

products (hydrogen-transfer reactions of $C_2H_5^+$)—all point to the operation of a carbonium ion chain mechanism.

Since paraffin alkylation is thermodynamically less favorable than olefin polymerization (6), the latter side reaction has frequently been encountered (5). Large amounts of brown adsorbate were also observed when ethylene *alone* was reacted over REHX at 121–149°C, but white, essentially organic-free catalysts were obtained after treatment with isobutane alone under similar conditions. These facts suggest ethylene polymerization as a major source of the brown adsorbate formed under alkylation conditions, but with the added complexity of the known (4) hydrogen-transfer reactions of rare earth faujasites superimposed.

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Reaction Probabilities for Methane and Oxygen on (111) Silicon Single-Crystal Surfaces

Molecular dynamics of gas–solid reactive collisions is very poorly known. Yet, it is essential to a quantitative understanding of surface catalysis. In this note we report the rates of reaction of cold methane and oxygen molecules with a single-crystal wafer of pure silicon at surface temperatures between 1030° and 1150°K. These data were obtained with a nozzle-produced beam apparatus described in detail elsewhere (1, 2, 3).

In the present work, the potential of the beam instrument was not fully used since the number of collisions of background molecules with the target equaled or even exceeded the number of collisions of beam

molecules with the surface under study. Yet the results are interesting in that they demonstrate a rather high reactivity of silicon surfaces with methane.

Target wafers were heated by radiation from a projection lamp placed at one focus of an ellipsoidal aluminum reflector, with the target placed at the other focus. Changes in the mass of the target from reaction with the impinging molecules were measured by observing changes in the extension of a quartz spiral spring, following the method of Koros *et al.* (4). Hot filament ionization gauges used to measure the beam fluxes and the background pressures were calibrated for methane and oxygen

with the nozzle as an oven source, according to a method described elsewhere (1, 5).

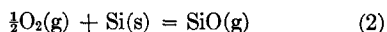
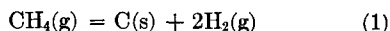
In a preliminary run, with a high background pressure in the beam chamber, methane was found to react with a silicon target at 1060°K, causing a gain in weight of the target. But reaction stopped after 2.5 hr. An attempt to restore activity by exposing the target to a beam of oxygen (to burn off carbon presumed to cover the surface) failed.

Conditions of operation were then adjusted so that the background pressure in the beam chamber was $\sim 10^{-6}$ torr, and

Table 1. In all cases, weight gains or losses were linear with time.

No detectable weight change of a graphite target at 1150°K could be observed either in oxygen or in methane.

The results reported in Table 1 can be interpreted by the following surface reactions:



According to this interpretation, methane decomposes on the surface to hydrogen

TABLE 1
RATES OF REACTION OF SILICON IN METHANE AND OXYGEN^a

Gas	Target temperature (°K)	Duration of run (hr)	Linear rate of weight change (mg/hr)	Probability of reaction γ
CH ₄	1120	4.4	+0.18	0.44
CH ₄	1060	4.9	+0.058	0.14
CH ₄	1090	4.9	+0.097	0.24
O ₂	1090	2.0	-0.22	0.05
CH ₄	1150	4.9	+0.27	0.66
O ₂	1150	4.1	-0.16	0.036
CH ₄	1030	5.4	+0.020	0.05
C ₂ H ₆	1120	4.9	+0.28	0.12
O ₂	1120	2.8	-0.15	0.032
CH ₄	1150	3.6	+0.25	0.61
CH ₄	1060	3.2	+0.065	0.16

^a Runs are listed in chronological order.

all subsequent runs were performed under these conditions. A second silicon target was tried at 1120°K and found to be unreactive in methane but reactive with an oxygen beam; the weight of the target decreased linearly with time. Rates of weight loss were: 0.12, 0.09, and 0.14 mg/hr at 1040°, 1120°, and 1140°K, respectively. A fresh target that had never seen methane was also found to react with oxygen at about the same rate: 0.16 mg/hr at 1150°K.

Another fresh target was found to react in methane, ethane, and oxygen, and eleven runs are reported in chronological order in

which desorbs into the gas phase and to carbon which stays with the target, causing the target to gain weight. Oxygen reacts with the silicon surface to form volatile silicon monoxide, causing the target to lose weight. This reaction of oxygen with silicon has been observed previously (6) and should occur at a sufficient rate under the conditions of this work. The reaction of oxygen with silicon rather than with surface carbon is further substantiated by the unreactivity of the graphite target at 1150°K in oxygen.

Following the above interpretation, prob-

abilities of reaction for methane and oxygen on silicon can be calculated with the following equations:

$$\gamma_{\text{CH}_4} = \frac{\text{Rate of target weight increase, in carbon atoms per second}}{\text{Methane flux from beam and background, in methane molecules per second}} \quad (3)$$

$$\gamma_{\text{O}_2} = \frac{1}{2} \frac{\text{Rate of target weight decrease, in silicon atoms per second}}{\text{Oxygen flux from beam and background, in oxygen molecules per second}} \quad (4)$$

γ is the probability that a molecule on a collision course with the target wafer will react on the surface before it leaves to join the surrounding Knudsen gas. Therefore, if there are multiple collisions with the surface due to surface roughness, the probability of reaction as defined here is a composite of the probabilities of reaction for each single collision. Values for γ_{CH_4} and γ_{O_2} are given in Table 1. They are listed in chronological order to illustrate reproducibility of the probabilities of reaction for methane.

The values of γ for methane can be approximated by the empirical Arrhenius equation based on surface temperature:

$$\gamma_{\text{CH}_4} = 2 \times 10^7 \exp(-40,000/RT) \quad (5)$$

Although this appears to represent a clear-cut case of activated adsorption, the reaction of methane on the surface cannot be rate-controlled by a single elementary step (such as activated adsorption), because in that case the preexponential factor in Eq. (5) would have to be less than or equal to unity. There is no clear interpretation of the data summarized by Eq. (5) in the absence of a theory accounting for the role of thermal accommodation in the adsorption of cold molecules on a hot surface.

The values of γ for oxygen are not as nearly reproducible as those for methane and do not show any trend as target temperature is changed. The mean value is 0.04 averaged over the values in Table 1 and those calculated from the data given above for the second target. This value is in agreement with the value of 0.04 found recently by Madix *et al.* (7) using a comparable molecular beam technique (8). It is also in reasonable agreement with reported values of the sticking probability

of molecular oxygen on "clean" silicon surfaces at room temperature: 0.017 (9); 0.01–0.02 (10); 0.04, 0.02, 0.18, 0.16, 0.10

(11); and 0.01 (6). A lack of temperature dependence for γ can be inferred from the agreement between γ at 1100°K and sticking probabilities at room temperature. This supports our belief that the measured values of γ refer to the sticking probability of O₂ on silicon rather than the rate at which SiO evaporates from an oxygenated monolayer, since, in the latter case, γ would be expected to be temperature-dependent.

The good agreement between the results of others and those of the present work for the case of the oxygen-silicon interaction, confers special significance to the novel results on methane. We were surprised to find that an unreactive molecule like methane, at low temperature, would decompose at such a high rate on a hot semiconductor surface. The very large values of γ (from 0.14 to 0.66) indicate a high reactivity. In the light of these findings studies of the sticking probability of methane on other surfaces would seem very rewarding, especially for catalytic applications.

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Statistics of Site Trapping in Adsorption of Triatomic Molecules

It is known that random adsorption of diatomic molecules on adjacent pairs of surface sites will, if the adlayer is immobile, lead to the trapping of a fraction of the surface as single sites not available for adsorption. Roberts (1) has estimated this fraction as 8% for both square and close-packed arrangements of surface lattice sites. The analogous result for triatomics does not seem to be available, but is of interest in the interpretation of the low coverages reached (2, 3, 4) in the adsorption of CO₂ on metal films. In some cases it is found that less than 50% of the surface sites can be filled, even though the differential heat of adsorption may be quite large at the highest coverages reached (3). Since it is possible to achieve complete coverages of O₂ or CO on similar surfaces (5) it seems unlikely that steric effects due to the size of the molecule are important. A possible explanation of the low CO₂ coverages would be site trapping due to formation of an immobile adsorbed layer.

We report here the results of a computer investigation of the trapping of vacant sites by immobile adsorption of triatomics on square and close-packed plane lattices. A triatomic molecule might occupy three adjacent sites in either a linear or triangular configuration. We have investigated layers of each configuration alone, and also

randomly mixed layers having equal probabilities for the two configurations.

The procedure used was to set up in computer storage a two-dimensional array of storage locations, one for each surface site, and to record in the appropriate location the state of each site. Storage for the close-packed lattice was organized according to the strategy of Dean (6). Initially all sites were recorded as vacant. Random numbers were then generated to select a surface site. If this site was found to be already filled, the trial was rejected. If it was vacant, further random numbers were generated to select the configuration, for a mixed layer, and one of the possible orientations on the surface. The two neighboring sites defined by the configuration and orientation thus selected were examined for occupation. If both were vacant, the trial was successful, and all three sites were recorded as filled; otherwise the trial was rejected. This procedure was repeated until a large number of trials led to no further filling. All the sites were then investigated systematically for all possible orientations, and any triple vacancies consistent with the chosen configuration were filled. The final coverage so obtained was taken as that which would have been reached in an infinite number of strictly random trials. Provided at least 90% of the