†Present address: Redstone Arsenal, Huntsville Ala. 35809.

‡Work supported by the Fannie and John Hertz Foundation.

[1] See, for example, J. B. Pendry, *Low Energy Electron Diffraction* (Academic, New York, 1974).

[2] P. J. Jennings, Surface Sci. 20, 18 (1970), and 26, 509 (1971), and 27, 221 (1971); P. J. Jennings and B. K. Sim, Surface Sci. 33, 1 (1972).

[3] R. Feder, Phys. Status Solidi (b) 46, K31 (1971), and 49, 699 (1972), and 56, K43 (1973), and 62, 135 (1974).

[4] J. Kessler, Rev. Mod. Phys. 41, 3 (1969).

[5] M. R. O'Neill and F. B. Dunning, Rev. Sci. Instrum. 45, 1611 (1974).

[6] J. van Klinken, Nucl. Phys. 75, 161 (1966).

[7] N. Sherman, Phys. Rev. 103, 1601 (1956).

[8] M. Fink and A. C. Yates, At. Data 1, 385 (1970); M. Fink and J. Ingram, At. Data 4, 129 (1972); D. Gregory and M. Fink, At. Data Nucl. Data Tables 14, 39 (1974).

[9] P. S. P. Wei, J. Chem. Phys. 53, 2939 (1970).

[10] R. Loth and W. Eckstein, Phys. Lett. 20, 390 (1966); W. Eckstein, Z. Phys. 203, 59 (1967).

[11] J. Kessler, in *Atomic Physics 3*, edited by S. J. Smith and G. K. Walters (Plenum, New York, 1973), p. 524.

Oxidation of Clean Ge and Si Surfaces*

R. Ludeke and A. Koma†
IBM Thomas J. Watson Research Center, Yorktown Heights, New York 10598
(Received 10 March 1975)

The low-energy-electron loss spectra of oxygen adsorbed at room temperature on clean Si and Ge (100) and (111) surfaces suggest that each oxygen atom is doubly bonded to a surface atom. Using a chemical-bonding argument, it is shown that this complex is also energetically more favorable than previously proposed oxidation models.

The room-temperature oxidation mechanism of clean Si and Ge surfaces has been the source of considerable speculation[1-8] and a number of models have been proposed.[1-5] Of these, the peroxide bridge[2,3] between adjacent surface atoms and the Green-Maxwell model[1] have generally been favored based on experimental evidence. Since it is now believed that full coverage corresponds to at least one oxygen atom per surface atom,[1,7,9] the monoxide-bridge model[2,3] can be eliminated, except for a variation of this model proposed by Mayer and Vrakking.[4]

We propose in this Letter an entirely new model and present convincing evidence that the arrangement of the oxygen and surface atoms consists of a double-bonded IV=O complex, where IV denotes either Ge or Si. We furthermore argue that this model is energetically favored at room temperature over the previously proposed arrangements.

We have measured the low-energy-electron loss spectra (LELS) of Ar$^+$-ion-cleaned and annealed Ge and Si surfaces as a function of oxygen coverage θ. The technique consists of measuring the second derivative of the energy spectrum of electrons inelastically backscattered into a cylindrical-mirror analyzer.[8,10] The estimated energy resolution is ~0.5 eV and the accuracy of the loss measurement ~0.2 eV. The oxidation and measurements were performed in an ultrahigh-vacuum system. The oxygen coverage was obtained from the ratio of the Auger intensities of the oxygen and Si (or Ge) lines relative to the saturation ratio, which is assumed to correspond to monolayer coverage.

Figure 1 shows the loss spectra for the Ge(100) surface. Figure 1(a) is that for the clean surface, which exhibits the 2×1 surface reconstruction, as observed by reflection high-energy-electron diffraction. The 2.5- and 4.5-eV loss peaks are attributed to bulk interband transitions and those at 1.3, 7.3, and 9.1 eV to surface states.[10,11] The spectrum is already considerably changed at a coverage of a third of a monolayer [Fig. 1(b)]: The surface states have largely disappeared; the 4.5-eV peak is narrowed and shifted to 4.7 eV; and new peaks have appeared at 11, 8.6, and 6.7 eV. Only minor changes are observed upon further coverage [Fig. 1(c)]. The energy location of the peaks agrees, to within the experimental error of 0.2 eV, with the bond-electron excitation spectrum of the GeO molecule,[12-14] which generally exhibits broad bands due to vibrational excitations at energies hatched in at the bottom of Fig. 1.

Although the 2.5-eV peak of the covered sur-

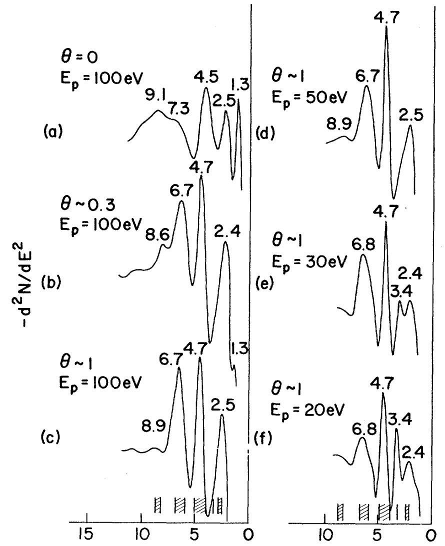

FIG. 1. LELS of the Ge(100) surface for several oxygen coverages θ and primary-electron energies E_p.

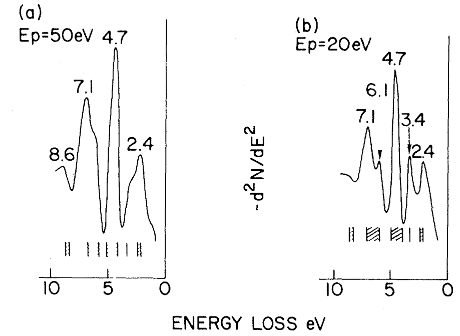

FIG. 2. LELS of the Ge(111) surface with monolayer coverage of oxygen.

face may have contributions from Ge bulk transitions, it is definitely an oxygen-related structure since it is observable down to the lowest primary-electron energies, E_p [Figs. 1(d)-1(f)], where bulk transitions are not resolvable within the sensitivity of our measurements. Bulk contributions are, of course, to be expected at all energies; however, because of the increased importance of indirect transitions for low primary-electron energies[10] the interband contributions to the spectrum are smeared out. The fact that the loss spectra remain quite intense at low values of E_p is indicative of the nearly nondispersive nature of the electronic levels[11] and supports a localized, molecular character of the oxygen-surface-atom complex. A new feature appears in the spectra of Figs. 1(e) and 1(f) at 3.4 eV. This structure, we believe, corresponds to the optically forbidden triplet-state excitation ($a\,^3\Sigma^+ \rightarrow X\,^1\Sigma^+$) of the GeO molecule, recently observed at 3.41 eV in a reaction process.[15] It is well known that the opticlike selection rules in electron-energy-loss spectroscopy of gases can be broken at low values of E_p because the first Born approximation is no longer valid and exchange and detailed coupling mechanisms must be considered.[16]

Figure 2 shows loss spectra of the Ge(111) surface for $\theta \sim 1$. The spectra are nearly identical to those of the (100) surface, with the exception that the 6.8-eV peak of Fig. 1 is shifted to 7.1 eV and a separate peak emerges at 6.1 eV at low E_p's. Actually evidence for a similar peak on the (100) surface can be seen on the low-energy side of the 6.8-eV structure in Fig. 1(f). We have no satisfactory explanation for this shift in energy, although both peaks still fall within the range of the molecular excitation band near 7 eV.

The notion of a quasi-molecular GeO surface complex is further supported by mass-spectrometric analysis of the flash-desorbed species. Near 400°C the surface oxide was removed and the species identified to be GeO molecules, in agreement with previous observations.[7]

The loss spectra of oxygen-covered Si surfaces have been reported previously.[8] Our results, shown in Fig. 3, are in general agreement with those of Ref. 8, with the exception that we see additional structure at 8.3 and 9.4 eV and at 2.9 eV at low primary-electron energies [Fig. 3(c)]. The peak at 5.7 eV seems to be spurious, and could result from the double differentiation of two adjacent sharp peaks. We have also indicated the location of excitation bands of the SiO molecule.[14, 17, 18] As with GeO, the agreement is ex-

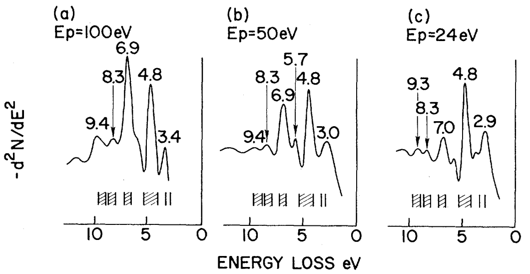

FIG. 3. LELS of the Si(100) and (111) surfaces with monolayer coverage of oxygen. The spectra for the two different surfaces are identical.

TABLE I. Heats of formation in kilocalorie/mole of O_2 for various proposed semiconductor-oxygen complexes. The values in parentheses are the calculated configurational strain energies included in the heats of formation. The chemical-bond data used to derive these results are also given.

	Peroxide Bridge[a]	MV[b]	GM[c]	Monoxide (Present model)
Ge (111)	-50 (35)	-	-	- 113 ($\sim$0)
Ge (100)	-52 (3)	-	-	- 173 ($\sim$0)
Si (111)	-88 (49)	-135 (136)	-141 (40)	- 159 ($\sim$0)
Si (100)	-99 (1)	-	-	- 228 ($\sim$0)

	Ge-Ge	Ge-0 Tetrag.	Ge = 0	Si - Si	Si - 0 quartz	Si = 0	0 = 0	0 - 0
Bond energy[d] (Kcal/mole)	45	85	161	53	111	192	119	34
Bond length[d] (Å)	2.45	1.89	1.65	2.35	1.61	1.51		1.48
$k_\theta r^2$[e] (eV/rad^2)	2.84[f]	7.4[g]	-	3.16[f]	8.1[g]	-	-	-
Bond angles: (degrees)	Ge - $\hat{0}$ - Ge = 130[h], Si - $\hat{0}$ - Si = 144[i], IV - $\widehat{IV}$ - IV = 109.50[h]							

[a] Neglects bending of IV-Ô-O; see Ref. 21.
[b] Ref. 4.
[c] Ref. 1.
[d] Ref. 20.
[e] Bond-bending force constant about group-IV atom.
[f] Ref. 22.
[g] Calculated by method of Ref. 23.
[h] Ref. 23.
[i] Ref. 24.

cellent. As the primary-electron energy is decreased, the 3.4-eV peak diminishes in intensity and a new peak near 2.9 eV emerges and becomes fully established for $E_p \sim 24$ eV [Fig. 3(c)]. We believe that this peak is associated with the optically forbidden $^1\Sigma$-$^3\Pi$ excitation, which has been identified in the gas phase at this energy.[19] Another forbidden transition has been reported near 4.2 eV.[15] Its presence would explain the asymmetry on the low-energy side of the 4.8-eV loss peak in Fig. 3(c).

The above experimental evidence clearly indicates that oxygen is chemisorbed on Si and Ge surfaces into a monoxidelike bound state. The monoxide molecules are believed to be doubly bonded[20] (IV = O) which leaves two electrons on the group-IV atom which could participate in the formation of other covalent bonds without seriously affecting the electronic properties of the double bond. In the adsorption process the oxygen molecule dissociates and each atom is bonded to a different surface atom by a double bond. This process requires that a back bond be broken on the (111) surface to achieve the desired bonding. We have calculated the heats of formation[3] of the various proposed oxygen complexes, including the double-bonded monoxide model. The results, shown in Table I, further indicate that the IV = O monoxide model is energetically favored over others. The parameters used in the calculations are also listed. The values obtained for the Ge-peroxide model differ from those of Green and Lee[3] because of the use of more recent bond data. The values in parentheses are the calculated configurational strain energies. We have also tried to estimate the strain contributions in the Mayer-Vrakking and Green-Maxwell models. Because of the complexities of these models, the values are only approximate. The data for the (100) surfaces also include recalculated contributions of 30 and 37 kcal/mole for the respective breakup of paired Ge and Si surface atoms[3] prior to the oxidation process.

The proposed model is consistent with a correspondence of one oxygen to one surface atom and generally agrees with the large heats of adsorption, ~ 210 and 125 kcal/mole, measured, respectively, for Si and Ge surfaces.[25] It is furthermore consistent with results from ion-reflection mass spectroscopy[26] which indicate that the oxygen atoms are on top of the silicon surface atoms. This observation eliminates the Green-Maxwell model[1] from consideration, particularly for room-temperature adsorption since the model requires the breaking of three Si-Si bonds.

The results of Ibach *et al.*[5] may also be reinterpreted to support our Si = O model. For low oxygen coverages these authors observed loss peaks at 125 and 90 meV using high-resolution LELS. They attributed these to vibrational levels of a peroxide structure. However, the vibrational levels of the $^1\Sigma^+$ ground state and the most prominent excited $^1\Pi$ state near 5 eV of the free SiO molecule have vibrational frequencies corresponding to 154 and 106 meV, respectively.[14] Since the frequency $\nu \propto \mu^{-1/2}$, where μ is the reduced mass, a simple calculation shows that for a rigidly attached Si = O molecule (i.e., infinite mass attached to the Si) the vibrational energies correspond to 123 and 85 meV, in excellent agreement with experimental observations.

We thank J. A. Van Vechten and H. Lüth for helpful discussions and comments.

---

*Research sponsored in part under contract with U. S. Army Research Office, Durham, N. C.

†On leave from the Department of Applied Physics, University of Tokyo, Japan.

[1] M. Green and K. H. Maxwell, J. Phys. Chem. Solids 13, 145 (1960).

[2] M. Green and A. Liberman, J. Phys. Chem. Solids 23, 1407 (1962).

[3] M. Green and M. J. Lee, in *Solid State Surface Science*, edited by M. Green (Marcel Dekker, New York, 1969), Vol. 1, Chap. 3.

[4] F. Mayer and J. J. Vrakking, Surface Sci. 38, 275 (1973).

[5] H. Ibach, K. Horn, R. Dorn, and H. Lüth, Surface Sci. 38, 433 (1973).

[6] G. A. Bootsma, Surface Sci. 15, 340 (1969).

[7] A. A. Frantsuzov and N. I. Makrushin, Surface Sci. 40, 320 (1973).

[8] H. Ibach and J. E. Rowe, Phys. Rev. B 9, 1951 (1974), and 10, 710 (1974).

[9] A. H. Boonstra, Philips Res. Rep., Suppl. 3, 1 (1968).

[10] R. Ludeke and L. Esaki, Phys. Rev. Lett. 33, 653 (1974), and Surface Sci. 47, 132 (1975).

[11] R. Ludeke and A. Koma, in Proceedings of a Conference on the Physics of Compound Semiconductor Interfaces, Los Angeles, California, February 1975 (to be published).

[12] D. P. Tewari and H. Mohan, J. Mol. Spectrosc. 39, 290 (1971).

[13] W. Jevons, L. A. Bashford, and H. V. A. Briscoe, Proc. Phys. Soc., London 49, 543 (1937).

[14] R. F. Barrow and H. C. Rowlinson, Proc. Roy. Soc., Ser. A 224, 374 (1954).

[15] G. Hager, L. E. Wilson, and S. G. Hadley, Chem. Phys. Lett. 27, 439 (1974).

[16] N. F. Mott and H. S. W. Massey, *The Theory of Atomic Collisions* (Clarendon Press, Oxford, England, 1965).

[17] W. Jevons, Proc. Roy. Soc. 106, 174 (1924).

[18] R. Cornet and I. Dubois, Can. J. Phys. 50, 630 (1972).

[19] R. D. Verma and R. S. Mulliken, Can. J. Phys. 39, 908 (1961).

[20] R. T. Sanderson, *Chemical Bonds and Bond Energy* (Academic, New York, 1971).

[21] This bending is about the soft oxygen bonds of unknown bending force constants. The estimated bending angle is only 10°–15° and hence the total contribution to the strain energy may be neglected.

[22] J. A. Van Vechten, Phys. Rev. 170, 773 (1968), and Phys. Rev. B 10, 4222 (1974).

[23] R. W. G. Wykoff, *Crystal Structures* (Interscience, New York, 1963), Vol. 1.

[24] A. G. Revesz, Phys. Rev. Lett. 27, 1578 (1971).

[25] L. Brewer, Chem. Rev. 52, 1 (1953).

[26] H. H. Brongersma and P. M. Mul, Surface Sci. 35, 393 (1973).