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Reactive Scattering of Halogen Molecules from ⟨111⟩ Surfaces of Silicon and Germanium: Comparison with Oxygenic Species

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The values of the reaction probabilities of Cl_2, Br_2 and I_2 were determined to be 0.3–0.5 independent of surface temperature at low gas pressures and surface temperatures above about 900 and 1100°K for single-crystal surfaces of germanium and silicon, respectively. These values were the same magnitude as those for O and O_3 and were at least an order of magnitude higher than the reaction probability of molecular oxygen. The differences in reactivity of O, O_2, O_3 and the halogens was interpreted in terms of *virtual* dangling surface bonds which account qualitatively for the chemical interaction between the gas and solid during collision. In these terms the reactivity of molecular oxygen was low due to the severe steric requirement imposed by the necessity for interaction with adjacent surface orbitals to effect chemisorption. Atomic oxygen and the halogens were easily chemisorbed on a single site. Ozone interacted through its terminal oxygens with adjacent surface orbitals to produce dissociation.

INTRODUCTION

Previous studies of the high temperature reactivity of oxygenic species with clean silicon and germanium surfaces showed the reaction probability of molecular oxygen to be low and without an activation energy (*1–3*). As the product of the reaction was the monoxide, dissociation of the molecule was required, and it seemed likely that the overlap of the orbitals between the incoming molecules and the surface atoms could be sufficiently low as to produce severe steric requirements for the reaction (*1, 4*). The reactions of the halogens series (Cl_2, Br_2 and I_2) with single crystal slices of germanium and silicon were studied in order to determine the effect of variation in bond length and bond strength on reactivity. Previous work suggested that the reactivity of the halogens was high, but little data was available for comparative purpose, particularly at high temperatures (*5, 6*). The reactions to form the halides were known to be overall exothermic, as were the reactions with oxygen, so that a low activation energy was anticipated for the halogen reaction probabilities. Both dc and ac molecular beam techniques were employed in this work. The results of the modulated beam experiments are reported elsewhere (*8, 9*). This paper presents the results obtained for the high temperature reaction probabilities of Cl_2, Br_2 and I_2. The difference in reactivity observed between the halogens, ozone, oxygen atoms and molecular oxygen is discussed.

EXPERIMENTAL PROCEDURE

Silicon and germanium single-crystal samples were obtained as described previously (*4*). In this work the samples were supported by a tungsten harness and suspended from a microbalance or a rigid support for gravimetric or mass spectrometric studies, respectively. The sample area was about 4 cm². They were positioned approximately 4 cm from the effusion orifice (and 2 cm from the mass-spectrometer ionizer in the case of the mass spectrometer studies). The crystals were heated by a high intensity tungsten iodine lamp placed directly behind the sample. The temperature on about seven-tenths of the sample surface was uniform; the variation in temperature near the sample edges was ±30°C as determined with a calibrated infrascope.

The experimental procedure used to determine the reaction probability gravimetrically was described previously (*7*). The beam flux was varied using low temperature slurries of liquid nitrogen and liquid organics to maintain a static vapor pressure of halogen gas in the molecular beam source region. Care was taken to calibrate the pressure in the source chamber for each gas. In addition to the gravimetric studies the reaction probabilities, α, were measured by observing the relative decrease in the mass spectrometer ion current of the reflected beam resulting from heating the sample to temperatures above room temperature. The agreement between both methods was very good.

Results

Results typical of the gravimetric studies are shown for the reaction of silicon with molecular bromine in Fig. 1. As noted previously for chlorine (*8*) the reaction probability was independent of surface temperature above about 900°K at the lower beam pressures employed. Figure 2 shows data for the reaction of bromine at a high beam pressure of about 10^{-5} Torr with germanium typical of the mass spectrometer results. In cases in which the value of α appeared to drop at higher surface temperatures the ratio of Br^+ to Br_2^+ signals did not change with temperatures. Table 1 shows the result obtained for each reaction

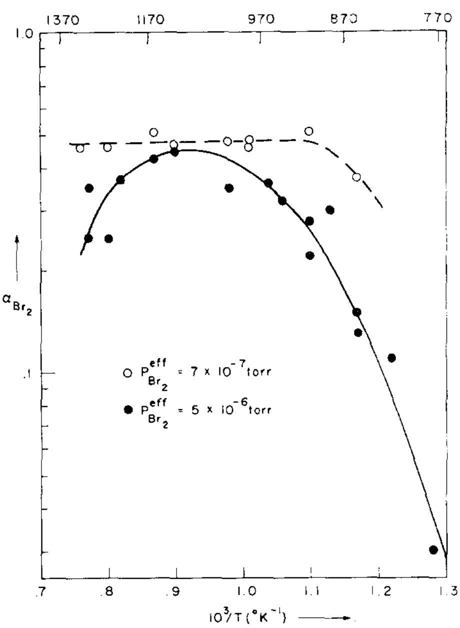

FIG. 1. Plot of α_{Br_2} on ⟨111⟩ oriented silicon against inverse surface temperature.

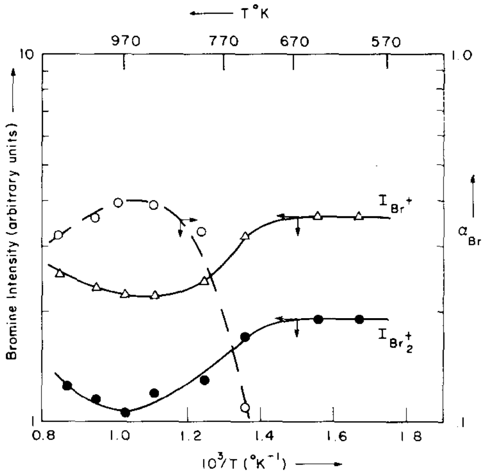

FIG. 2. Plot of α_{Br_2} on ⟨111⟩ oriented germanium against inverse surface temperature.

TABLE 1

Substrate	Method employed	α Reactant gas					
		Cl_2	Br_2	I_2	O_2	O	O_3
Germanium 800–1050°K	Gravimetric	0.25	0.3	0.3	0.02	0.4	0.3
	Mass spec	0.35	0.4	0.5	—	—	—
Silicon 1000–1350°K	Gravimetric	0.35	0.35	—	0.04	0.5	0.4

studied. In each case the maximum value of α is reported as measured without corrections for possible differences in product distributions in the gravimetric studies. The values previously obtained for the oxygenic species are included for comparison.

DISCUSSION OF RESULTS

It is important to note that the values of α reported above were obtained under low coverage conditions on a heavily reacted surface. The coverages were calculated to be the order of magnitude of 10^{-2} as described previously (*8, 11*). The crystal plane exposed to the gas was predominantly the ⟨111⟩ plane (*6, 10*). Furthermore, it was recently shown that the Si ⟨111⟩-1 surface structure prevails at the temperatures and pressures employed here (*11*). The surface can thus be viewed as primarily ⟨111⟩ oriented without surface reconstruction, though, to be sure, there must be a substantial concentration of facets of large dimension, ledges, and kinks. The following discussion idealizes this complex surface to a single ⟨111⟩ crystal plane.

The results given in Table 1 show that the reactivity of the halogen gases with the semiconductor surfaces was quite high. The values of α were nearly identical for all the halogens studied on the respective substrates. Furthermore, among all of the gases studied molecular oxygen was the only species whose reactivity differed appreciably from atomic oxygen—a reaction not requiring bond dissociation. The low reactivity of molecular oxygen and the higher reactivity of the other gases can be explained in terms of the interaction of O_2 with adjacent surface orbitals to form isolated *virtual* bonds which introduces a stringent steric requirement for the reaction.

That this low value was probably not due to the interaction with point defects in equilibrium on the surface was apparent from the independence of α_{O_2} on gas or surface temperature. Furthermore, the constancy of α_{O_2} and α_{X_2} with surface temperature at low beam pressure indicated that there was no reversibly adsorbed molecular precursor for the dissociative adsorption. This temperature independence would exist fortuitously if desorption of the intermediate and dissociation on the surface required identical activation energies. On the basis of arguments given below it seems likely that the activation energy for X_2 dissociation is at most 1 or 2 cal/g mole so that the lifetime of a molecular precursor at the temperatures studied would be of the order of magnitude of the collision time, in any event. The values of α in all the cases given in Table 1 therefore reflected the value of the "steric factor" associated with the gas solid *collision*. The differences in the values of α observed were therefore associated with the details of the potential energy surface for the chemical reaction at close distances.

The symmetries of the lowest unoccupied molecular orbitals about the plane through the internucleus axis are identical, and symmetry arguments based on the principle of maximum bonding cannot be invoked to explain the difference in reactivity between O_2 and X_2 for the bridge-bond collision complex, even if the surface orbitals can be grouped into molecular orbitals of well-defined symmetry. Furthermore, any symmetry argument based on differences in the activation energies predicted from correlation diagrams such as those employed by Kearns (*12*) to suggest differences in reactivities between $'\Delta$ and $^3\Sigma O_2$ are inapplicable here, as no activation energies were observed. The low steric factor for molecular oxygen appears to arise from strict orientation requirements of the surface collision for dissociative adsorption or a low probability of passing from the electronic surface representing reactants to that representing the adsorbed state due to the triplet multiplicity of ground state molecular oxygen (*13*).

It is well known from gas phase kinetics that the halogens are easily dissociated by methyl radicals and alkali metal atoms (*14, 15*). The corresponding dissociation reactions with molecular oxygen are endothermic, but the cross section for the exothermic reaction,

$$CH_3 \cdot O_2 \rightarrow CH_3O_2, \qquad (1)$$

is known (*16*), and it is 40 times smaller than that for

$$CH_3\cdot + X_2 \rightarrow CH_3X + X. \qquad (2)$$

The cross sections for reactions of the type

$$M + X_2 \rightarrow MX + X, \qquad (3)$$

where M is an alkali metal atom are also quite large compared to that for reaction (1) above (*15*). To draw the analogy with the gas phase reactions it is quite reasonable to view the ⟨111⟩ surface as a collection of dangling bonds directed normal to the surface. In this respect it is noteworthy that the work function of silicon and germanium is quite close in energy to the ionization potential of the alkali metals which could permit long-range charge transfer interactions and dissociation of the halogen molecule as is believed to occur with alkalai metal atoms (*17, 18*). It is difficult to assign electron occupation numbers to these orbitals to make the analogy more complete due to uncertainty in their position with respect to the Fermi level; existing evidence suggests that two surface states exist which are both partially and fully occupied (*19–21*). The available evidence does suggest that it is unlikely that the surface analogue of reaction (1) above leads to chemisorbed oxygen on silicon surfaces. The ESR studies of Haneman (*21*) and Chung and Haneman (*22*) at room temperature showed that molecular oxygen did not chemisorb on silicon in a fashion that either quenched the surface ESR signals or changed their *g* values. There was no evidence for the formation or destruction of "surface free radicals" upon chemisorption. It is, of course, difficult to extrapolate these results to high temperatures.

The same interpretation of the difference in reactivities can be reached from a slightly different point of view. The calculations of Haneman and Heron (*23*), Elias (*24*) and Falick (*25*) indicate that the interaction energy between adjacent surface orbitals on the ⟨111⟩ silicon surface is of the order of RT at most in agreement with the observation by Florio and Robertson (*6*) that the surface structure of ⟨111⟩ silicon is Si(1 × 1) at high temperatures. Chemically these orbitals can thus be regarded as "dangling bonds" in the absence of an approaching reactive species. The spatial degree of interaction of the surface orbitals with incoming gaseous species can be qualitatively assessed by constructing *virtual bonds* in the vicinity of each surface lattice point. As the representative distance for strong chemical interaction a distance equal to the gas phase bond length of Ge–O or Ge–X was chosen. Figure 3 shows the ⟨111⟩ surface lattice of germanium with circles drawn about each lattice point of radius equal to the Ge–O or Ge–X bond length. In this construction it is assumed that the same degree of bond overlap between the diatomic molecule and the surface orbital will produce approximately the same force for dissociation. From Fig. 3 illustrating the virtual bonds it is easily seen that the spatial extent of the interaction of the halogens with the surface dangling bonds is significantly larger than that with molecular oxygen. In fact, neighboring virtual bonds for the halides overlap so that the site distinction for halogen dissociation is obscured by the strong site *interaction* during the collision. In the case of molecular oxygen chemisorption, however, each site is relatively isolated and the orientation requirements are more severe. It is interesting to note that the fraction of the ⟨111⟩ surface contained within the Ge–O bond length of each lattice point is 0.6 which corresponds quite closely to the oxygen atom reaction probability.

It was unlikely that the low value of α_{O_2} was due to a spin forbidden process that required a non-adiabatic transition for reaction. According to Nikitin (*13*) the probability of curve crossing normally associated with non-adiabatic reactions is of the order of 10^{-1}–10^{-2}, which is similar in magnitude of $\alpha_{O_2}/\alpha_{X_2}$ observed here. In this regard, the value of α_{O_2} did not decrease with increasing gas-temperature as expected from the Landau-Zener formulation (*12*), but this effect could be masked by a small activation energy. In previous work it was shown that there was no enhancement in the reactivity of discharged molec-

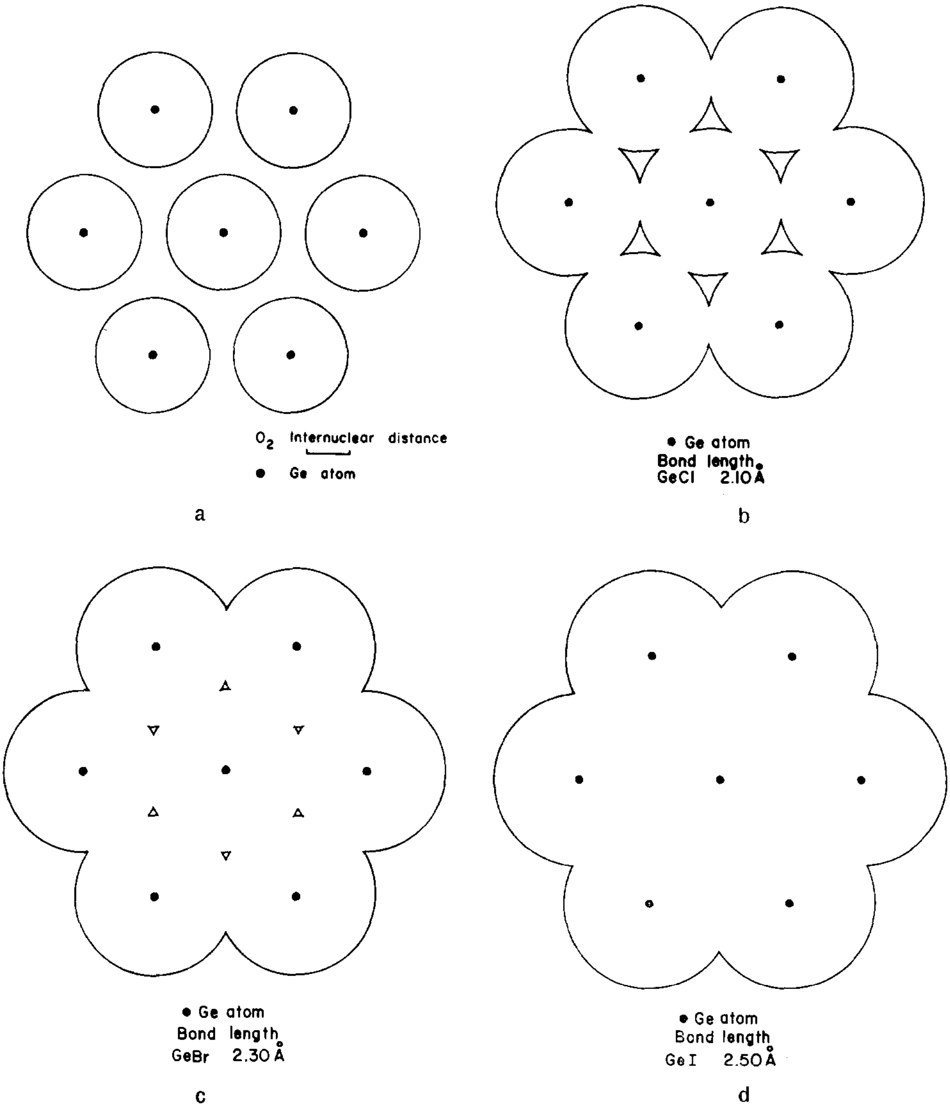

FIG. 3 a, b, c, d. Virtual bond plot for the dissociation of O_2, Cl_2, Br_2 and I_2 on the ⟨111⟩ surface of germanium, respectively.

ular oxygen when the atoms were titrated out with NO_2 (*4*). At the atom concentrations obtained with the RF discharge, significant concentrations of $'\Delta O_2$ were expected (*24, 25*). The high reactivity of $O(^3P)$ indicated that spin conservation was not a dominant effect for the formation of adsorbed oxygen. It therefore appears that the reactivity of $O_2(^3\Sigma)$ was not due to a non-adiabatic curve crossing. The high reaction probability of ozone can be interpreted in a similar manner. In this regard ozone differs from molecular oxygen in two significant respects: (1) the distance between its terminal oxygens is 2.2 Å compared to 1.2 for molecular oxygen; (2) the bond dissociation energy is 24 kcal/g mole compared to 118 kcal/g mole for O_2. The greater distance between terminal oxygens ensure stronger interaction between the oxygen atoms of the molecule and adjacent surface bonds. Furthermore, the reduced bond energy requires a lower overlap between molecular and surface orbitals to produce an equivalent force toward dissociation. In effect the virtual bonds are longer, and the surface can pull the terminal ozone oxygens with relatively greater force to produce dissociated oxygen atoms and chemical reaction.

SUMMARY

On the basis of the existing evidence it appears that molecular oxygen and ozone are chemisorbed on germanium and silicon surfaces by interaction with neghboring surface orbitals, whereas the halogens are dissociatively adsorbed at a single site. This conclusion was drawn by regarding the ⟨111⟩ surface as a collection of isolated dangling *virtual* bonds whose spatial extent depends on the length of the bond formed during chemisorption. With the surface viewed in this fashion the reactivities of O, O_2, O_3, and the halogens were easily understandable. This qualitative discussion of relative chemical reactivities awaits further refinement with more quantitative quantum mechanical calculations.

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