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CRITICAL CONDITIONS FOR THE
GROWTH OF SiC, Si₃N₄, AND SiO₂

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F.W. Smith

Physics Department
The City College of New York
New York, N.Y. 10031

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F.W. Smith

Physics Department

The City College of New York

New York, N.Y. 10031

Abstract

The UHV system in use for Si surface reaction studies is described and experimental results obtained during the last year using this system are presented.

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I. Introduction

This Annual Progress Report will describe the UHV system for Si surface reaction studies in operation in our laboratory, experimental results obtained during the last year on the $\text{NH}_3 + \text{Si}(100)$, $\text{O}_2 + \text{Si}(111)$ and $\text{Si}(100)$, and $\text{N}_2 + \text{Si}(111)$ reactions, and the use of Rutherford Backscattering Spectrometry as an analytical tool. Also included is an Appendix with a brief abstract on the $\text{O}_2 + \text{Si}(111)$ work.

II. UHV System for Silicon Surface Reaction Studies

The UHV system for Si surface reaction studies is shown schematically in Fig. 1 as it has been assembled in our laboratory. In operation, the system is utilized essentially as follows:

1. Up to four chemically cleaned Si substrates are mounted on the sample insertion flange (C2). The system is roughed using the sorption pumps, followed by a crossover to the UHV pumps (200 l/s ion pumps, Ti sublimation pump, and cryopump). After a 24-hour bakeout at 250C (if necessary), a base pressure of about 5×10^{-10} Torr is obtained within 24 hours.
2. The Si substrates are cleaned thermally under UHV conditions by heating at 1350C for five minutes using the d-c power supply (E2). The poppet isolation valve is closed, and the reacting gas is then admitted to the UHV chamber. The desired pressure of the reacting gas is maintained by adjusting the inlet valve and also the valve (E4) to the turbomolecular pump (E1). The Si substrate temperature is then lowered to the reaction temperature.

3. Observation of growth and measurement of substrate temperature are made by an optical pyrometer through a viewport into the UHV chamber. The partial pressures of the reacting gases are monitored by the IQ 200 residual gas analyzer (E6). Use of the IPC 1 pressure converter (E7) allows these observations to be made with total pressures in the reacting chamber between about 10^{-7} and 10^{-1} Torr.

4. After completion of growth studies on a given Si substrate, up to three additional substrates are available for further studies under different experimental conditions, without opening the UHV chamber.

III. Experimental Results

A. NH_3 + Si(100) Reaction

The reaction of ammonia (NH_3) with Si(100) under UHV conditions leads to the formation of a Si_3N_4 film on the Si surface. For these studies we have employed n-type Si(100) substrates, NH_3 pressures between 3×10^{-5} and 2×10^{-3} Torr and substrate temperatures T_s between 1200 and 1395C. The observed critical conditions for growth are shown as $\ln P_c(T_s)$ vs $1/T_s$ in Fig. 2. In Fig. 3 we present an SEM micrograph of some of the silicon nitride growth features observed on the Si(100) surface.

From Fig. 2, we obtain $P_o = 3.2 \times 10^{-18}$ Torr and $\Delta E = 7.0$ eV, defined by the equation

$$P_c(T_s) = P_o \exp(-\Delta E/k_B T_s), \quad (1)$$

from the straight line drawn tangent to the data at high T , as shown. These values of P_0 and ΔE are in good agreement with values obtained earlier¹ for the $\text{NH}_3 + \text{Si}(111)$ reaction, namely, $P_0 = 9.4 \times 10^{18}$ Torr and $\Delta E = (7.0 \pm 0.7)$ eV. Thus, for the reaction of NH_3 with $\text{Si}(111)$ and (100) , there does not appear to be the same surface structure sensitivity as observed² for the reaction of C_2H_4 with $\text{Si}(111)$ and (100) .

We note that the $P_c(T_s)$ data in Fig. 2 deviate above the drawn straight line for $1/T > 6.3 \times 10^{-4} \text{ K}^{-1}$ ($T < 1315^\circ\text{C}$). This may signal a decreasing tendency for the NH_3 molecules to dissociate on the $\text{Si}(100)$ surface as T decreases below 1315°C . Further investigations will be needed to clarify this point.

We have repeated the $\text{NH}_3 + \text{Si}(111)$ reaction for three samples in the new UHV system. The results obtained are in very good agreement with our previous results¹, well within the experimental error.

B. $\text{O}_2 + \text{Si}(111)$ and $\text{Si}(100)$ Reactions

The technologically-important reaction between oxygen and the surface of single crystal Si has been studied under UHV conditions for $5 \times 10^{-5} < P_{\text{O}_2} < 3 \times 10^{-2}$ Torr and values of T_s between 890 and 1175°C , for both the $\text{Si}(111)$ and (100) surfaces and for both n-type and p-type doping. In spite of the fact that the actual growth mechanism for SiO_2 on Si is quite different from the case of hydrocarbons reacting with the Si surface to form SiC, we have nevertheless observed clear critical growth conditions $P_c(T_s)$ for the formation of SiO_2 on the Si surface.

These values for $P_c(T_s)$ appear to be independent both of substrate orientation ((111) or (100)) and of substrate doping (n- or p-type).

Experimental results for $\ln P_c(T_s)$ as a function of $1/T_s$ are given in Fig. 2, and some novel SiO_2 growth features are presented in Fig. 3. For $\text{O}_2 + \text{Si}(111)$ or (100), n- or p-type doping, we obtain $P_o = 2 \times 10^{12}$ Torr and $\Delta E = 3.83$ eV. These results are consistent with related observations of Lander and Morrison³ obtained at lower values of P_{O_2} . A detailed discussion of these results will be published.

The novel growth features shown in Fig. 3, in the form of cones, occur on the substrate at the boundary between the region of the substrate where growth occurs and the region which remains free of growth. In this latter region, the net reaction $\text{O}_2(\text{g}) + 2 \text{Si}(\text{s}) \rightarrow 2 \text{SiO}(\text{g})$ dominates and the Si substrate is rapidly etched by the O_2 . Thus, these growth features should provide clues to the nature of the competing processes occurring on the Si surface which give rise to the observed critical conditions for growth. We plan to determine the structure of these growth features using x-ray diffraction.

C. $\text{N}_2 + \text{Si}(111)$ Reaction

The reaction of N_2 with $\text{Si}(111)$ leading to the formation of a surface Si_3N_4 film proceeds at much higher pressures than for the corresponding case of nitridation of Si using NH_3 . This is essentially due to the relatively high stability of the N_2 molecule to decomposition as compared with the NH_3 molecule.

Preliminary results for $P_c(T_s)$ for this reaction are shown in Fig. 2. Estimates for P_o and ΔE are 3×10^9 Torr and 2.6 eV, respectively. There seems to be a clear tendency for the Si_3N_4 clusters to nucleate at preferred sites, possibly dislocations, on the Si surface. We are continuing our studies of this reaction.

D. Rutherford Backscattering Spectrometry Studies

Preliminary RBS studies have been undertaken at Brookhaven National Labs on Si samples with surface films of SiC, SiO_2 , and Si_3N_4 in the laboratory of Dr. Keith Jones. The interpretation of these spectra is not yet complete, but their potential for determining depth profiles of C, O, and N in Si is clear⁴.

E. References

1. F.W. Smith and B. Meyerson, Thin Solid Films 60, 227 (1979).
2. F.W. Smith, Surface Science 80, 388 (1979).
3. J.J. Lander and J. Morrison, J. Appl. Phys. 33, 2089 (1962).
4. W.-K. Chu, J.W. Mayer, and M.-A. Nicolet, "Backscattering Spectrometry", (Academic Press, New York, 1978).

IV. Effort of Principal Investigator

The principal investigator has devoted the equivalent of approximately full time effort for two months and 20% effort for six months to the contract work. He will continue to devote approximately 20% effort to the contract work for the remaining four months of the contract.

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UHV System for Silicon Surface Reaction Studies

Schematic Diagram

Fig. 1

Not shown: vacuum gauges (UHV-24 nude ion gauge, Millitorr gauge, T/C gauge)
 feedthrough ports (total of ten 1 1/2" ports below base plate and eleven 2 3/4",
 four 8", and one 6" ports in UHV chamber).

Fig. 2

Fig. 3

$\text{NH}_3 + \text{Si}(100)$
Growth Features

$\overline{1\text{cm}} = 2.5\mu$

$\text{O}_2 + \text{Si}(111)$
Growth Features

$\overline{1\text{cm}} = 24\mu$