1 or PM3 and the new parametrization, which we will refer to as "new oxygen parametrization" (NOP), we use six Gaussians, four repulsive and two attractive, instead of two Gaussians, both repulsive in AM1 or repulsive and attractive in PM3 parametrization. Figure 1 shows the correction function for various parametrizations. The associated values of adjustable parameters are listed in Table II. It is interesting to note that the NOP correction function gives two artificial minima at 1.6 Å and 2.9 Å of pair distance $R_{AB}$; however, for the Si-O pair distance stabilization in defect occurs at 1.65 Å (interstitial oxygen) and 1.69 Å (*A* center).

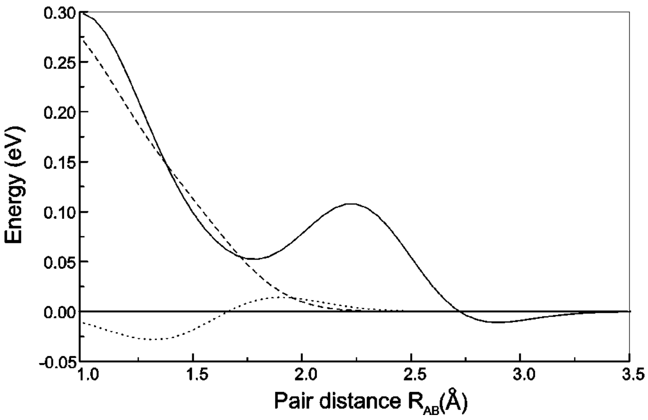

FIG. 1. Correction function $E_{AB}$ as a function of pair distance $R_{AB}$: NOP, solid line; AM1, dashed line; PM3, dotted line. The correction function works outside the quantum-mechanical framework with the aim to adjust the nuclear-nuclear interaction. The shape of the compensation function depends on the adjustable parameters. The associated parameters are listed in Table II.

TABLE II. List of adjustable parameters for oxygen in various parametrizations.

| Parameter | AM1 | PM3 | NOP |
|---|---|---|---|
| $a_1$ | 0.2809620 | −1.1311280 | −0.217867 |
| $b_1$ | 5.0000000 | 6.0024770 | 5.150000 |
| $c_1$ | 0.8479180 | 1.6073110 | 2.358491 |
| $a_2$ | 0.0814300 | 1.1378910 | 0.317213 |
| $b_2$ | 7.0000000 | 5.9505120 | 6.000000 |
| $c_2$ | 1.4450710 | 1.5983950 | 2.302430 |
| $a_3$ | | | −1.019130 |
| $b_3$ | | | 5.200000 |
| $c_3$ | | | 0.984307 |
| $a_4$ | | | 1.048130 |
| $b_4$ | | | 5.848000 |
| $c_4$ | | | 1.005118 |
| $a_5$ | | | 0.281000 |
| $b_5$ | | | 5.000000 |
| $c_5$ | | | 0.848000 |
| $a_6$ | | | 0.070814 |
| $b_6$ | | | 7.000000 |
| $c_6$ | | | 1.445000 |

The value of the formation energy of the interstitial oxygen and *A* center is used as a test of the new parametrization of oxygen. However, first we need to distribute the total cluster energy between the silicon and hydrogen atoms. For this we employ two different size clusters, in particular, $Si_{75}H_{64}$ and $Si_{102}H_{82}$ clusters. Using simple algebra we obtained energies for silicon and hydrogen which we will refer to as the

TABLE III. Formation energies of the interstitial oxygen and *A* center complexes in silicon calculated by various techniques.

| Method | AM1 | PM3 | NOP | LDA [a] |
|---|---|---|---|---|
| $E_f(O_i)$(eV) | 2.1 | 1.57 | 1.6 | 1.6 |
| $E_f$(OV)(eV) | 1.8 | 0.36 | 2.5 | 3.7 |

[a] Reference 22.

TABLE IV. Bond length (Å), angle (deg), and formation energy (eV) for oxygen dimer ($O_{2i}$) and substitutional oxygen dimer ($VO_2$) center in silicon.

| | $O_{2i}$ | | $VO_2$ |
|---|---|---|---|
| Si-O | Staggered | Skewed | |
| This work | 1.65 | 1.66 | 1.69 |
| Coutinho *et al.* [a] | 1.63, 1.65 | 1.61, 1.62 | 1.70 |
| Öberg *et al.* [b] | | 1.62, 1.65 | |
| Ewels *et al.* [c] | 1.52, 1.67 | | |
| Si-O-Si | | | |
| This work | 151, 153 | 147 | 137 |
| Coutinho *et al.* [a] | 126, 131 | 166 | 150 |
| Öberg *et al.* [b] | | 166 | |
| Ewels *et al.* [c] | 170 | | |
| $E_f$ | | | |
| This work | 2.86 | 3.06 | 3.73 |
| Coutinho *et al.* [a] | 2.0, 3.0 | 2.1, 3.4 | 3.93 |
| Pesola *et al.* [d] | | | 3.70 |

[a] Reference 13.
[b] Reference 23.
[c] Reference 24.
[d] Reference 22.

TABLE V. Bond lengths and angles for the four-oxygen-atom defect (di-Y-lid) in silicon shown in Fig. 2.

| Distance (Å) | $Si_2-O_1$ | $Si_2-O_2$ | $Si_3-O_2$ | $Si_4-O_2$ |
|---|---|---|---|---|
| NOP | 1.657 | 1.787 | 1.731 | 1.734 |
| AIMPRO [a] | 1.658 | 1.686 | 1.694 | 1.984 |
| Angle (deg) | $Si_1-O_1-Si_2$ | $Si_2-O_2-Si_4$ | $Si_3-O_2-Si_2$ | |
| NOP | 143 | 130 | 112 | |
| AIMPRO [a] | 133 | 147 | 117 | |

[a] Reference 25.

lattice energy $E_L(\mathrm{Si})$ and $E_L(\mathrm{H})$. The oxygen lattice energy $E_L(\mathrm{O})$ is computed employing the total energy of $Si_8H_{12}O_2$ cluster as

$$E_L(\mathrm{O})=\frac{1}{2}\{E_t-8E_L(\mathrm{Si})-12E_L(\mathrm{H})\}, \tag{2}$$

where $E_t$ is the total energy of the $Si_8H_{12}O_2$ cluster after relaxation. The formation energy $E_f$ of an oxygen defect is given by

$$E_f=n_{Si}E_L(\mathrm{Si})+n_HE_L(\mathrm{H})+n_OE_L(\mathrm{O})-E_T, \tag{3}$$

where $n_X$ is the number of $X$ atoms in the cluster ($X=$Si, H, and O) and $E_T$ is the total cluster energy after relaxation. In Table III we report the formation energies of both interstitial oxygen and $A$ center computed in the large cluster together with *ab initio* and other semiempirical calculations. It is observable that the NOP gives a result in excellent agreement with the LDA calculation in the case of interstitial oxygen. In the case of the $A$ center, the result is comparable with the LDA calculation. Both parametrizations AM1 and PM3 give worse results.

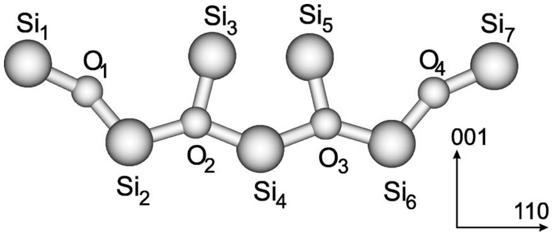

FIG. 2. The calculated structure of the four-oxygen-atom (di-Y-lid) defect. The defect consists of a pair of oxygen dimers, both in the same ⟨110⟩ plane and is in the 2+ charge state. Distances and angles are shown in Table V. Large and small balls denote silicon and oxygen atoms, respectively.

As a test of transferability we used oxygen defects that are not included in the parametrization ensemble, but that are well characterized and may serve as a reference to test the quality of the parametrization. In particular, we use the oxygen dimer ($O_{2i}$) and the substitutional oxygen dimer ($VO_2$). These dimers were recently examined very carefully by *ab initio* methods.[13,22] The dimer was positioned in the large hydrogenated silicon cluster and relaxed by the Broyden-Fletcher-Goldfarb-Shanno (BFGS) technique. The relaxation is allowed in two shells of atoms around the defect. Table IV gives the geometry and formation energy of the dimers. We find that results obtained are in the good agreement with the available *ab initio* data.

As a demonstration of the NOP we have modeled a four-oxygen-atom defect known as di-Y-lid thermal donor. The defect consists of a pair of oxygen dimers, both in the same ⟨110⟩ plane. The defect creates a double-donor-level very close to the conduction band. Following the computation reported by Ewels[25] we have modeled the defect in the +2 charge state. The defect was embedded in the $Si_{185}H_{118}$ cluster and relaxed by the BFGS technique. The calculated geometry of the oxygen complex is shown in Fig. 2. The bond lengths and angles are given in Table V and are compared with the previous study. The geometry of the oxygen complex computed in the frame of the NOP is in good agreement with previous results given by Ewels. It should be note that both AM1 and PM3 parametrizations give an incorrect geometry of the complex. We find that the calculated formation energy per oxygen for the di-Y-lid complex equals 0.36 eV and is in good agreement with the formation energy of 0.61 eV reported by Pesola *et al.*[26]

In conclusion, we have presented a new parametrization for the oxygen in the framework of the MNDO technique. We use the NOP in a silicon cluster model to study the geometry and energy of some oxygen defects in silicon. We find that NOP gives good results in comparison with the LDA computation. This implies that MNDO in combination with the NOP is accurate enough to have predictive powers. On the other hand, semiempirical methods are fast enough to allow to study large systems.

This work was supported by the Slovak Grant Agency under Grant No. 1/9042/02.

[1] S.G. Louie, M. Schlüter, J.R. Chelikowsky, and M.L. Cohen, Phys. Rev. B **13**, 1654 (1976).

[2] J.C. Inkson, *Many-Body Theory of Solids* (Plenum Press, New York, 1984).

[3] G. Schrag, M. Rebmann, C. Wurster, F. Zeller, K. Lassmann, and W. Eisenmenger, Phys. Status Solidi A **168**, 37 (1998).

[4] J. Kuriplach, A.L. Morales, C. Dauwe, D. Segers, and M. Šob, Phys. Rev. B **58**, 10 475 (1998).

[5] D. Watkins and J.W. Corbett, Phys. Rev. **121**, 1001 (1961).

[6] D.R. Bosomworth, W. Hayes, A.R.L. Spray, and G.D. Watkins, Proc. R. Soc. London, Ser. A **317**, 133 (1970).

[7] R.C. Newman, J. Phys.: Condens. Matter **12**, R335 (2000).

[8] S. Canuto and A. Fazzio, Phys. Rev. B **33**, 4432 (1986).

[9] D.J. Chadi, Phys. Rev. Lett. **77**, 861 (1996).

[10] A.B. van Oosten, A.M. Frens, and J. Schmidt, Phys. Rev. B **50**, 5239 (1994).

[11] E. Artacho, F. Ynduráin, B. Pajot, R. Ramz, C.P. Herrero, L.I. Khirunenko, K.M. Itoh, and E.E. Haller, Phys. Rev. B **56**, 3820 (1997).

[12] R.B. Capaz, L.V.C. Assali, L.C. Kimerling, K. Cho, and J.D. Joannopoulos, Phys. Rev. B **59**, 4898 (1999).

[13] J. Coutinho, R. Jones, P.R. Briddon, and S. Öberg, Phys. Rev. B **62**, 10 824 (2000).

[14] M. Needels, J.D. Joannopoulos, Y. Bar-Yam, and S.T. Pantelides, Phys. Rev. B **43**, 4208 (1991).

[15] J.W. Corbett, R.S. McDonald, and G.D. Watkins, J. Phys. Chem. Solids **25**, 873 (1964).

[16] B. Pajot, in *Oxygen '96*, Vol. 17 of *NATO Advanced Study Institute, Series B: Physics*, edited by R. Jones (Kluwer Academic, Dordrecht, 1996), p. 283.

[17] D.K. Schröder, *Semiconductor Material and Device Characterization* (Wiley, New York, 1998), p. 321.

[18] M.J.S. Dewar and W. Thiel, J. Am. Chem. Soc. **99**, 4899 (1977).

[19] M.J.S. Dewar, E.G. Zoebish, E.F. Healy, and J.J.P. Stewart, J. Am. Chem. Soc. **107**, 3902 (1985).

[20] J.J.P. Stewart, J. Comput. Chem. **10**, 221 (1989).

[21] Ch. Kittel, *Introduction to Solid State Physics* (Wiley, New York, 1996).

[22] M. Pesola, J von Boehm, T. Mattila, and R.M. Nieminen, Phys. Rev. B **60**, 11 449 (1999).

[23] S. Öberg, C.P. Ewels, R. Jones, T. Hallberg, J.L. Lindström, L.I. Murin, and P.B. Briddon, Phys. Rev. Lett. **81**, 2930 (1998).

[24] C.P. Ewels, R. Jones, and S. Öberg, in *Early Stages of Oxygen Precipitation in Silicon*, edited by R. Jones (Kluwer Academic, Dortrecht, 1996), p. 141.

[25] C.P. Ewels, Ph.D. thesis, University of Exeter, Exeter, U.K., 1997.

[26] M. Pesola, Young Joo Lee, J von Boehm, M. Kaukonen, and R.M. Nieminen, Phys. Rev. Lett. **84**, 5343 (2000).