PHYSICAL REVIEW B VOLUME 48, NUMBER 3 15 JULY 1993-I

Oxygen-hydrogen donor complexes in germanium

P. Deák,* B. Schröder, A. Annen, and A. Scholz
Fachbereich Physik, University of Kaiserslautern, Erwin-Schrödinger Strasse, D-6750 Kaiserslautern, Germany

(Received 30 November 1992; revised manuscript received 9 February 1993)

Semiempirical cluster calculations are reported on the interaction of interstitial oxygen complexes with hydrogen in germanium. It has been found that—unlike in silicon—the configuration in which the oxygen and one of its neighbors are threefold coordinated is not the saddle point in the diffusion of interstitial oxygen, but a metastable state which can be stabilized by a trapped hydrogen. The resulting structure is a single donor. It is also shown that dioxygen interstitial complexes form readily in germanium. The interaction of such complexes with hydrogen also produces single donors. These findings explain why oxygen acts as a donor in hydrogenated amorphous germanium (*a*-Ge:H) in contrast to *a*-Si:H.

I. INTRODUCTION

The effectivity and stability of thin-film solar cells can be increased and the selective absorption improved by the application of tandem structures integrating a-$Si_{1-x}Ge_x$:H or a:Ge:H layers. Therefore, the investigation of *a*-Ge:H has intensified in recent years.[1-5] Recently, it has been found[6] that—in contrast to *a*-Si:H—oxygen is a very effective donor in *a*-Ge:H. The doping effect of oxygen depends strongly on the substrate temperature and it is probably related to the formation of oxygen-hydrogen complexes.

Oxygen complexes in *crystalline silicon* have been intensively studied in the past, mainly because of their role as thermal donors (for a recent review see, e.g., Ref. 7). Although oxygen thermal donors—very similar to those in silicon—have been found in germanium as well (see, e.g., Ref. 8), much less is known about complex formation of oxygen in *crystalline* germanium. The simple interstitial oxygen defect,[9] the oxygen thermal donors,[10] and the vacancy-oxygen complex (*A* center)[11-13] have been identified, but both infrared[12] and deep-level transient spectra[13] reveal further oxygen-related complexes. It has been speculated early on[14] that a donor level around $E_c - 0.2$ eV may originate from a dioxygen precursor to the thermal donors. The interaction of hydrogen with oxygen is known to produce donor centers in crystalline germanium. The trapping of hydrogen at a substitutional oxygen results in a very shallow donor level (see, e.g., Ref. 15), but the interaction of hydrogen with oxygen may give rise[16] to deep levels around midgap as well.

The question arises of why does oxygen give rise to deep donor levels in hydrogenated crystalline germanium, while only thermal donors appear in pure silicon, and even those are being passivated through interaction with hydrogen.[17] The answer to that question could then explain the similar difference between the hydrogenated amorphous forms of the two materials. Based on semiempirical quantum chemical cluster calculations, it will be shown that the differences of oxygen diffusion in germanium and silicon are the reason for the formation of stable donor complexes in germanium if hydrogen is present.

II. COMPUTATIONAL METHOD

Semiempirical quantum chemical methods have been proven to be successful in describing the behavior of oxygen[18] and hydrogen[19,20] in silicon. Parameter sets for germanium are available in the MNDO (modified intermediate neglect of differential overlap),[21] AM1 (Austin model),[22] and the PM3 (parametric MNDO) (Ref. 23) method (encoded into the package MOPAC 6.0).[24] Although the performance of the three methods is similar on small molecules, our preliminary calculations on crystalline germanium (using the cyclic cluster model[25] with a 32-atom supercell) have shown that both AM1 and PM3 underestimate the interatomic distance and overestimate the binding energy, while MNDO reproduces very accurately the former and underestimates the latter (see Table I). since only the MNDO method was able to reproduce the characteristics of the *A* center (vacancy-oxygen complex) in crystalline germanium, that one has been chosen for the study of oxygen complexes in germanium.

The host has been represented by a molecular cluster consisting of 53 germanium atoms and 44 additional hydrogens to saturate the dangling bonds on the perimeter of the cluster. Since we have been interested primarily in amorphous germanium, this molecular cluster model was selected in favor of a cyclic cluster model which is also more restrictive on the cluster size.[7] The total energy of this $Ge_{53}H_{48}$ cluster has been minimized with respect to all bond distances and bond angles (assuming only C_{2v} symmetry). The perimeter germanium atoms and their hydrogen neighbors have been kept fixed in further calculation, while the remaining ones were allowed to relax as required by the presence of various defect complexes.

TABLE I. Interatomic distance, binding energy, and ionization threshold obtained by three different semiempirical methods in a 32-atom cyclic cluster calculation on crystalline germanium.

	PM3	AM1	MNDO	Expt. (Ref. 23)
$d_{\text{Ge-Ge}}$ (Å)	2.366	2.390	2.451	2.450
E_b (eV)	4.79	4.38	2.62	3.87
I (eV)	11.0	9.8	7.5	~5.3

III. RESULTS AND DISCUSSION

The equilibrium site of an isolated interstitial oxygen in germanium was found at the bond-center (BC) site between two nearest-neighbor Ge atoms, slightly off axis. The Ge-O distances are 1.671 and 1.702 Å (the asymmetry originates from the asymmetry of the cluster). For comparison, the calculated and observed[26] Ge-O distance in the $(CH_3)_3Ge\text{-}O\text{-}Ge(CH_3)_3$ molecule are 1.762 and 1.770 Å, respectively. The shortening of the Ge-O bond is obviously the effect of the confinement in the solid. The related one-electron energy levels are in the valence band of the cluster, i.e., the defect is electrically inactive as expected. For substitutional oxygen the equilibrium position is calculated to be off center by 1.027 Å in the [001] direction (C_{2v} symmetry). The oxygen is bonded to two of the four germanium neighbors with a bond distance of 1.790 Å and a Ge-O-Ge angle of 152°. The other two germanium atoms relax toward each other and form a weak bond with a bond distance of 3.558 Å. The antibonding orbital of this bond is in the gap. All these features of interstitial and substitutional oxygen are in agreement with experimental observations in germanium and are very similar to those observed[27] and calculated[28] in silicon. The calculated asymmetric stretching modes in germanium are 1107 and 834 cm^{-1} for the interstitial and substitutional oxygen, respectively. Comparing the ratio of the two calculated frequencies, 1.33, to the ratio of the experimentally observed values, $862/620=1.39$ (see Ref. 12), it can be seen that the relative error in the calculated frequencies is approximately constant, as noted earlier in the case of oxygen in silicon.[29]

The diffusion of oxygen in silicon as well as in germanium proceeds by jumps from one interstitial site to the next. In silicon the saddle point of the motion is a configuration of C_{2v} symmetry [cf. Fig. 1(a)] in which the oxygen and one of its silicon neighbors are threefold coordinated. The energy of this structure has been calculated in a similar semiempirical cluster calculation[30] (using a $Si_{47}H_{60}$ molecular cluster and the MNDO/3 method) to be 2.49 eV higher than that of the interstitial, in good agreement with the experimentally observed[31] 2.53 eV. In the case of oxygen in germanium we find that the structure depicted in Fig. 1(a) is metastable. The energy barrier for diffusion is 0.22 eV above the energy of this threefold-coordinated-oxygen structure, and is located at a configuration where the oxygen is off the [001] axis by about 0.3 Å toward the interstitial site. The barrier is calculated to be 0.85 eV above the energy of the stable interstitial configuration. This is much lower than the experimentally observed diffusion activation energy,[32] 2.08 eV. The main source of error is probably the underestimation of the strengths of Ge-Ge bonds by ~1.2 eV (see Table I). The energy difference between the interstitial and the threefold-coordinated-oxygen structure consists, to a first approximation, of the energy required to break a second Ge-Ge bond in the vicinity of the interstitial and of the energy gained through substituting it by a Ge-O bond. The underestimation of the former shows up in the barrier height.

The oxygen structure in Fig. 1(a) is a double donor but it is not stable with respect to the interstitial. However, if hydrogen is introduced into the system, a stable complex may form. We have calculated the equilibrium position of a positively charged hydrogen atom in a "pure" $Ge_{53}H_{48}$ cluster and in the $Ge_{53}H_{48}{:}O_Y$ cluster containing the threefold-coordinated oxygen (indicated by a subscript Y). The stable structure of H^+ is the on-axis BC site (just as in silicon[18]) with Ge-H distances of 1.631 and 1.582 Å, while the stable structure of O_YH^+ is shown in Fig. 1(b) (the Ge-O distances are 1.998, 1.939, and 1.817 Å, the Ge-H distance is 1.458 Å). The energy balance

$$\{E[Ge_{53}H_{48}{:}O_YH^+]+E[Ge_{53}H_{48}]\}$$
$$-\{E[Ge_{53}H_{48}{:}O_i]+E[Ge_{53}H_{48}{:}H^+]\}=-0.36\ \mathrm{eV}$$

shows that the complex O_YH^+ may be stable with respect to isolated interstitial oxygen and interstitial hydrogen. Therefore, if the conditions for oxygen and hydrogen diffusion are favorable, such complexes may form and remain stable thereafter. The complex is a single donor. The occupancy level is estimated to be in the upper half of the band gap. The calculated oxygen vibration frequency in the positive charge state is 815 cm^{-1}. Its ratio to the calculated frequency of the interstitial, 0.74, would indicate a band near 640 cm^{-1} in the experimental infrared spectrum.

We have also investigated the interaction of two oxygen interstitials in germanium. It has been found that, similarly to the case in silicon, the interstitial dioxygen complex $(O_i)_2$ [see Fig. 2(a)] is more stable than two isolated oxygen interstitials. The energy gain in the formation of this dioxygen complex was calculated to be 1.35

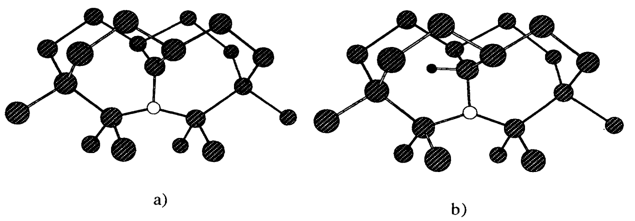
a) b)

FIG. 1. The O_Y (a) and O_YH^+ (b) defects in germanium. Large dark circles are Ge atoms, oxygen is denoted with small white circles, hydrogen with small black circles.

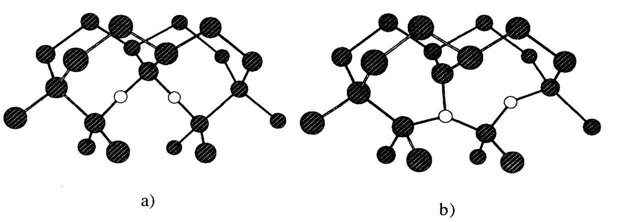
a) b)

FIG. 2. The $(O_i)_2$ (a) and $(O_i\text{-}O_Y)$ (b) defects in germanium. The threefold-coordinated germanium in $(O_i\text{-}O_Y)$ is a trap for hydrogen [see Fig. 1(b)].

eV, significantly higher than the one found in silicon (0.1 eV in Ref. 28, or 1.0 eV in a more sophisticated calculation by Needels *et al.*[33]). A second metastable complex (O_i-O_Y) [see Fig. 2(b)], has also been found with an energy 1.75 eV above $(O_i)_2$. The bond distances of the threefold-coordinated oxygen are 1.869, 1.863, and 1.834 Å; those of the twofold-coordinated one are 1.689 and 1.763 Å. This complex is very similar to the metastable (single) interstitial oxygen defect found in silicon by Dal Pino *et al.*[34] We find, however, that without the support of the second oxygen, this structure does not correspond to a local minimum of the total energy in germanium, and relaxes back into the ideal threefold-coordinated-oxygen structure. The metastable structure depicted in Fig. 2(b) is again a double donor and it can also capture a hydrogen atom. The hydrogen bonds to the threefold-coordinated germanium atom in a similar manner as in the O_YH^+ complex [cf. Fig. 1(b)]. The energy of the $(O_i\text{-}O_YH)^+$ complex is about the same as the energy of isolated $(O_i)_2$ and H^+. Therefore $(O_i)_2$ and (O_i-O_YH) may coexist in hydrogenated germanium. The (O_i-O_YH) complex is a single donor with its occupancy level also in the upper part of the band gap. The calculated oxygen vibration frequencies are 994 cm^{-1} (for the divalent O) and 833 cm^{-1} (for the trivalent O). Their ratio to the calculated frequency of the single interstitial would indicate bands at 774 and 650 cm^{-1} in the experimental infrared spectrum.

IV. CONCLUSION

We have found that the details of the diffusion mechanism of oxygen in germanium differ from the one in silicon. Beside the lower activation energy for diffusion (2.08 eV in Ge in comparison to 2.53 eV in Si), the potential barrier in germanium has a "camel's-back" shape. The intermediate metastable state is a threefold-coordinated-oxygen configuration which can serve as a trap for hydrogen atoms. If a hydrogen atom is captured, the arising single donor structure is more stable than isolated oxygen and hydrogen interstitials. This is in contrast to the situation in silicon, where hydrogen only accelerates the motion of oxygen, but no bond is formed.[35–38] It has also been found that, due to the faster diffusion of oxygen (eight orders of magnitude at room temperature) and the higher binding energy of interstitial dioxygen complexes in germanium, such dioxygen complexes should form more easily than in silicon. These complexes may also capture a hydrogen atom and give rise to single donor levels.

The results outlined above explain why donor complexes arise due to oxygen in hydrogenated germanium and not in silicon. Since the phenomenon depends principally on the local bonding environment, the explanation applies equally to both crystalline and amorphous material. The central role in both oxygen-hydrogen donor complexes found is played by trivalent oxygen atoms (cf. Ref. 7). The corresponding vibration frequencies are estimated to be around 640 cm^{-1}. It should be noted that a band at 670 cm^{-1}, found in *a*-Ge:(H,O) layers, was identified as a Ge-O vibration at a Ge atom bonded to one H atom as well by Lucovsky *et al.*[39]

ACKNOWLEDGMENT

This work has been supported by the German "Bundesministerium für Forschung und Technologie," Project No. 03219116A.

---

*Permanent address: Physical Institute of the Technical University Budapest, Budafoki út 8, Budapest H-1111, Hungary.

[1] F. Karg, H. Böhm, and K. Pierz, J. Non-Cryst. Solids **144**, 477 (1989).

[2] W. Paul, J. Non-Cryst. Solids **137&138**, 803 (1991).

[3] W. Kusian, H. Pfleiderer, and E. Günzel, J. Non-Cryst. Solids **137&138**, 813 (1991).

[4] W. Krühler, Appl. Phys. A **53**, 54 (1991).

[5] T. Drüsedau, J. Non-Cryst. Solids **137&138**, 821 (1991).

[6] B. Schröder, A. Annen, T. Drüsedau, and P. Deák, Appl. Phys. Lett. (to be published).

[7] P. Deák, L. Snyder, and J. W. Corbett, Phys. Rev. B **45**, 11 612 (1992).

[8] P. Clauws and J. Vennik, Phys. Rev. B **30**, 4837 (1984).

[9] W. Kaiser and C. D. Thurmond, J. Appl. Phys. **32**, 115 (1961).

[10] C. S. Fuller, W. Kaiser, and C. D. Thurmond, J. Phys. Chem. Solids **17**, 301 (1961).

[11] J. A. Baldwin, Jr., J. Appl. Phys. **36**, 793 (1965).

[12] R. E. Whan, Phys. Rev. **140**, A690 (1965).

[13] N. Fukuoka, H. Saito, and Y. Kambe, Jpn. J. Appl. Phys. **22**, L353 (1983).

[14] C. S. Fuller and F. H. Doleiden, J. Phys. Chem. Solids **19**, 251 (1961).

[15] E. E. Haller, in *Festkörperprobleme, Advances in Solid State Physics,* edited by P. Grosse (Vieweg, Braunschweig, 1986), Vol. 26, p. 203.

[16] A. J. Tavendale and S. J. Pearton, J. Appl. Phys. **54**, 3213 (1983).

[17] N. M. Johnson and S. K. Hahn, Appl. Phys. Lett. **48**, 709 (1986).

[18] P. Deák, L. Snyder, and J. W. Corbett, Phys. Rev. B **37**, 6887 (1988).

[19] P. Deák, C. R. Ortiz, L. Snyder, and J. W. Corbett, Physica B **170**, 223 (1991).

[20] M. J. S. Dewar, G. L. Grady, and E. F. Healy, Organomet. **6**, 186 (1987).

[21] M. J. S. Dewar and C. Jie, Organomet. **8**, 1544 (1989).

[22] J. J. P. Stewart, J. Comp. Chem. **12**, 320 (1991).

[23] *CRC Handbook of Chemistry and Physics*, 67th ed., edited by R. C. Weast (CRC, Boca Raton, 1987).

[24] J. J. P. Stewart, Quantum Chem. Prog. Exchange **23**, 455 (1990).

[25] P. Deák and L. Snyder, Phys. Rev. B **36**, 9619 (1987).

[26] L. V. Vikov and N. A. Tarensenko, Zh. Struk. Khim. **10**, 102 (1969).

[27] J. W. Corbett, G. D. Watkins, and R. S. McDonald, Phys. Rev. A **135**, 1381 (1964).

[28] G. G. DeLeo, W. B. Fowler, and G. D. Watkins, Phys. Rev. B

29, 3193 (1984).

[29] L. C. Snyder, R. Z. Wu, and P. Deák, Radiat. Eff. Defects Solids **111-112**, 393 (1989).

[30] L. C. Snyder, J. W. Corbett, P. Deák, and R. Z. Wu, in *Defects in Electronic Materials,* edited by M. Stavola, S. J. Pearton, and G. Davies, MRS Symposia Proceedings No. 104 (Materials Research Society, Pittsburgh, 1988), p. 179.

[31] J. C. Mikkelsen, Jr., in *Oxygen, Carbon, Hydrogen and Nitrogen in Silicon,* edited by S. J. Pearton, J. W. Corbett, and J. C. Mikkelsen, Jr., MRS Symposia Proceedings No. 59 (Materials Research Society, Pittsburgh, 1986), p. 19.

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

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

[34] A. Dal Pino, M. Needels, and J. D. Joannopoulos, Phys. Rev. B **45**, 3304 (1992).

[35] R. C. Newman, in *Proceeding of the 20th International Conference on the Physics of Semiconductors,* edited by E. M. Anastassakis and J. D. Joannopoulos (World Scientific, Singapore, 1991), Vol. 1, p. 332.

[36] R. Murray, Physica B **170**, 115 (1991).

[37] S. K. Estreicher, Phys. Rev. B **41**, 9886 (1990).

[38] R. Jones, S. Öberg, and A. Umerski, Mater. Sci. Forum. **83-87**, 551 (1992).

[39] G. Lucovsky, S. S. Chao, J. Yang, J. E. Tyler, R. C. Ross, and W. Czubatyj, Phys. Rev. B **31**, 2190 (1985).