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# Sticking Probability of Oxygen Molecules on Single Crystals of Germanium

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The sticking probability $\alpha$ of oxygen molecules in a molecular beam impinging on single-crystal wafers of germanium was determined by a gravimetric technique. The value of $\alpha = 0.04$ was obtained for surface temperatures between 460° and 900°C and for gas temperatures between 30° and 450°C prior to expansion in generating the molecular beam. Under the conditions of this work, the molecules of oxygen sticking to the surface formed volatile germanium monoxide. It is believed that $\alpha$ represents a steric factor, oxygen molecules being adsorbed only if they lie flat on the surface prior to adsorption.

## INTRODUCTION

Valuable information on the kinetics of adsorption has been obtained in recent years by measurements of the sticking probability of various molecules on solid surfaces that are well defined both physically and chemically. The chemical interaction between oxygen and germanium is particularly interesting because germanium monoxide evaporates relatively readily from an oxygenated germanium surface.

Thus, Law and Meigs (*1*) have demonstrated that oxidation of germanium with oxygen pressures of 7 to 115 mm Hg at 500° to 700°C takes place through the formation of the monoxide which evaporates and diffuses away through the gas phase. At these high pressures, diffusion controls the rate of oxidation. Rosenberg, Robinson, and Gatos (*2*) found that, at high temperatures, desorption of oxygen from oxygenated germanium surface does not occur but oxygen removal takes place by evaporation of GeO.

By operating at very low pressures of oxygen and at sufficiently high surface temperatures, it might then be possible to measure the sticking probability of oxygen on a surface of germanium kept clean by continuous evaporation of GeO formed as a result of adsorption. It was decided to try this experiment in a molecular beam apparatus.

## EXPERIMENTAL APPARATUS AND PROCEDURE

The experimental study of germanium oxidation was performed in an apparatus designed to produce a molecular beam by directing a jet of gas in supersonic flow through an orifice into a high-vacuum chamber. Molecular beams formed in this manner were directed onto single-crystal

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germanium wafers heated by thermal radiation. The losses in weight of the targets, due to formation and evaporation of germanium monoxide, were measured by observing the changes in extension of a quartz spring used to suspend the targets.

**Molecular beam apparatus.** The molecular beam apparatus has been described in detail elsewhere (*3*, *4*). The principal elements are shown in Fig. 1. Each gas was fed to a nozzle at a pressure of 10 to 100 mm Hg. The gas flowed into the nozzle exhaust chamber and expanded into supersonic flow. During the expansion the gas molecules transferred most of their translational energy and a part of their rotational energy into translational energy in the direction of flow. During operation the pressure in the nozzle exhaust chamber was maintained at about $2 \times 10^{-3}$ mm Hg. The core of the expanding jet of gas was directed through a cone-shaped skimmer into a second chamber maintained at a pressure of about $1 \times 10^{-6}$ mm Hg. After passing through the skimmer the gas was essentially in free molecular flow and the molecules entered the target chamber as a molecular beam.

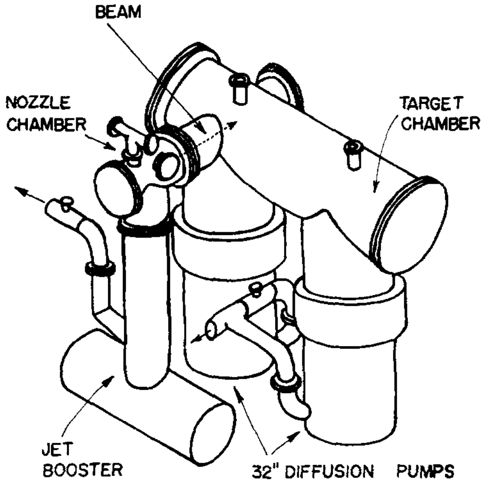

Fig. 1. Molecular beam apparatus.

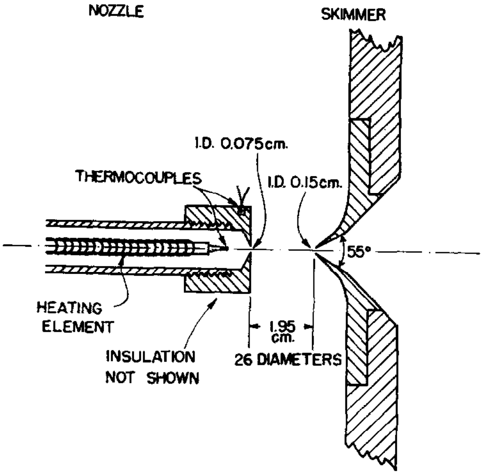

Fig. 2. Details of nozzle and skimmer.

Details of the nozzle and skimmer are shown in Fig. 2. The nozzle assembly was made of stainless steel with the exception of a brass electrical connection box. The diameter of the nozzle orifice was 0.075 cm. The skimmer was made of steel. The cone of the skimmer tapered to an entrance diameter of 0.15 cm.

A nichrome resistance wire wound around alumina tubing was installed within the nozzle to heat the nozzle and the gas flowing through it. Power input to the heater was controlled with a Variac. Chromel-alumel thermocouples were placed in the gas chamber upstream of the orifice and in the nozzle block. A cooling water coil protected the electrical connection box from overheating.

The first chamber was exhausted through a Stokes Series 150, 16-inch diameter, Jet Booster oil diffusion pump with a Kinney Type 220 mechanical vacuum pump serving as a forepump. The pumping fluid in the Jet Booster was Aroclor 1254 (Monsanto Chemical Co.), a chlorinated hydrocarbon.

The second chamber was exhausted through two NRC H-32-SP, 32-inch diameter, fractionating oil diffusion pumps operating in parallel. The forepump was a Stokes 412-H mechanical vacuum pump. The pumping fluid in these diffusion pumps was Dow Corning DC-704 Silicone Oil. Backstreaming of oil was limited by a water-cooled baffle above each diffusion pump.

Background pressures were measured in

the first chamber with an NRC Alphatron gauge and in the second chamber with an NRC Type 518 ionization gauge.

**Target suspension system.** Germanium wafers were suspended in the path of the molecular beam as shown in Fig. 3. A collimating orifice was placed between the skimmer and target to limit the area of the target exposed to the molecular beam. Each target was placed in a platinum or tungsten wire harness touching only the edges of the target. The targets were hung on a platinum wire suspended from a helical quartz spring. The spring was in turn suspended from a support whose position could be adjusted for centering the target in the molecular beam.

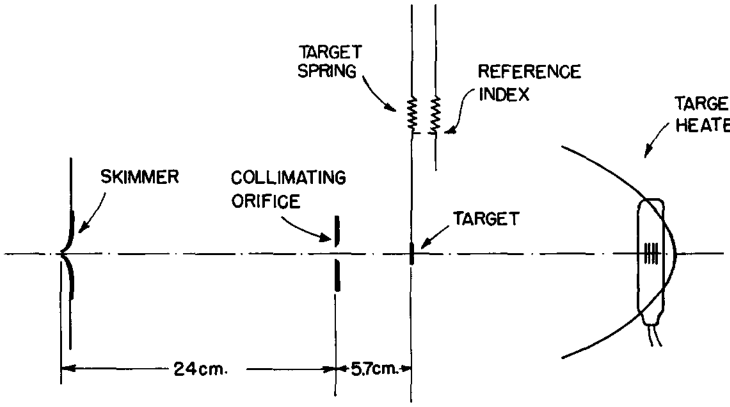

Fig. 3. Target suspension system.

The extension of the quartz spring was measured in order to determine the change in weight of the targets during oxidation. The spring (Warden Laboratories) had a sensitivity of approximately 0.1 mm/mg. A second spring identical to the target spring was suspended beside the target spring in order to provide a temperature insensitive reference point for extension measurements. The images of platinum index wires attached to the lower end of each spring were formed outside the chamber by a double convex lens. These images were observed with a Misco micrometer-type optical reader (*5*). The distance between target index and reference index was measured on the scale of the optical reader giving target spring extension in reader scale divisions. This extension measurement system was calibrated directly and in place by adding known weights to the target and measuring changes in extension with the optical reader. The sensitivity was 9.2 scale divisions/mg. The limit of detection was about 0.5 scale divisions or 0.05 mg.

**Target heating system.** The targets were heated with radiation from a 1500-watt projection lamp (General Electric Co., Type DTJ) located in a 20 cm diameter, polished-aluminum, ellipsoidal reflector located behind the targets as shown in Fig. 3 (*5*). The filament of the lamp was placed at one focus of the reflector; the target was placed at the other. Target temperature was varied by varying power input to the projection lamp. This power input was controlled with a Variac and measured with an ammeter and a voltmeter. A target temperature of 937°C was obtained with a power input of about 1100 watts. No cooling was provided for the projection lamp. Target temperature was measured with a chromel-alumel thermocouple inserted between the halves of a split germanium wafer sandwiched between two whole germanium wafers (*5*). Calculation shows that the temperature drop across the three wafers was less than 1°C. Target temperature was related to power input to the projection lamp and to lamp filament temperature as determined with an optical pyrometer (Leeds and Northrup No. 8622-C). The temperature thus measured was checked against the melting point of germanium, 937°C (*6*), with both the three-wafer sandwich and single-wafer targets. As measured with the thermocouple assembly, temperatures could be reproduced within 10°C.

**Materials.** Semiconductor grade germanium wafers with varying resistivity and doping agents were supplied by Merck and Co., Inc. The wafers were cut from single crystals parallel to the 111 plane. One crystal cut parallel to the 110 plane (Run 32) was obtained from Radio Corporation of America. With the exception of one target (Run 31), the targets were polished on one side and lapped on the other. Shape and thickness of the targets was varied. Targets were rinsed with carbon tetrachloride and acetone.

Gases were supplied in cylinders by Liquid Carbonics Co. (oxygen, C.P. grade) and Matheson Co. (nitrous oxide, regular grade; carbon dioxide, bone-dry grade; nitrogen, dry grade; hydrogen, ultra-pure grade; methane, C.P. grade). Mass spectograph analyses were as follows (mole per cent): oxygen—$O_2$, 99.1; $N_2$, 0.6; Ar, 0.3; nitrous oxide—$N_2O$, 99.5; $N_2$, 0.4; $O_2$, 0.1; carbon dioxide—$CO_2$, 99.99+; no impurities detected.

**Procedure.** For each germanium oxidation run the target was placed in proper position and the system evacuated. A period of 12 to 24 hr was required to reach a pressure of $5 \times 10^{-7}$ mm Hg (ionization gauge reading). The target heater was turned on and gas was fed to the nozzle (the sequence was reversed in several runs). Readings of target spring and reference positions were made at intervals of 10 or 20 min during the run. Pressure readings for the nozzle, nozzle exhaust chamber, and beam chamber; temperature readings from the nozzle thermocouples; and power input and filament temperature readings for the target heater were recorded at various intervals. For runs in which oxidation was continued on successive days, the gas flow was stopped and the target heater turned off overnight while the pumping system remained on.

**Measurement of beam characteristics.** A modified NRC Type 518 ionization gauge with an NRC model 710 gauge control was used to measure the intensity of the molecular beam. As shown in Fig. 4, a cone-shaped extension was attached to the neck of the gauge bulb. The gauge was mounted on a three-axis translation chassis having remote control.

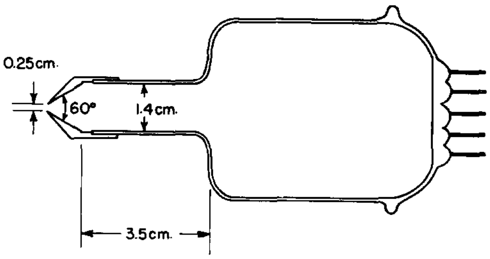

FIG. 4. Modified ionization gauge.

The principle of operation is as follows: When the gauge is placed in the path of the beam, incoming beam molecules pass directly into the gauge bulb where their velocities and directions of motion are randomized. Since the molecules leave the gauge in random free-molecular flow, the net random flow out is proportional to the pressure within the gauge less the background pressure outside the gauge as measured by a second gauge outside the beam flow. At steady state the molecular beam flow in is equal to the net random flow out and is thus proportional to the difference in pressure readings of the gauges.

The modified ionization gauge was calibrated as a flux measuring device with a molecular beam of known intensity. The first chamber of the molecular beam apparatus was filled with each of the gases used in this work and served as the source for a conventional effusion molecular beam. The source pressure was measured with a McLeod gauge. A 0.152 cm diameter, sharp-edged, circular orifice was substituted for the skimmer. Flux at the modified gauge was calculated by assuming ideal effusion through the orifice.

Correction factors to be applied to gauge readings to give true pressures for gauges used in background pressure measurements were obtained by relating the pressure indicated by the gauge in the above calibrations to that required for effusive flow out of the gauge at the known rate. Random flow through the conical extension was taken as 88% of that for an ideal effusion orifice of the same diameter (*7*). The correction factors calculated in this way agreed with those obtained by NRC for Type 518 gauges in direct calibration against a McLeod gauge (nitrogen, 13% discrepancy; helium, 1% discrepancy; no other available).

The majority of beam flux measurements were made with the modified gauge at a horizontal distance of 19 cm from the skimmer entrance. For calculating flux at other distances, flux was assumed to be inversely proportional to the square of distance (*3*, *8*). Flux measurements were made with nozzle pressures of 10 to 100 mm Hg and nozzle-to-skimmer distances of 8 to 32 nozzle diameters.

## EXPERIMENTAL RESULTS

Germanium targets were found to react with molecular beams of oxygen as indicated by loss of weight of the targets. The rates of weight loss were found to correspond to the removal of 0.04 atoms of germanium for each one-half molecule of oxygen impinging on the target. This result was independent of target temperature between 470° and 900°C, independent of oxygen flux between 2.5 and $6.6 \times 10^{15}$ molecules/cm$^2$ sec, independent of nozzle temperature from 25° to 450°C, independent of crystal orientation (111 or 110), and independent of crystal doping (0.02

TABLE 1

REACTION RATES: OXYGEN BEAM, ROOM TEMPERATURE NOZZLE

| Run | Reaction period (hours) | Target temp. (°C) | Flux at target (molec/cm$^2$ sec) $\times 10^{-15}$ | Sticking probability |
|---|---|---|---|---|
| 23 | 2.3 | 650 | 6.6 | 0.046 |
| 25 | 5.7 | 650 | 6.6 | 0.038 |
| | 1.7 | 650 | 2.5 | 0.043 |
| | 2.0 | 550 | 6.6 | 0.037 |
| | 3.0 | 650 | 6.6 | 0.037 |
| | 2.3 | 650 | 6.6 | 0.036 |
| 28 | 2.0 | 650 | 6.6 | 0.045 |
| | 4.0 | 650 | 6.6 | 0.045 |
| | 3.0 | 650 | 6.6 | 0.045 |
| | 1.0 | 820 | 6.6 | 0.045 |
| | 1.5 | 820 | 6.6 | 0.045 |
| | 1.2 | 650 | 6.6 | 0.038 |
| | 1.5 | 650 | 6.6 | 0.045 |
| | 0.7 | 650 | 6.6 | 0.045 |
| | 0.5 | 740 | 6.6 | 0.045 |
| | 0.8 | 740/840 | 6.6 | 0.045 |
| | 0.7 | 840 | 6.6 | 0.045 |
| | 1.0 | 650 | 6.6 | 0.045 |
| | 1.0 | 500 | 6.6 | 0.045 |
| | 1.0 | 480 | 6.6 | 0.045 |
| 29 | 3.0 | 690 | 5.9 | 0.045 |
| 30 | 3.0 | 690 | 5.9 | 0.045 |
| | 0.8 | 900 | 5.9 | 0.045 |
| 31 | 2.3 | 690 | 5.9 | 0.045 |

TABLE 2

REACTION RATES: OXYGEN BEAM, HOT NOZZLE, TARGET AT 650°C

| Run | Reaction period (hours) | Target temp. (°C) | Flux at target (molec/cm$^2$ sec)$10^{-15}$ | Sticking probability |
|---|---|---|---|---|
| 25 | 2.3 | 30 | 6.6 | 0.036 |
| | 2.3 | 450 | 14 | 0.037 |
| | 1.5 | 230 | 11 | 0.039 |

TABLE 3

REACTION RATES: $N_2O$, $CO_2$, $CH_4$, ROOM TEMPERATURE NOZZLE

| Run | Reaction period (hours) | Target temp. (°C) | Flux at target (molec/cm$^2$ sec) × $10^{-15}$ | Observed reaction rate |
|---|---|---|---|---|
| | | $N_2O$ | | |
| 28 | 1.0 | 650 | 3.8 | 0 |
| | 1.3 | 820 | 3.8 | 0 |
| | 1.3 | 650 | 3.8 | 0 |
| | 1.0 | 740 | 3.8 | 0 |
| | 1.0 | 840 | 3.8 | 0 |
| | 2.0 | 550 | 3.8 | 0 |
| 32 | 1.0 | 690 | 3.4 | 0 |
| | | $CO_2$ | | |
| 28 | 2.0 | 840 | 4.4 | 0 |
| 32 | 1.0 | 690 | 4.0 | 0 |
| | | $CH_4$ | | |
| 23 | 2.0 | 650 | 9 | 0 |
| 32 | 0.7 | 690 | 8 | 0 |

ohm cm *p*, 4 ohm cm *p*, or 20 ohm cm *n*). No reaction was observed with either nitrous oxide, carbon dioxide, or methane beams.

Detailed experimental data are presented in Tables 1 to 3. Figures 5–8 show changes in target weight with time for several typical runs. Figure 9 is a photograph of typical targets before and after reaction. Figures 10–12 are photomicrographs of target surfaces.

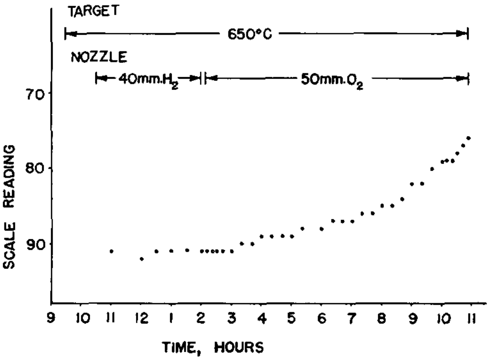

FIG. 5. Run 23 showing protracted induction period.

An induction period of up to several hours during which the heated target was exposed to an oxygen beam was required before reaction took place on fresh targets. This was also true for some cases in which the heated target remained under vacuum overnight. The reaction rate on one target (Fig. 5) increased slowly from zero to a constant rate after several hours; on other targets the transition from no reaction to reaction at a constant rate took place within 10 to 15 min (Fig. 6). The length of the induction period was apparently unaffected by the temperature of the target.

The results of experiments with an oxygen beam from a room temperature nozzle are summarized in Table 1. The targets for

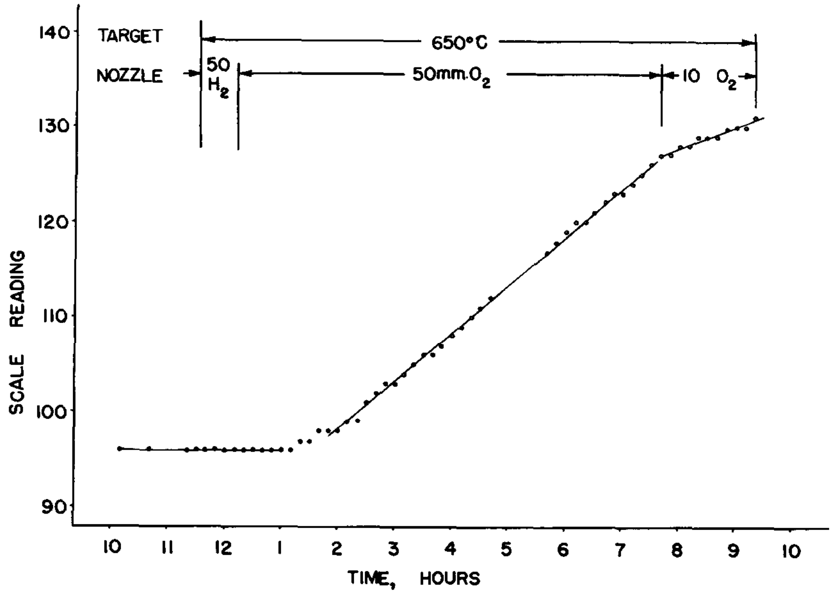

FIG. 6. Run 25. Heating *in vacuo* or hydrogen is not sufficient to clean the sample. After heating with the oxygen beam turned on, the target reacts and the rate reaches its steady state rather quickly.

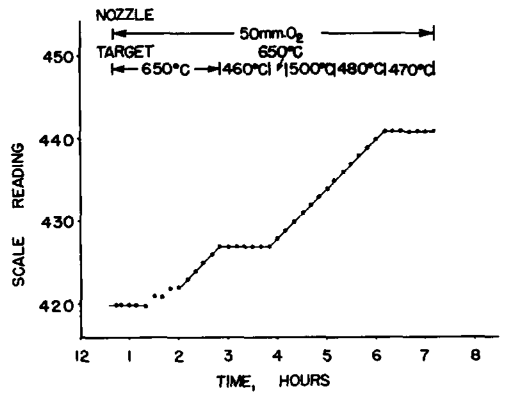

FIG. 7. Run 28. The rate of reaction does not depend on target temperature above 460° to 470°C.

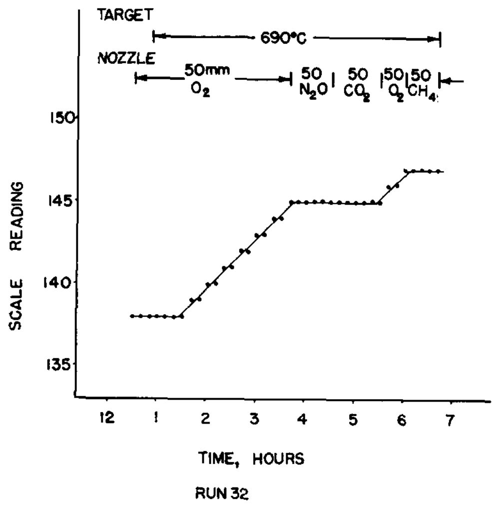

FIG. 8. Run 32. Germanium reacts with oxygen but not with nitrous oxide, carbon dioxide or methane.

Runs 23, 25, and 28 were identical 111 plane, polished, 0.02 ohm cm *p*-type wafers. It may be seen in the table that the oxidation rate was independent of target temperature above about 460°C.

In Run 25, the oxidation was performed at two flux levels ($6.6 \times 10^{15}$ molecule/cm$^2$ sec with 50 mm Hg nozzle pressure; $2.5 \times 10^{15}$ molecule/cm$^2$ sec with 10 mm Hg pressure). The reaction rate was directly proportional to the rate at which molecules impinged on the target (Fig. 6).

The effect of varied doping agents and concentrations may be compared in Runs 28–31. The reaction rates were the same for a 20 ohm cm *n*-type 111 plane polished target (Run 29), 0.02 ohm cm *p*-type 111

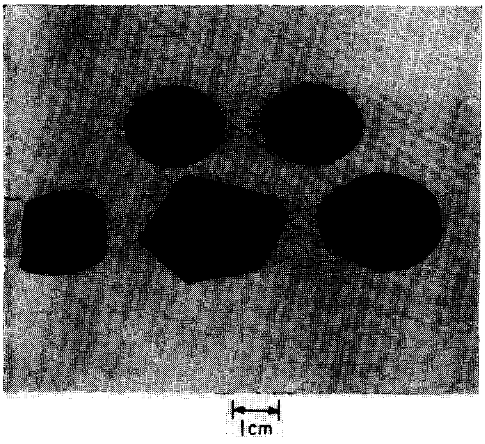

FIG. 9. Typical targets before and after exposure to oxygen beams. In this photograph the targets were lighted from the side with a dark background—polished areas appear black. Top row, left to right: an unexposed lapped wafer, an unexposed polished wafer. Bottom row, left to right: an exposed polished wafer (Run 32), an exposed polished wafer (Run 30), an exposed lapped wafer (Run 31).

plane lapped target (Run 30), and 4 ohm cm *p*-type 110 plane polished target (Run 31).

The crystal orientation was varied in Run 31. The oxidation rate for this target with the 110 plane exposed was identical to the rates in other runs where the 111 plane was exposed.

A lapped surface was employed in Run 30 in order to compare oxidation rates on this rough surface with rates on the polished surfaces of other runs. The observed rates were the same. However, the polished surfaces became rough during oxidation, and after oxidation the appearance of both types of surface was similar.

Nozzle temperature was varied with an oxygen beam in Run 25. As shown in Table 2, the reaction probability remained essentially constant for nozzle temperatures of 30° to 450°C. The reaction rate remained proportional to the rate at which molecules impinged on the target.

The lower limit of target temperature at which oxidation took place was investigated in Run 28. No reaction was observed in 1 hr at 420°C, 1 hr at 450°C, or 1 hr at 460°C. Reaction took place at 470°C and above with a reaction probability of 0.04 (Fig. 7).

Nitrous oxide ($N_2O$), carbon dioxide, and methane were employed as reactant gases in Runs 23 and 28, with the results summarized in Table 3 and Fig. 8. The target used in Run 32 was a 110 plane, 4 ohm cm *p*-type, polished wafer. No reaction was observed for any of these gases. Reaction took place with oxygen both before and after nitrous oxide and carbon dioxide were used. Reaction took place with oxygen before methane was used but not after exposure of the target to the methane beam.

Three targets were found to be nonreactive. In Run 24 (111 plane, 0.02 ohm cm *p*-type, polished), the target was heated under vacuum for 17 hr with no beam; no reaction occurred with an oxygen beam in 8 hr following. In Run 27 (111 plane, 0.02 ohm cm *p*-type) no reaction was observed in 11 hr with an oxygen beam. In Run 29 (111 plane, 20 ohm cm *n*-type, polished) no reaction occurred in 5 hr with an oxygen beam.

Surface roughening occurred on all targets for which reaction with oxygen was observed (Figs. 9 and 10). Sections of target surfaces which were shielded from the beam by either the collimator or by support wires were roughened to a much lesser degree (Figs. 10 and 11). Flux on these shielded surfaces was about $4 \times 10^{14}$ molecule/cm$^2$ sec (due to a background oxygen pressure of 0.9 to $1.3 \times 10^{-6}$ mm Hg) or about one-tenth the flux of beam molecules. Triangular etch pits were observed on the shielded surfaces of several runs (Fig. 12).

## DISCUSSION

Perhaps the most striking result of this work is the finding that the sticking probability $\alpha$ of oxygen on germanium crystals does not depend on surface temperature, gas temperature, beam flux, crystallographic orientation, conductivity type, or doping. The value of $\alpha$ is constant and equal to 0.04 within experimental error.

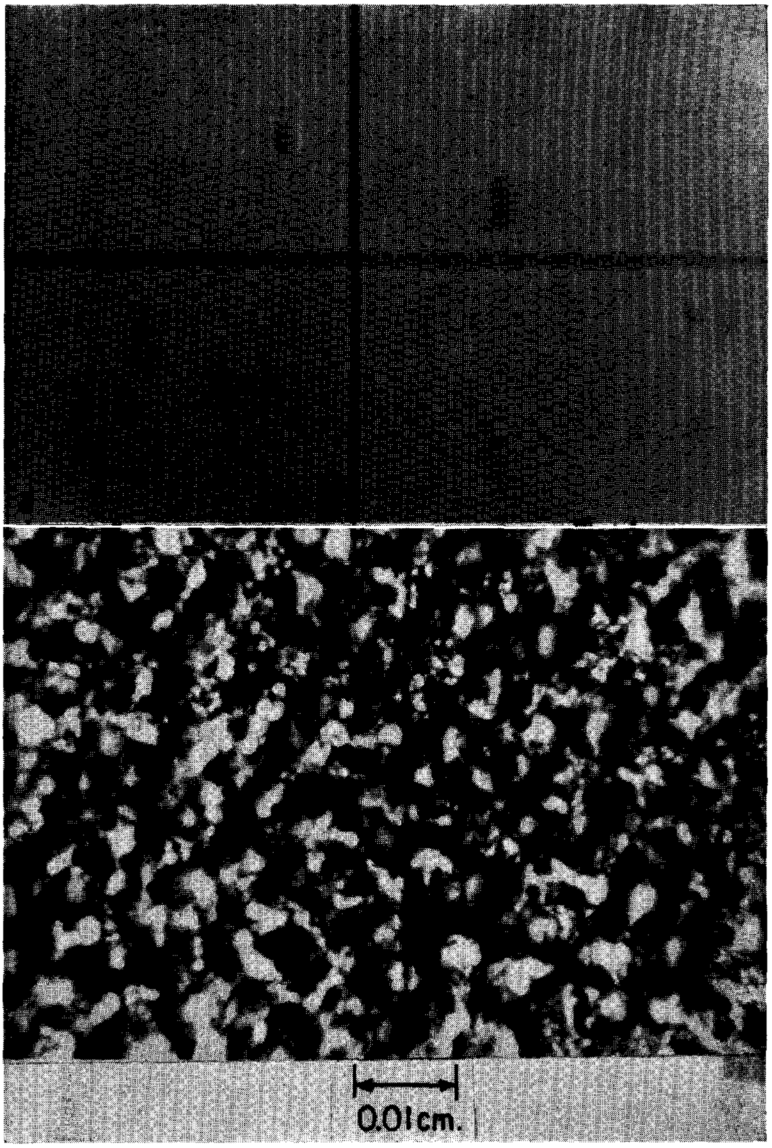

FIG. 10. (a) A polished 111 $p$-type target surface. Imperfections seen are due to the microscope. (b) A 111 $p$-type surface after 22 hr of reaction with an oxygen beam (Run 25).

On further thought, this fact does not appear so surprising. Because the surfaces exposed to the beam became rough, any possible effect due to orientation or crystal face became obscured. Also, if thermal accommodation of the cold molecules hitting the hot surface is not a prerequisite for adsorption, then surface temperature is not likely to affect sticking probability. Further, at the high temperatures used in this work, effects of doping and conductivity type are not likely to be as important as they might be at lower temperatures. Finally, the lack of dependence of $\alpha$ on beam intensity is precisely what is expected if the adsorption process is indeed the rate process that is measured.

One of the difficulties lies with the lack of dependence of $\alpha$ on the gas temperature. Unfortunately, the latter is not known.

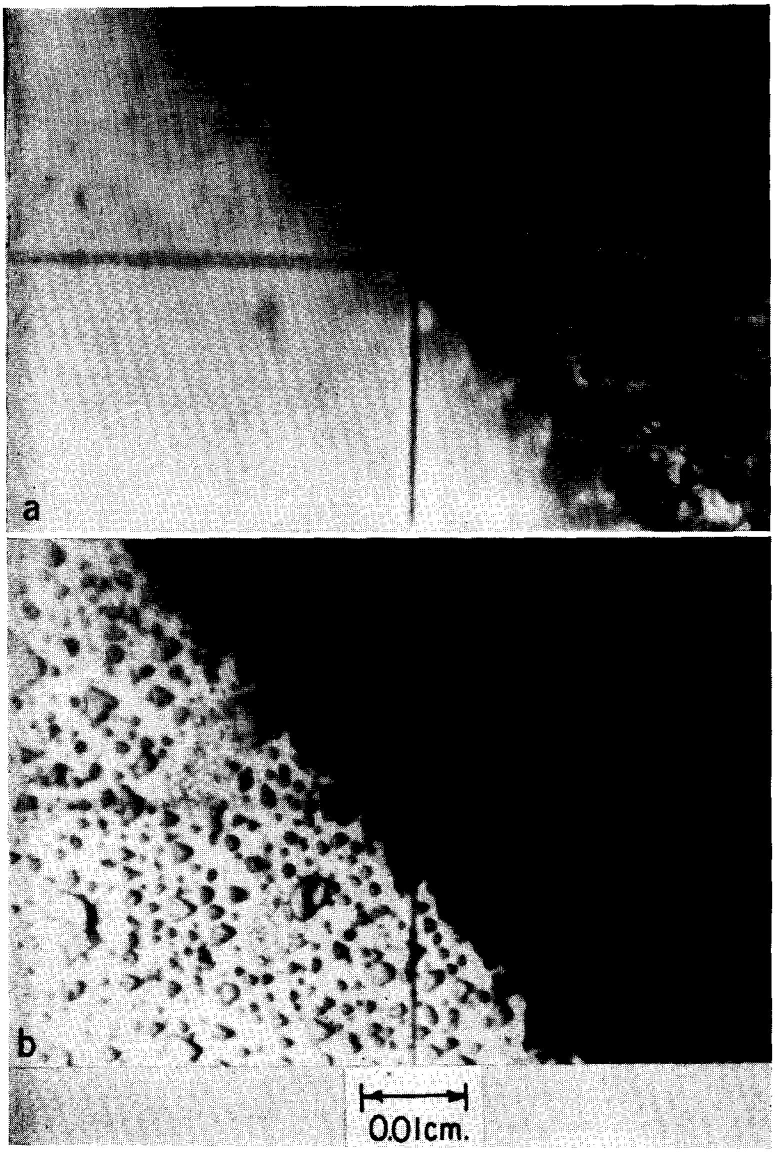

FIG. 11. Surface of a 111 $p$-type target after reaction. The lower left half of the surface shown was shielded from the beam by a support wire (Run 25). (a) Focused on exposed area. (b) Focused on shielded area.

There is little doubt that it varied when the nozzle temperature was changed from 30° to 450°C but the state of the molecules in the supersonic molecular beam used here has not yet been determined.

The other difficulty lies with the state of the surface. Several investigators have determined the sticking probability of oxygen on a clean germanium surface at room temperature. Their data are summarized in Table 4. Values of $\alpha$ reported by others vary somewhat but are definitely *smaller* than the value found in the present investigation. Since other workers have also observed that $\alpha$ decreased sharply as the clean germanium surface became covered with oxygen, it seems reasonable to believe that the germanium surfaces used in the

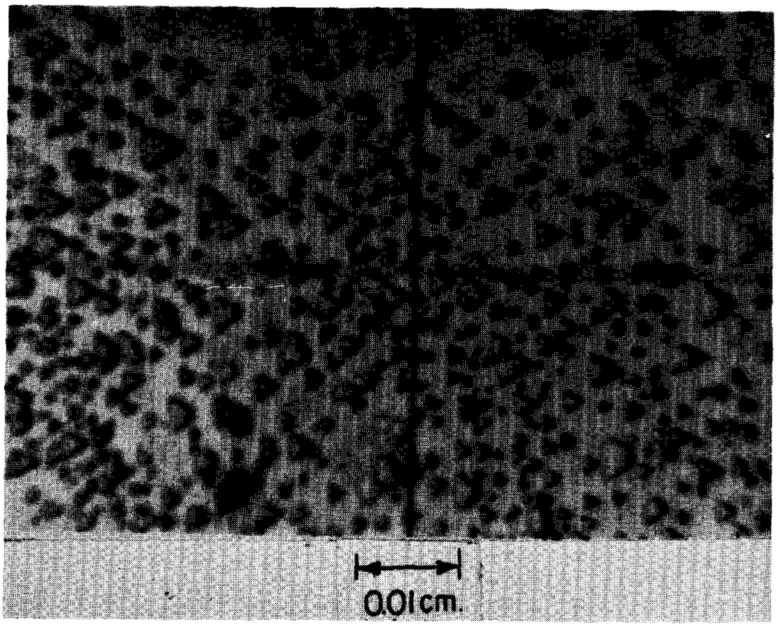

FIG. 12. Triangular etch pits formed on the unexposed area of a heated target (Run 25).

present study were as clean as the clean surfaces of others.

TABLE 4
STICKING PROBABILITY OF OXYGEN ON GERMANIUM SINGLE CRYSTALS

| Investigator and reference | $\alpha$ |
|---|---|
| Dillon and Farnsworth (*9*) | |
| Ge (100) | $1.5\text{–}4 \times 10^{-3}$ |
| Wolsky (*10*) | |
| Ge (100) | $10^{-2}\text{–}10^{-4}$ |
| Schlier and Farnsworth (*11*) | |
| Ge (100) | $<2.4 \times 10^{-3}$ |
| Ge (111) | $\sim 10^{-4}$ |
| Hagstrum (*12*) | |
| Ge (111) quenched | $8 \times 10^{-4}$ |
| This work | $4 \times 10^{-2}$ |

There is little doubt that if the germanium surfaces used here could be freed from their surface oxide layer to start with, during the observed induction period, then the surface could be kept clean at the low pressures of this work and at surface temperatures above 470°C, by the well-investigated process of "thermal restoration" involving evaporation of GeO into a vacuum. Thus complete thermal restoration of germanium surfaces requiring a certain time at a certain temperature has been reported for the following conditions: 530°C for 30 min (*13*), 330 to 430°C for 1 min (*14*), 530°C for 30 min (*11*), 530°C for 15 min (*9*), 530°C for 1 min (*12*). On the other hand, thermal restoration could not be achieved under the following conditions: 480°C for 15 min (*10*), 280°C for 1 min (*12*).

In fact, the most natural explanation of the rather abrupt change in reactivity around 450°C (Fig. 7) is that above this temperature the surface of germanium is clean whereas below that temperature it rapidly becomes covered with oxygen so that $\alpha$ falls rapidly and is too small to be measured by our technique.

It therefore appears also that the germanium wafers could be cleaned or "activated" by heating them during the induction periods shown on Figs. 5 to 8. It appears significant that heating *in vacuo* was not sufficient but that it was found necessary to heat with the oxygen beam turned on. Also, as mentioned above, three targets could not be activated in this way.

They may well have been contaminated. Such a contamination was indeed achieved by treating an activated target with a methane beam (Run 32). On the other hand, the lack of activation for these three targets as well as the apparent need for oxygen during the activation may well be related to the belief of Harvey and Gatos *(15)* that a germanium surface exposed to the atmosphere becomes covered with a layer of $GeO_2$ which may occur in two crystalline forms: a stable tetragonal form and a less stable hexagonal form. Then removal of a layer of tetragonal $GeO_2$ may necessitate undermining this layer by reaction of germanium with oxygen followed by the well-known reaction $GeO_2 + Ge \rightarrow 2\ GeO$ *(16)*.

In summary, the need for a rather specific activation process, the observation that an active target could be inactivated with methane, the existence of a rather sharp cutoff temperature for reaction with oxygen and the high measured values of $\alpha$ are all facts that militate in favor of the idea that the value $\alpha = 0.04$ was obtained on a clean germanium surface.

If this is so, how can this value be compared to the other values listed in Table 4? In a recent study of cleaved silicon and germanium surfaces, Lander, Gobeli, and Morrison *(17)* show by means of low-energy electron diffraction that these surfaces change their structure at high temperatures, around 300°C in the case of germanium. It is suggested that in the present work, all oxygen molecules striking the hot disordered surface in the proper orientation could be adsorbed whereas on the presumably more organized low-temperature surfaces of other investigators, oxygen molecules must not only be in the proper orientation but also hit appropriate pairs of sites fewer in number.

It is further suggested that, prior to adsorption, oxygen molecules must lie flat on the germanium surface so as to be able to form two bonds with adjacent surface atoms. In this view, the sticking probability represents a pure steric factor and can be treated as a condensation coefficient following Herzfeld *(18)* and Wanlass and Eyring *(19)*. The fact that nitrous oxide did not react with germanium substantiates this view since $N_2O$ cannot lie flat on the surface and form two Ge–O bonds, although the bond dissociation energy $N_2$–O is smaller than the dissociation energy of $O_2$.

Although the "temperature" of the beam molecules was not known, this work indicates that $\alpha$ did not vary when it was changed. Then, in the spirit of transition state theory *(19)*, $\alpha$ will be equal to the ratio of partition functions for internal motion of the transition state and of the gaseous reactant. A value of $\alpha$ independent of temperature then follows from the assumption that free rotation of $O_2$ is replaced in the transition state by two vibrations: a stiff one perpendicular to the surface and a weak one parallel (frequency $\nu$) to the surface. Then

$$\alpha = \frac{kT/h\nu}{8\pi^2 Ikt/2h^2} = \frac{h}{4\pi^2 I\nu}$$

where $I = 19.5 \times 10^{-40}$ g cm$^2$, the moment of inertia of $O_2$. To obtain $\alpha = 0.04$, it is necessary to postulate $\nu = 2.1 \times 10^{12}$ sec$^{-1}$, a not unreasonable figure. If, because of surface roughness, the true value of $\alpha$ were smaller, perhaps by a factor of two *(20)* than the apparent value of 0.04, the value of $\nu$ would have to be multiplied by the same factor. But a discussion of such refinements does not seem warranted.

## CONCLUSION

This work illustrates the usefulness of a nozzle molecular beam in the kinetic study of gas–surface reactions. In the case of oxygen reacting with germanium, the sticking probability of oxygen could be measured over a wide range of conditions, in a reproducible way and during many hours of steady state reaction.

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