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Sticking Probabilities by an Effusive Beam Technique

The Germanium-Oxygen System

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The sticking probability α of oxygen molecules on a germanium (100) wafer heated at 525°C was measured with an effusive beam technique allowing independent and precise variation of the oxygen temperature. As GeO evaporated continuously to yield a restored clean surface, the weight loss of the wafer was recorded with an electrobalance. Values of α calculated from this weight loss and the incident beam flux increased by a factor of 40 when the absolute temperature of the gas was raised by a factor of about 6. The value of α equal to 0.04 measured at the highest gas temperature investigated (536°K) was in complete agreement with that found earlier with a supersonic molecular beam.

INTRODUCTION

The study of adsorption kinetics has been for many years an important source of concepts applicable to the description of catalytic phenomena at surfaces. More recently, the kinetics of adsorption has been investigated with atomically clean surfaces at very low pressures. The rate of adsorption is then expressed in terms of a sticking probability α which is defined as the probability that a given collision of a molecule with the surface will produce a specified adsorbate–adsorbent complex. A further refinement in the measurement consists in controlling the energy states of the molecules hitting a solid target by means of a molecular beam.

In these fundamental studies of gas–solid interactions, certain systems lend themselves particularly well to experimentation and ultimately to theoretical interpretation. Such is the germanium-oxygen system. Thus, the sticking probability, α, of oxygen molecules on germanium surfaces has been reported by several investigators, whose results are shown in Table 1. In only one investigation was α measured above the temperature necessary for the thermal restoration of the surface, due to evaporation of GeO, as reported in the literature (*1–6*).

In that study, Anderson *et al.* (*2*) directed a supersonic nozzle molecular beam of oxygen on a heated germanium target. From the known beam flux and the steady loss of weight of the target due to evaporation of GeO, values of α could be calculated. They were approximately equal to 0.04, independent of wafer temperature, wafer orientation, wafer purity, beam flux, and the source chamber temperature.

This last result was particularly surprising. In view of the difficulty of defining and controlling the internal temperature of molecules in such nozzle beams, it was decided to extend the work of Anderson *et al.* by means of an effusive beam technique that allowed precise control of the gas temperature over an extensive range. This technique was developed successfully and values of α as low as 10^{-3} were determined readily.

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TABLE 1
STICKING PROBABILITIES OF OXYGEN ON GERMANIUM REPORTED BY PREVIOUS INVESTIGATORS UNDER DIFFERENT CONDITIONS

Investigator(s) (Ref.)	Technique	α(crystal face) exposed
Anderson and Boudart (*2*)	Nozzle beam	0.04 (111, 110, 100)
Dillon and Farnsworth (*6*)	Work function change during O_2 adsorption	0.015 (100)
Hagstrum (*7*)	Flash filament and Auger electron emission change with O_2 adsorption	0.0008 (111)
Schlier and Farnsworth (*4*)	Low-energy electron diffraction intensity data	0.0024 (100) 0.0001 (111)
This work	Effusive beam	0.001–0.04 (100)

The effusive beam constructed for this investigation allowed independent control of the reaction variables. Oxygen in effusive flow was directed on a heated single-crystal germanium wafer cut parallel to the desired crystal plane; the wafer temperature T_W was varied independently from the oxygen temperature T_S. The molecular flux of oxygen was altered simply by changing the pressure P_S in the source chamber. The sticking probability was calculated from the known beam flux and the weight loss of the germanium wafer due to the evaporation of GeO formed as a result of the adsorption of beam and background oxygen molecules.

This paper describes this novel beam technique and its operation, presents results obtained with the germanium-oxygen system, and establishes the dependence of the sticking probability on the temperature of the molecules hitting the surface at a constant higher temperature.

EXPERIMENTAL

Molecular beam system. The apparatus necessary for the formation and control of the effusive beam consisted of a main vacuum chamber into which the beam issued and a source assembly from which the beam issued. The apparatus is shown schematically in Fig. 1. The oxygen was admitted continuously to the source chamber, SC, at steady state pressures between 0.025 and 0.25 torr, depending on the temperature of the gas in the chamber. The temperature and pressure were interrelated by the condition that the gas mean free path must be greater than the characteristic effusion hole dimension for effusive flow to occur. The gas effused through a thin-walled orifice into the main vacuum chamber, MC. During operation, the main chamber pressure was 1.5×10^{-7} to 9×10^{-7} torr depending on the beam flux into the main chamber. The gas impinged directly on the germanium wafer which was suspended in front of the orifice at a distance of 4.2 cm.

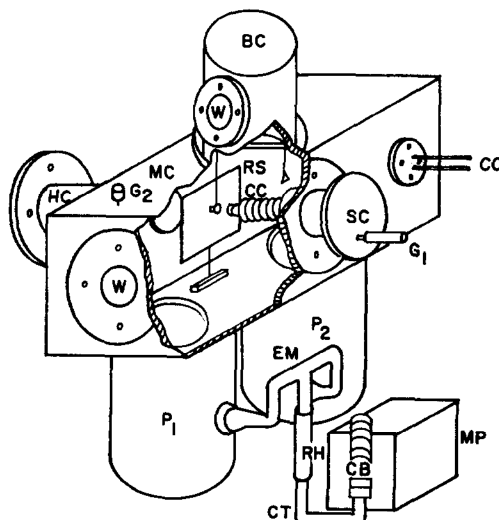

FIG. 1. Schematic drawing of the molecular beam apparatus.

The source chamber is shown schematically in Fig. 2. The beam issued through a sharp-edged circular orifice, 0.0356 cm in diameter, drilled in 0.0025 cm thick gold foil. The diameter of the orifice was measured with an optical micrometer. The foil was stretched tightly by means of a stainless steel tongue-and-groove assembly. This assembly separated the vacuum chamber in which the wafer was hanging from the higher-

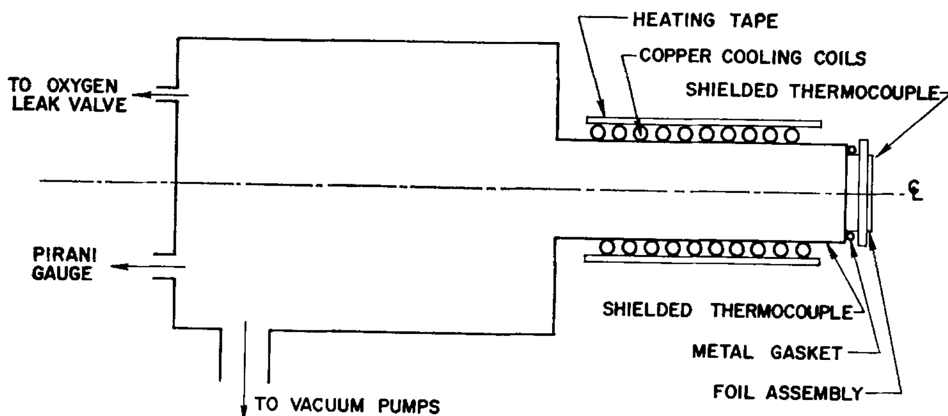

FIG. 2. Schematic drawing of the source chamber assembly.

pressure in the source chamber. Gas temperatures below room temperature were achieved by circulating liquid nitrogen or ice water through the copper cooling coils, shown as CC in Fig. 1, hard-soldered to the source chamber snout. A high-temperature heating tape was wrapped around the cooling coils at all times. This tape was used to achieve temperatures above room temperature. The temperature of the gas in the source chamber was measured with two shielded chromel-P/alumel thermocouples. One thermocouple was embedded in solder in the wall of the source chamber snout; the other was pressed firmly against the front face of the foil assembly. The location of these thermocouples is shown in Fig. 2. The agreement between these thermocouples was within ±5°C.

In order to prevent developing a damaging pressure differential across the thin foil, the source chamber and the main vacuum chamber were connected through the source system vacuum manifold. The source chamber could be evacuated through the main chamber or independently. During pumpdown or repressuring of the system, this connection was opened. During operation with the beam, it was closed. The source system vacuum manifold was constructed of hard-drawn copper tubing. Both hard- and soft-solder joints were used. The manifold was pumped by an NRC H-2-SP oil diffusion pump. The pump fluid used was DC 704. A Veeco water-cooled baffle was located above the pump. The pump was backed by a Welch 1405 mechanical pump. This pumping system produced pressures of less than 10^{-7} torr in the source chamber and the oxygen introduction system. The pressure was measured by a CVC Philips Gauge type PHG-026. The gauge was mounted on the source manifold.

No difficulty was experienced in maintaining steady state pressure and temperature in the source chamber. Oxygen was expanded from a high-pressure gas cylinder to 500 torr in a 35-liter stainless steel oxygen breathing tank. The gas was admitted to the source chamber through a Veeco variable leak valve. The pressure in the source chamber was changed by adjusting the leak rate. The source pressure was measured with a CVC Pirani Gauge type GP-105. This gauge is shown as G_1 on Fig. 1. The gauge was calibrated in oxygen with a McLeod gauge at pressures up to 0.500 torr. Calibrations were performed at both room temperature and liquid nitrogen temperature. The source assembly produced oxygen beams with temperatures between 85° and 540°K.

The chamber into which the beam issued was constructed of 0.75-inch aluminum plate. The overall dimensions of the chamber, MC, were 40 × 46 × 100 cm. All weld seams were made internally with the exception of the seams for the two end plates. The chamber was pumped by two NRC HS10-4200 oil diffusion pumps in parallel. The pumps are shown as P_1 and P_2 on Fig. 1. The pump fluid was DC 704. Above each pump was a 10-inch NRC Optical Baffle Cold

Trap. These traps were water-cooled during operation. The diffusion pumps were backed by a single Welch 1397 mechanical pump. The mechanical pump is shown as MP, on Fig. 1. Pressures less than 10^{-7} torr were obtained routinely without bakeout. The pressure in the main chamber was measured with a CVC Philips Gauge. This gauge is shown as G_2 on Fig. 1. The gauge was mounted on top of the main chamber. All accessories necessary for control and measurement of the reaction variables were mounted on this chamber. Viton and Buna-N "O-ring" seals were used throughout. Glass windows, shown as W on Fig. 1, were located at each end of the main chamber.

The main chamber was mounted on a frame constructed of aluminum I-beams and aluminum channel. The chamber was insulated from floor vibration, and transmission of vibration from the large mechanical pump was reduced.

Wafer suspension and balance assembly. The germanium wafer was suspended from a microbalance, counterweighed, and aligned with the effusion hole as shown in Fig. 3. The high sensitivity of the microbalance made the high intensity of the supersonic beam unnecessary. The maximum sensitivity of the Cahn RG Electrobalance was 2×10^{-7} g/scale division. However, due to vibration noise it was necessary to operate the balance at a sensitivity of 4×10^{-7} g/scale division. A weight loss of 10^{-5} g/h was measured to 10% accuracy.

The balance was rigidly mounted in the chamber on top of the main vacuum chamber. This chamber is shown as BC in Fig. 1. A glass window was provided in the balance chamber. A slit was cut in the bottom of the balance chamber to allow passage of the suspension wires for the wafer and the counterweights. All suspension wires were tungsten. The wafer was supported by a tungsten wire harness. The counterweights were placed in an aluminum pan supported by a tungsten wire stirrup. The balance was calibrated before each run with class M wire calibrating weights. The output voltage from the balance was monitored with a Leeds and Northrup Speedomax H 1-mV recorder accurate to 0.3%. The balance output voltage was filtered to eliminate excessive noise from vibration.

Beam deflection assembly. A beam flag was employed to deflect the beam so that, when desired, it did not impinge directly on the suspended wafer. The flag was alternately changed from an Up position (beam deflection) to a Down position (no interference with beam) by mechanical operation external to the vacuum chamber.

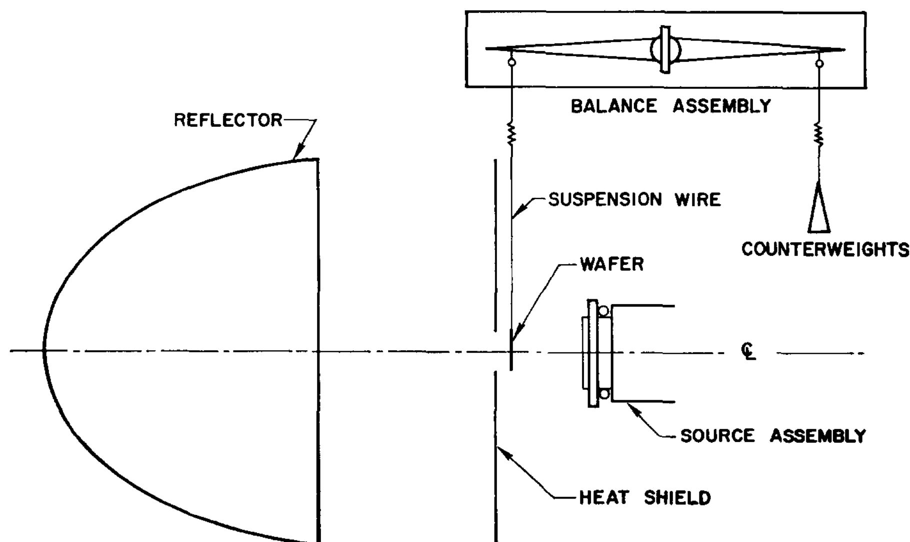

FIG. 3. Schematic drawing of the water suspension and heater assembly.

The flag was constructed of stainless steel. No increase in chamber pressure was observed at 10^{-7} torr when the flag position was changed.

Wafer heating system. The wafer was heated with a General Electric Type DTJ projection lamp. The radiation from this lamp was focused on the side of the wafer opposite the effusion hole, as shown in Fig. 3. The lamp filament was fixed at one focus of a chrome-plated copper ellipsoidal reflector; the wafer was located at the other. The minor diameter of the reflector was 20 cm. The reflector was mounted so that its distance from the wafer could be adjusted. The distance between the end of the reflector and the point of focus was 10 cm. The radiation from the lamp was collimated by a 0.75-inch hole cut in a 1/16-inch stainless steel plate, shown as RS in Fig. 1. The lamp, reflector, and sliding mount assembly were located in an aluminum chamber, shown as HC in Fig. 1. This chamber was cooled externally. Water at 20°C was circulated through rubber hose wrapped around the chamber. Absorption of radiation by the walls of the heater chamber, the radiation shield, and the main vacuum chamber heated the walls of the apparatus to about 50°C.

The wafer temperature was changed by changing the power input to the projection lamp. The wafer temperature was calibrated against a Powerstat used to control the power input. This calibration was accomplished as follows: A chromel-P/alumel thermocouple was sandwiched between two germanium wafers. This sandwich was placed in a harness and aligned with the effusion hole. The system was evacuated to 10^{-6} torr, and the wafer temperature was calibrated against the power input to the lamp. The melting point of germanium was used as a reference point in the calibration. The calibration data were poorly reproducible. The lack of accurate reproducibility was due to (1) the difficulty of placing the reflector at the same distance from the wafer before each run, and (2) the change in the reflectivity of the reflector with usage. Thus, during a run, the wafer temperature was constant and known to an accuracy of ±50°C.

In all the discussion that follows, the temperature cited is the minimum wafer temperature after taking into account the inaccuracies of the calibration.

Materials and surface pretreatment. One semiconductor grade germanium wafer was supplied by Knapic Electrophysics Corp. The *p*-type wafer was cut parallel to the (100) crystal plane and lapped. The room-temperature resistivity was between 0.25 and 0.33 ohm-cm. The wafer was 1.85 cm in diameter and 0.051 cm thick. The area of the wafer was measured graphically to be 2.59 cm^2. The target was degreased with benzene and acetone and subjected to etching in a solution of concentrated nitric acid, 48% hydrofluoric acid, and water in a ratio of 5:5:1 for 15 sec.

A second germanium wafer was supplied by the Futurecraft Corp. It was cut parallel to the (100) plane of a single crystal of 60-ohm-cm resistivity, *p*-type germanium. The wafer was optically polished on the side exposed to the beam and lapped on the back side. This wafer was given no chemical treatment.

Oxygen was supplied in a cylinder by General Dynamics Corp. Mass spectrographic analysis of the gas showed oxygen 99.5%, argon 0.33%, nitrogen 0.03%, and carbon dioxide 0.14%.

Procedure. The wafer was aligned with the effusion hole and counterweighed within 1 mg. The radiation shield was centered on the wafer, and the radiation from the lamp was focused on the wafer. The calibration of the balance was completed electronically. The molecular beam system, balance chamber, and heater assembly were pumped down to 10^{-5} torr simultaneously. After water was admitted to the cooling coil on the heater chamber, the wafer heater was turned to the desired setting. The source heater was turned on, and the entire system was allowed to pump down.

The pressure in the apparatus reached 5×10^{-8} torr in about 12 hr. The balance was stabilized for 9 hr longer. No balance drift was observed during this period of time. The source chamber was isolated from the pumps and pressurized with oxygen. Pressures between 0.025 and 0.250 torr were

maintained, depending on the temperature in the source chamber. The ratio of the gas mean free path to the diameter of the effusion hole was maintained near 2 for runs at all temperatures.

The wafer was cleaned *in situ* by flashing to near the melting point and subsequently maintaining the wafer temperature at 525°C in a 67°C oxygen beam. The wafer was maintained above the temperature necessary for thermal restoration of the surfaces. The weight loss of the wafer was continuously recorded. Source temperature and pressure, power input to the wafer heater, and residual pressure in the chamber in which the wafer was suspended were recorded intermittently.

Calculation of Sticking Probability

The oxygen flux at the germanium wafer was calculated by elementary kinetic theory. Sticking probabilities were calculated according to Eq. (1)

$$\dot{w} = \left(\overline{\frac{dw}{dt}}\right) = \left[K\Phi\alpha \frac{p_s}{(2\pi mkT_s)^{1/2}} A_0 \frac{A_d}{\pi l_0^2} + 2\alpha' \frac{p_0}{(2\pi mkT_0)^{1/2}} A_d\right] \frac{72.6n}{N} \quad (1)$$

where the symbols are as follows:

$(\overline{dw/dt})$	average rate of weight loss of germanium (molecular wt.: 72.6) during run
K	correction factor for finite thickness of effusion orifice
Φ	correction factor for variation of effusing flux over the surface
p_s	pressure of oxygen in source chamber (dynes/cm^2)
p_0	pressure of oxygen in background gas in chamber (dynes/cm^2)
T_s	temperature of oxygen in source chamber (°K)
T_0	average temperature of chamber walls (°K)
m	molecular mass of oxygen (g)
k	Boltzmann constant
A_0	area of effusion hole (cm^2)
l_0	distance between effusion hole and wafer (cm)
N	Avogadro's Number
A_d	wafer area (one side) (cm^2)
n	number of Ge atoms leaving the surface per O_2 molecule sticking
α	average sticking probability of beam molecules
α'	average sticking probability of background molecules

For this apparatus K and Φ were taken to be unity. The Clausing factor, K, corrects for molecules that are scattered from the walls of the orifice. It was determined by the ratio of the thickness of the aperture to the aperture diameter. In this case, this ratio was 0.07. The value of K was certainly greater than 0.95 and was assumed to be unity. The correction factor, Φ, was calculated to be 0.94 for the wafer perfectly aligned on the center line of the source aperture. Since the alignment of the wafer was not perfect, Φ was taken as unity in all calculations. The values of K and Φ do not effect the relative values of α measured. A value of n equal to two was used, in accordance with previous work of others (*2*, *11*).

From Eq. (1), it is possible to define an apparent sticking probability

$$\alpha_{\text{apparent}}(T_s,t) = \alpha(T_s,t) + 1.11 \times 10^5 \times (p_0/p_s)(T_s/T_0)^{1/2}\alpha'(T_0,t) \quad (2)$$

where $\alpha_{\text{apparent}}(T_s,t)$ is the apparent sticking probability of oxygen gas at the source temperature, T_s, at exposure time t; $\alpha(T_s,t)$, the sticking probability of oxygen gas at the source temperature, T_s, at exposure time t; and $\alpha'(T_0,t)$, the sticking probability of the background oxygen gas at the temperature of the walls, T_0, at exposure time t. All other symbols in Eq. (2) are defined by Eq. (1). The numerical constant in Eq. (2) was obtained by substituting the measured values of A_0, A_d, and l_0 into Eq. (1). In physical terms, the apparent sticking probability was half the total molecular flux of products leaving the surface divided by the incident beam flux. The apparent sticking probability must be corrected for the reaction with background oxygen which was present in the main vacuum chamber due to nonreactive collisions on the surface. This correction allows calculation of the sticking probability of oxygen molecules in the beam alone at the source temperature, $\alpha(T_s,t)$.

The sticking probability of oxygen in the beam on the (100)-oriented, 0.25-ohm-cm wafer was determined by first measuring the total weight loss rate with a room-temperature beam in order to determine α'. Subsequent values of $\alpha(T_s)$ were calculated using this value of α'. However, as p_0 and T_0 were difficult to determine exactly, a different procedure was followed with the (100)-oriented, 60-ohm-cm wafer. In this case, the beam flag described earlier was turned up so that the beam could be deflected, and the weight loss due solely to the background oxygen, $\dot{w}_b$, was measured. Combined with the total weight loss rate, $\dot{w}$, $\dot{w}_b$ allowed calculation of the weight loss rate due to the beam molecules alone, $\dot{w}_s$. Under these conditions, it was necessary to consider only the first term of Eq. (1). Substitution of the geometric parameters into the first term of Eq. (1) yields

$$\alpha = 2.17\dot{w}_s(T_s^{1/2}/p_s) \tag{3}$$

RESULTS

Figure 4 shows sample data from a run. In this case, a run was taken as a weight loss of 0.04 mg. This weight loss corresponded to a single traversal of the recorder chart. The recorder tracing was returned to full scale by making a simple adjustment of the balance electronics. This adjustment did not change the characteristics of the balance. Thus, several runs were made at identical experimental conditions.

The (100)-oriented, 0.25-ohm-cm wafer was first investigated. Initially the wafer temperature was fixed at 525°C, and a 67°C oxygen beam was directed upon the surface. No reaction was observed for 4.5 hr. The wafer temperature was increased to about 650°C for 1 min; the temperature was returned to 525°C. At this time the reaction began.

The apparent sticking probability increased from zero to 0.045 over a period of 118 hr. The details of this increase are shown in Fig. 5. The apparent sticking probability increased initially from 1.6×10^{-3} to 1.0×10^{-2}. This change amounted to a rate of increase in the apparent sticking probability of 7.1×10^{-4} hr^{-1}. The sharp decrease in α_{apparent} to 2.4×10^{-3} was followed by an increase rate in α_{apparent} of 7.9×10^{-4} hr^{-1}.

The effect of the wafer temperature on the sticking probability was not investigated in detail. The apparent sticking probability decreased sharply from 4.40×10^{-2} to 9.1×10^{-3} when the wafer temperature was decreased from 525° to 440°C. The sticking probability increased to 3.6×10^{-2} when the wafer temperature was increased from 440° to 575°C.

The effect of gas temperature on the sticking probability was investigated in Runs 1 through 12. The values of sticking probability, $\alpha(T_s,t_0)$, listed in Table 2 are the values corrected for the slow increase of α_{apparent} between 87.5 and 118 hr. The reference time was chosen as 87.5 hr. This correction was made by assuming a tempera-

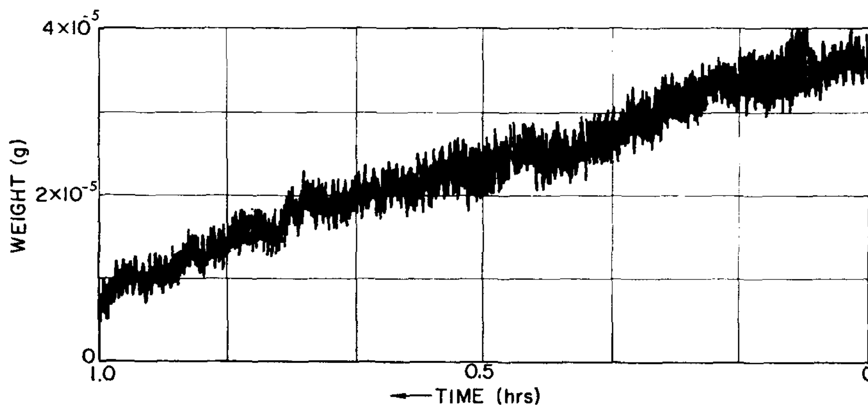

FIG. 4. Typical recorder tracing of wafer weight against time.

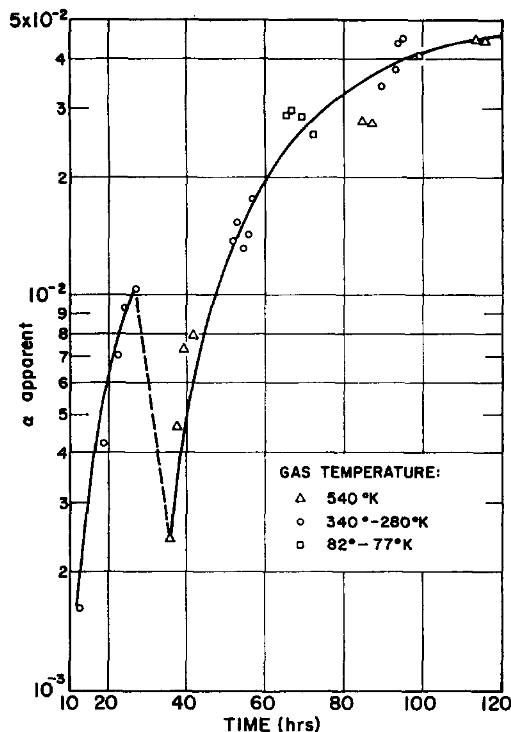

FIG. 5. Plot of the apparent sticking probability against target exposure time at various oxygen temperatures. Wafer temperature: 525°C.

ture-independent, linear increase in the apparent sticking probability between Runs 1 and 12. The corrected value of the sticking probability, $\alpha(T_s,t_0)$, increased from a low value to 0.032 at gas temperatures of 82° and 536°K, respectively. The details of this small correction are given in the Appendix.

In order to calculate the value of $\alpha(T_s,t_0)$ from α_{apparent}, the sticking probability of the background molecules was calculated. This value was obtained by assuming

$$\alpha(298°\text{K},t_0) \approx \alpha(341°\text{K},t_0).$$

Because of the weak dependence of α on the gas temperature, at least above room temperature, this was a reasonable assumption. The accuracy of the data did not justify iteration to obtain $\alpha(341°\text{K},t_0)$ from the observed temperature dependence.

The dependence of the sticking probability on gas temperature above 536°K was not investigated.

The beam flux in Runs 11 and 12 had values of 8.94×10^{14} and 3.10×10^{15} molecules/cm² sec, respectively. It may be noted that the Knudsen number (mean free path of the gas in the source chamber divided by the diameter of the effusion orifice) was 6.7 and 1.79 in these two runs, respectively. As seen in Table 2, no significant variation of the sticking probability was noted in these runs.

Straightforward results were then obtained with the second wafer. Due to use of the beam flag, no corrections were necessary and values of α shown were calculated directly by means of Eq. (3). These results are summarized in Table 3.

The value of α calculated in Run 14 was obtained from the difference in weight loss between Runs 13 and 14. Similarly, the values obtained in Runs 15, 17, 19, and 22 were obtained from weight loss differences between Runs 14 and 15, 16 and 17, 18 and 19, and 21 and 22, respectively. Runs 13–15 and 20–23 illustrated the excellent reproducibility of the weight loss measurements. It should be noted that the background pressure p_0 was constant in the weight measurements at a given temperature regardless of the beam flag position.

The main result of this investigation was that the sticking probability α of oxygen molecules on germanium surfaces, while independent of surface temperature above 500°C, increased with gas temperature. Values of α went up from 0.00091 at 85°K,

TABLE 2

EFFECT OF OXYGEN TEMPERATURE, T_s, ON THE STICKING PROBABILITY, $\alpha(T_s,T_0)$: WAFER TEMPERATURE AT 525°C

Run No.	T_s (°K)	$\alpha(T_s,t_0)$
1	538	2.9×10^{-2}
2	278	2.0×10^{-2}
3	278	2.0×10^{-2}
4	278	2.2×10^{-2}
5	278	2.2×10^{-2}
6	278	2.7×10^{-2}
7	285	2.8×10^{-2}
8	82	—
9	82	0
10	82	1.1×10^{-2}
11	536	3.2×10^{-2}
12	536	3.0×10^{-2}

TABLE 3
SUMMARY OF DATA OBTAINED WITH THE BEAM FLAG UP OR DOWN

Run No.	Position of beam flag	$\dot{w} \times 10^4$ (g/hr)	$p_s \times 10^3$ (torr)	T_s (°K)	$p_0 \times 10^6$ (torr)	$\alpha \times 10^2$
13	Down	5.70	275	536	2.8	5.14
14	Up	2.89	250	536	2.8	4.35
15	Down	5.10	275	536	2.8	
16	Up	1.86	135	283	1.9	2.04
17	Down	2.70	150	283	1.8	
18	Up	0.660	32	85	1.2	9.1×10^{-2}
19	Down	0.676	35	85	1.2	
20	Down	4.05	290	534	2.0	
21	Down	4.05	290	534	2.0	4.18
22	Up	1.63	—	534	2.0	
23	Down	4.00	290	534	2.0	

to 0.020 at 283°K, to 0.042 at 536°K. Thus α changes by a factor of about 40 when the absolute temperature increases sixfold.

DISCUSSION

Before examining the results, it is essential to review critically the conditions of the work with respect to obtaining a clean surface and keeping it clean during the steady state measurements of the sticking probability. Then the essential results of the present study concerning the gas temperature dependence of α will be discussed in comparison with those of others and especially those of Anderson *et al.* (*9*). Finally, the theoretical significance of the work will be briefly explored.

The nature of the surface under the conditions used in this investigation has been discussed elsewhere (*2*, *3*, *8*). Anderson *et al.* demonstrated that above 470°C the sticking probability of oxygen on germanium was independent of the surface temperature. The results of Runs 12 through 14 are plotted in Fig. 6 with the results of Anderson *et al.* Though the effect of surface temperature on sticking probability was not thoroughly investigated in this work the results here closely follow the temperature in dependence above 470°C observed by Anderson *et al.*, with their supersonic beam. The apparent sticking probability becomes independent of wafer temperature above about 500°C. The value obtained in Run 13 may have been too low for detection in the work of Anderson *et al.* According to this study, the surface reaches steady reactivity between 440° and 525°C. This temperature range is consistent with temperatures cited by others (*3*–*6*) for "thermal restoration" of the oxygenated germanium surface.

The results of Runs 11 and 12 also strongly suggest that the surface was sparsely covered

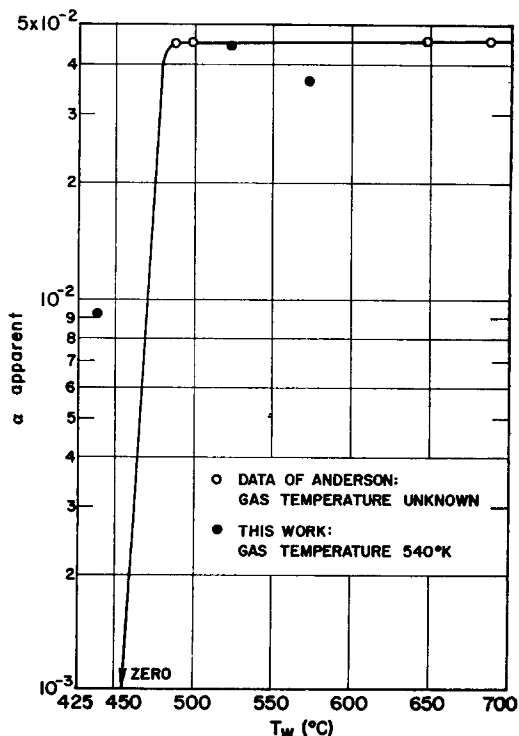

FIG. 6. Plot of apparent sticking probability against the wafer temperature at various gas temperatures.

with adsorbed oxygen during reaction, since the two runs were performed at values of the incident flux differing by a factor of over 3 without any noticeable change in the value of α observed. The observations of this work confirm amply those of others and indicate strongly that continuous thermal treatment was capable of maintaining a clean germanium surface during the steady state measurements of α.

Further evidence that α was measured on an atomically clean surface was obtained by low-energy electron diffraction (LEED). In our laboratory at Stanford, LEED patterns characteristic of a clean (100) germanium face have been obtained by heating the optically polished germanium wafers without prior chemical treatment to 900°C in a modest vacuum of 10^{-8} torr. Furthermore, after this initial cleaning and subsequent exposure of the surface to oxygen, at room temperature, the patterns were restored thermally at 700°C even in the presence of 10^{-6} torr oxygen. The work of Jona (*8*), and Lander and Morrison (*1*), further supports these observations. It is quite probable, then, that the conditions employed to study α afforded a clean surface.

The rapid increases of the sticking probability initially and after the sudden decrease appeared to be associated with the initial cleaning of the surface. The increase of α_{apparent} with wafer exposure time is shown in Fig. 5. After 28 hr of operation, the source snout heater was turned on. This heater had not been previously heated *in vacuo*. The quantitative similarity between the increases noted above suggests that the sudden decrease in α_{apparent} at 28 hr exposure time was due to surface contamination. This contamination was caused by the brief outgassing of the source snout heater. During this outgassing the chamber pressure rose to about 10^{-4} torr. Contamination of the surface at these pressures is consistent with the data of Lander and Morrison (*1*). This activation period was not investigated further. Pressure surges of this nature were eliminated in all subsequent runs. Finally, it must be noted that Anderson *et al.* showed that CO_2 neither reacts nor contaminates the hot germanium surface. Thus, the presence of a small amount of CO_2 in our beam did not effect our experimental observations.

Let us now consider the salient results of the present work. It was found that values of α for oxygen on germanium increased from a low value near 10^{-3} to about 4×10^{-2} as the beam temperature was raised from 85° to 536°K. The dependence of α on beam temperature is given in Tables 2 and 3. The large uncertainty in the value of α at 85°K in the case of the data of Table 2 was reduced decisively in the data shown in Table 3 by the use of the beam flag and direct measurement of the rate of weight loss due to the reaction of the wafer with background oxygen.

The data of Table 3 show that α increases by a factor of 20 when the absolute temperature of the beam molecules is raised from 85° to 283°K—a threefold increase. But α increases only by a factor of 2 when the absolute temperature of the beam molecules is raised further from 283° to 536°K,—a twofold increase.

It appears that the effect of temperature on α is strong at very low temperatures but becomes very weak at temperatures above room temperature. This behavior is clear from the expression

$$\alpha = 0.08 \exp(-760/2T)$$

which is found empirically to fit the data of Table 3 extremely well. While the Arrhenius form of this expression may have no theoretical significance, it illustrates the fact that no large variations in α are expected above say 500°K where α reaches a value of 0.04.

This is exactly the observation made by Anderson and Boudart, whose work should be strictly comparable to the present study. In the previous work, the effect of beam temperature was investigated by varying the nozzle temperature from 303° to 723°K. In this fashion, the distribution of energy between translation and rotation in the beam formed was certainly altered, but the state of development of nozzle beams did not allow precise calculation of the translational and rotational temperatures of the expanded beam. Recent measurements of rotational relaxation in the nozzle beam

verify that the rotational temperature of the beam employed by Anderson *et al.* was appreciably below the nozzle temperature. Further, the translational energy of the molecules in the nozzle beam was probably nearly twice that at the nozzle temperature (*9*). If this were the case, the beam translational "temperatures" of Anderson *et al.* were ~600°, 1000°, and 1400°K.

Though it is unlikely that expansion to the highest Mach numbers was achieved in the experiments of Anderson *et al.* in each case, the beam translational "temperature" was certainly well above room temperature, and the rotational temperature was well below room temperature. In view of these characteristics of the nozzle beam, two explanations of the temperature dependence of α are possible. First, it is possible that the rotational and translational temperatures of the oxygen molecules striking the surface did not vary with nozzle temperature. Such an effect may have occurred due to nozzle–skimmer interaction. If this were the case, the results would clearly have shown no dependence on nozzle temperature. The latter circumstance is highly unlikely, but it must be considered as possible. Second, the value of α is independent of the rotational temperature and reaches a limiting value of 0.04 at a translational temperature of approximately 540°K. Then, the results of the two investigations are entirely consistent and suggest that α is dependent exclusively on the translational energy of the oxygen molecules. Further theoretical elaboration of these conclusions seems premature.

First, in order to properly account for the results, it is necessary to consider multiple collisions on the roughened surface. This consideration necessitates knowledge of the surface topography and the trajectory of reflected molecules. It is very likely that unreacted molecules are not scattered specularly, but they are scattered toward the surface normal, since at all times the surface temperature was greater than the gas temperature. It is quite unlikely that molecules which reside on the surface long enough to lose their sense of origin should desorb without reacting. In fact, the sticking probability observed may be very closely related to the trapping probability of incident molecules in the *physical* adsorption potential well. Such a theory is presently being considered. However, given the sticking probability per collision, the number of collisions remains unknown. This problem of surface topography is also currently being studied by one of us.

Second, it must be emphasized that the sticking probability is not necessarily the same for each successive collision of a molecule with the surface. This fact arises from the energy exchange that accompanies the gas–solid collision (*10*). If the sticking probability depends on the gas temperature, its value must change with each collision event. As there is no satisfactory manner to predict the thermal accommodation coefficient for either internal or translational energy modes, the exact analysis of the collision kinematics remains unknown.

Third, the sticking probability can depend on the gas temperature in two ways. At the temperatures employed, the oxygen was in the ground vibrational state, and it is very unlikely that vibrational energy exchange was involved in the collisions. However, the effects of translation and rotation of the incident molecule were not separated in the experiments performed. A change in the beam temperature affected both the rotation and translation energy distributions identically. Further work must be done to sort out these multiple kinematic effects.

Conclusion

The values of the sticking probability of oxygen molecules on germanium surfaces, including those found in the present study, can now be critically reviewed. Because of the roughening of the surface and the high surface temperatures in the investigations of Anderson *et al.* and the present work, the results of the two beam studies are not directly comparable to those of the other workers, but they should agree with each other.

This they do remarkably well, at least for beam temperatures either known to be or suspected to be above 500°K. The sharp decrease in sticking probability of oxygen at low beam temperatures is the novel finding

made possible by the effusive beam technique first used in this work.

This study, then, and its predecessor demonstrate the detailed information that can be obtained by the study of adsorption kinetics with molecular beams.

APPENDIX

Correction for the Slow Increase of the Apparent Sticking Probability with Time

The increase in the apparent sticking probability between Runs 1 and 12 was assumed linear. This increase is shown in Fig. 5 in the text. Thus,

$$\frac{\alpha(536°\mathrm{C},t_1) - \alpha(538°\mathrm{C},t_0)}{t_1 - t_0} = \frac{\Delta\alpha}{\Delta t}$$

Furthermore,

$$\alpha(T_s,t_0) = \alpha(T_s,t') - (\Delta\alpha/\Delta t)\Delta t'$$

where

$$\Delta t' = t' - t_0$$

and t' is the time at which $\alpha(T_s,t')$ was measured. The value of $\Delta\alpha/\Delta t$ was calculated from the results of Runs 1 and 12. The expression used to correct $\alpha(T_s,t')$ to $\alpha(T_s, 87.5) = \alpha(T_s,t_0)$ was

$$\alpha(T_s,t_0) = \alpha(T_s,t') - q(t' - 87.5)$$

where $q = 3.5 \times 10^{-4}$.

The correction due to the time dependency of α_{apparent} was only about 10%. This correction did not effect the dependence of the sticking probability on gas temperature appreciably.

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