# CALORIMETRIC HEATS OF ADSORPTION OF OXYGEN ON ATOMICALLY CLEAN SURFACES OF GERMANIUM, SILICON, AND LEAD SULFIDE

G. B. Demidovich and A. A. Sklyankin

Vestnik Moskovskogo Universiteta. Fizika,
Vol. 35, No. 1, pp. 96-98, 1980

UDC 536.658

Direct measurements have been made of the differential heats of adsorption of oxygen on atomically clean surfaces of germanium, silicon, and lead sulfide, which have been produced by crushing the initial single crystals under ultrahigh vacuum. The high heats of adsorption for Ge and Si (115 ± 10 and 210 ± 30 kcal/mol, respectively) are associated with the formation of double bonds. The interaction of an atomically clean surface of Ge with oxygen is dependent on the presence of minute traces of water. No such relationship is observed for silicon.

Direct calorimetric measurements of the differential heats of adsorption Q on atomically clean surfaces are of particular interest, because they provide direct information on the interaction energies of surfaces with gases at the molecular level. Few studies on this have been made [1-3]. Measurements have been made of the heats of adsorption of oxygen on evaporated films of Ge and Si [1]. Similar measurements have been made [2] for powdered reduced Ge, but in the absence of an ultrahigh vacuum. The data of [1] were used for calibration purposes in measuring Q [3] in the adsorption of gases of $H_xA$ type on atomically clean surfaces of Ge and Si.

The clear deficiencies in such studies have led us to perform a series of studies on Q for oxygen on atomically clean surfaces of germanium, silicon, and lead sulfide made by cleavage under ultrahigh vacuum. The specimens were prepared by vibrational crushing of single crystals in a sealed glass system pumped after preliminary heating to a pressure of $10^{-8}$—$10^{-9}$ mm Hg by means of a titanium-molybdenum getter. The oxygen was produced by pyrolysis of CuO or $KMnO_4$, also previously outgassed by heating under the same vacuum (at 400 and 200°C, respectively). Known amounts of oxygen were admitted from known glass volumes via break seals. The heats of adsorption were measured with a Calvet microcalorimeter with a limit of detection of about $10^{-5}$ W. The uptake in adsorption was determined by a volumetric method. The oxygen pressure was measured with a Pirani gauge or an LT-2 thermocouple gauge.

Prolonged (about 40 hr) vibrational grinding of the Ge, Si, and PbS under ultrahigh vacuum produced specific surfaces as measured by the BET method (low-temperature adsorption of argon) of $1\text{-}5 \cdot 10^4$ $cm^2 \cdot g^{-1}$; the possible errors due to aggregation, which tends to occur with Ge and Si, were automatically eliminated

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in calculating the adsorption of $O_2$, since the dimensions of the argon atom and the oxygen molecule are similar.

One can estimate the contamination of a surface formally by means of coefficient $\varkappa$, equal to the ratio of the total number of residual-gas molecules in the volume of the system to the total surface of the specimen. The values for our experiments with specimens of 1-3 g were $\varkappa \sim 10^5 - 10^6$ mol·cm$^{-2}$; in an unheated glass system evacuated to about $10^{-5}$ mm Hg, $\varkappa$ was about $10^{10}$ mol·cm$^{-2}$.

The differential heats of adsorption in kcal/mol for $O_2$ on atomically clean Ge, Si, and PbS in the initial stages are given in Table 1 for various values of $\varkappa$ in mol·cm$^{-2}$. The values of Q correspond to the initial stages of oxidation with surface filling factors $\theta \geqslant 0{,}01$. Table 1 shows that atomically clean surfaces of silicon and lead sulphide produce considerable heat on adsorbing oxygen, which is characteristic of the formation of valency bonds. Under similar conditions, i.e., with $\varkappa \sim 10^5 - 10^6$ mol·cm$^{-2}$, an atomically clean surface of germanium did not interact with oxygen, in contrast to Si and PbS. In our experiments with Ge, there was no chemisorption corresponding to $\theta \leqslant 10^{-5}$ (on the assumption that the heat of possible chemisorption would be about 100 kcal/mol). On the other hand, admitting oxygen from an unheated glass system to the germanium (where the latter had $\varkappa \sim 10^{10}$ mol·cm$^{-2}$) resulted in appreciable adsorption with the production of considerable amounts of heat.

Table 1

| | $\varkappa \sim 10^5 - 10^6$ | $\varkappa \sim 10^{10}$ |
|---|---|---|
| Ge | 0 | 115±10 |
| Si | 210±30 | — |
| PbS | 80±20 | — |

Our results for Q for germanium and silicon agree well with the data of [1,2]; such high heats of adsorption cannot be explained satisfactorily by the formation of oxygen complexes on the surfaces of Ge and Si, which had been suggested by Green [4]. The observations can be matched to the calculated energies of such complexes by means of various corrections [3]. On the other hand, in our view the high heats of adsorption are related to the formation of Ge = O and Si = O double bonds on the Ge and Si. A rough estimate of the energies of these bonds is in agreement with this conclusion and also in good agreement with experiment:

$$2E_{Ge=O} - E_{O=O} - 2E_{Ge-Ge} \simeq 2 \cdot 159 - 118 - 2 \cdot 33 = 134 \text{ kcal/mole,}$$
$$2E_{Si=O} - E_{O=O} - 2E_{Si-Si} \simeq 2 \cdot 195 - 118 - 2 \cdot 34 = 204 \text{ kcal/mole.}$$

The formation of double bonds when atomically clean surfaces of Ge and Si interact with oxygen is also most likely from the viewpoint of the structure of the surface itself, where most of the atoms are in a state to form double bonds [5]. Indirect evidence for double bonds on the surfaces is provided by [6], where slow-electron diffraction measurements show that the adsorbed O atoms occupy locations on the surface exactly above the surface Si atoms, and the positions and intensities of the diffraction peaks were not altered until a monolayer covering was produced. A similar conclusion was obtained for the surfaces of Si [7] by IRMS.

Measurements on the characteristic-loss spectra for slow electrons [8] also indicated unambiguously that each oxygen atom forms a double bond to surface Ge

or Si atoms. These experimental results are confirmed by later study [9]. Finally, in [10] a study was made of the scope for formation of various types of surface structure and the adsorption of oxygen by these, and a similar conclusion was drawn, in which a model for the Si surface with double bonds was considered to be the best*. The result $Q \simeq 100$ kcal/mol for the adsorption of oxygen on PbS is in reasonable agreement with the energy calculated for associative adsorption in accordance with

$$E_{Pb=O} + E_{S=O} - E_{O=O} \simeq 94 + 124 - 118 = 100 \text{ kcal/mole.}$$

The oxidation mechanism for PbS is discussed in more detail in [12].

The following may be noted on the differences in adsorption of $O_2$ by germanium and silicon for various $\varkappa$; the literature data [2,13-15] show that the attachment coefficient k decreases from $10^{-2}$ to $10^{-5}$ as the vacuum improves ($\varkappa$ decreases) when oxygen interacts with an atomically clean surface of germanium. In our experiments k was zero** at the minimum value $\varkappa \sim 10^5$ mol·cm$^{-2}$. No such effect occurs for silicon, and data from various sources indicate that $k \simeq 10^{-2}$ and is independent of $\varkappa$. It will not be surprising that further improvement in the cleanness in our experiments with silicon, where $\varkappa \sim 10^5 - 10^6$ mol·cm$^{-2}$, should produce substantial changes in the interaction of $O_2$ with an atomically clean surface of Si. Differences in the interactions of atomically clean surfaces with oxygen are due to differences in the spin states of the surface atoms [17]. At room temperature, cleavage of germanium results in a nonradical atomically clean surface, whereas cleavage of silicon produces a high concentration of free radicals at the surface [5,17].

We are indebted to Professor V. F. Kiselev for initiating this research and for constant interest.

## REFERENCES

1. D. Brennan, D. O. Hayward, and B. M. W. Trapnell, J. Phys. Chem. Sol., vol. 14, p. 117, 1960.
2. M. Green, Semiconductor Surface Physics, Philadelphia, p. 326, 1957.
3. G. A. Bottsma, Surf. Sci., vol. 15, 340, 1969.
4. M. Green (editor), Solid State Surface Science [Russian translation], Moscow, 1972.
5. G. B. Demidovich and V. F. Kiselev, Vestnik Mosk. Univ., fiz. astron. [Moscow University Physics Bulletin], vol. 14, no. 2, p. 158, 1973.
6. F. Jona, Surf. Sci., vol. 8, p. 478, 1967.

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*Theoretical calculations [11] indicate that two-center adsorption of $O_2$ on atomically clean Ge is the most favored by energy, since the energy release is 6-10 eV (130-220 kcal/mol), but there may be a transition to one-center adsorption and activation-free dissociation of the adsorbed $O_2$ molecules as the degree of filling increases, although the latter ultimately also results in double bonds.

**The contamination coefficient $\varkappa$ to some extent characterizes the water content of the adsorbate; mass spectra of the residual gases in an unheated vacuum system [16] show a large water peak, whereas this peak falls almost to the noise level under ultrahigh vacuum.

7. H. H. Brongersma and P. M. Mul, Surf. Sci., vol. 35, p. 393, 1973.
8. R. Ludeke and A. Koma, Phys. Rev. Lett., vol. 34, p. 1170, 1975.
9. Y. W. Chung, W. Siekhaus, and G. A. Somorja, Surf. Sci., vol. 58, p. 341, 1976.
10. W. A. Harrison, Surf. Sci., vol. 55, 1, 1976.
11. A. I. Volokitin, G. V. Gadiyak, et al., Fiz. Tekh. Poluprov., vol. 10, 436, 1866, 1976.
12. G. B. Demidovich, A. A. Sklyankin and Yu. A. Zarif'yants, Vestnik Mosk. Univ., fiz. astron. [Moscow University Physics Bulletin], vol. 17, no. 6, p. 737, 1976.
13. R. E. Shlier and H. E. Farusworth, J. Chem. Phys., vol. 30, p. 917, 1959.
14. H. D. Hagstrom, J. Appl. Phys., vol. 32, p. 1020, 1961.
15. Yu. I. Belyakov, M. P. Volkov, and T. N. Kompaniets, Zh. Tekh. Fiz., vol. 44, p. 1298, 1974.
16. V. G. Erofeichev and L. N. Kurbatov, Fiz. Tverd. Tela, vol. 3, p. 595, 1961.
17. V. S. Kuznetsov, G. B. Demidovich, and V. F. Kiselev, Vestnik Mosk. Univ. fiz. astron. [Moscow University Physics Bulletin], vol. 16, no. 2, p. 177, 1975.

17 November 1978