

Reaction of Si(100) with NH₃: Rate-Limiting Steps and Reactivity Enhancement via Electronic Excitation

F. Bozso and Ph. Avouris

IBM T.J. Watson Research Center, Yorktown Heights, New York 10598

(Received 19 June 1986)

We report on the low-temperature reaction of ammonia with Si(100)-(2×1). The dangling bonds in the clean Si surface promote NH₃ dissociation even at temperatures as low as 90 K. The N atoms thus produced occupy subsurface sites, while the H atoms bind to surface Si atoms, tie up the dangling bonds, and inactivate the surface. Thermal or electronic-excitation-induced hydrogen desorption restores the dangling bonds and the reactivity of the surface. Silicon nitride film growth is achieved at 90 K by simultaneous exposure of the Si surface to NH₃ and an electron beam.

PACS numbers: 82.65.Jv, 68.45.Da, 68.55.Gi, 81.15.Gh

The understanding of surface chemistry and thin-film growth processes in technologically important gas-surface reaction systems is a subject of significant current interest.¹ One intriguing aspect revealed by studies in this area is the requirement of unusually high temperatures for sustained surface reactivity, in view of the fact that dangling bonds should render such surfaces very reactive even at low temperatures. For example, the reactions of Si(100) with NH₃ or hydrocarbons to give silicon nitride or silicon carbide films, respectively, require temperatures in the range of 800–1200 °C.^{2–5} The presence of surface dangling bonds, two in the case of the unreconstructed Si(100) surface or one in the case of the now generally accepted dimer model of the (2×1) reconstruction,^{6,7} should give to the surface radicallike reactivity characterized by low activation barriers.⁸ In principle, the need for high temperatures may reflect any of several reasons, such as an activated dissociated adsorption, formation of Schottky-type barriers at small surface coverages, higher diffusion barriers for surface ↔ bulk diffusion, etc. It is often undesirable (especially in applications to microelectronics) to carry out these reactions at high temperatures because of the simultaneous activation of unwanted side processes such as dopant diffusion. Thus, nonthermal activation mechanisms are actively being sought. However, in order to effectively develop nonthermal methods of activation, it is important to understand the mechanism of the reaction and especially the nature of the rate-determining step.

In this Letter, we present the analysis of a prototype gas-surface reaction system, the reaction of Si(100) with NH₃ to give silicon nitride, a technologically important electronic material. This analysis provides important insights into the nature of the rate-limiting steps in surface-reaction and thin-film-growth processes. Specifically, we determine the intrinsic reactivity of the Si(100) surface towards NH₃, the identity of the reaction sites, the causes of the self-limiting behavior of the surface reaction, and the role of the

thermal activation. Having understood the nature of the required activation we also have been able to activate the film growth process via an electronic excitation, and we have observed Si₃N₄ film growth at temperatures as low as 90 K.

The experiments described here were performed in an UHV system with a base pressure of $\sim 2 \times 10^{-10}$ Torr, equipped with facilities to perform x-ray photoemission spectroscopy (XPS), Auger-electron spectroscopy, LEED, electron-stimulated desorption (ESD), ion-scattering spectroscopy (ISS), and thermal desorption spectroscopy (TDS). The sample treatment and the crystal mounting arrangement which allows reaction studies in the temperature range 90–1500 K, as well as the microcapillary-array gas doser, have been described elsewhere.⁵

In Fig. 1(a) we show the N(1s) XPS spectra obtained when the Si(100)(2×1) surface is exposed to 10 L [1 L (Langmuir) = 10^{-6} Torr · sec] of NH₃ at 90 K, and after a short annealing to 300 K. The N(1s) signal at 90 K has two main components: a peak at a binding energy of 399.7 eV and a second one at 2 eV lower binding energy. The 399.7-eV peak is eliminated by heating of the sample to 300 K, but it reappears if the sample is cooled back to 90 K and reexposed to NH₃. TDS indicated desorption of NH₃ in the same temperature range [Fig. 2(a)]; this suggests that the N(1s) peak at 399.7 eV is due to molecularly adsorbed ammonia. The peak at 397.7 eV, on the other hand, does not change its energy or intensity upon annealing to temperatures as high as 1200 K. This XPS component is attributed to nitrogen atoms which are directly bonded to silicon. The value of the binding energy is in good agreement with literature values for silicon nitride.^{9–11} The above XPS results clearly demonstrate the high reactivity and ability of Si(100) surface dangling bonds to dissociate NH₃ even at 90 K. The reaction, however, is self-limiting to less than a monolayer of product. Further exposure to NH₃ at 90 K does not lead to any further increase of the 397.7-eV peak, i.e., no further reaction of Si with NH₃.

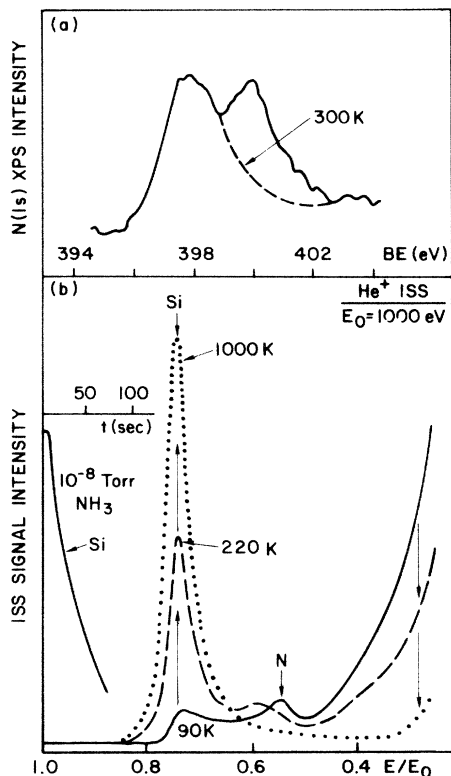


FIG. 1. (a) $N(1s)$ x-ray photoemission spectrum (XPS) of the $Si(100)-(2 \times 1)$ surface after exposure to 10 L NH_3 at 90 K (solid line), and after annealing of the NH_3 -exposed surface to 300 K (dashed line). (b) He^+ ion scattering spectra (ISS) of the $Si(100)-(2 \times 1)$ surface after exposure to 10 L NH_3 at 90 K (solid line), after subsequent annealing to 200 K (dashed line), and after annealing to 1000 K (dotted line). Inset: Si ISS peak intensity decrease in the course of a 10-L NH_3 exposure at 90 K. (Laboratory scattering angle 90° .)

In order to obtain insight into the nature of the rate-limiting process we have probed the state of the $Si(100)$ surface with He^+ ISS under reaction conditions. ISS is particularly suited in this respect because of its extreme surface sensitivity. In Fig. 1(b) we see that exposure of the $Si(100)$ at 90 K to $\sim 3 \times 10^{-8}$ Torr NH_3 results in the rapid attenuation of the Si ISS signal, indicating a high sticking probability (ca. $s > 0.5$). The ISS spectrum of the mixed nitride-molecular NH_3 phase at 90 K shows weak Si and N signals and a strong inelastic background at low energies. Mild annealing of this phase to 220 K and desorption of the molecularly adsorbed NH_3 leads to the increase of the Si ISS signal, which now has recovered approximately half of its original intensity, and the total elimination of the N ISS signal. (A small peak at $\sim E/E_0 = 0.6$ is due to a small oxygen contamination during the ISS experiment.) Simultaneously, the low-energy background is greatly reduced. No further significant change of the ISS spectrum is observed

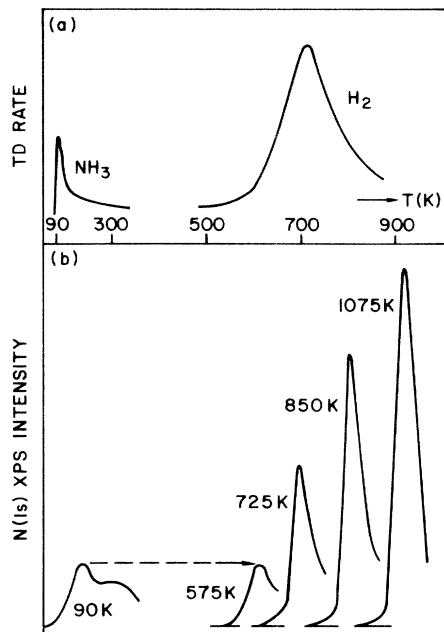


FIG. 2. (a) Thermal desorption spectra of NH_3 and H_2 from a $Si(100)-(2 \times 1)$ surface which has been exposed to 10 L NH_3 at 90 K. Heating rate $\sim 5 \text{ K sec}^{-1}$. (b) The intensity of the $N(1s)$ XPS peaks after sequential equivalent exposures of $400 \text{ sec} \times 10^{-8}$ Torr NH_3 at the indicated temperatures.

until the temperature is raised above ~ 700 K. At 1000 K [Fig. 1(b)] the Si ISS signal is as strong as that from the clean surface. The inelastic background has now been eliminated, but no surface nitrogen is detected by ISS. Parallel XPS measurements, on the other hand, show no decrease in the $N(1s)$ signal as a result of heating to 1000 K. The above observations indicate that the nitrogen resulting from the dissociation of NH_3 resides in subsurface sites and is thus shielded from the incident He^+ ions. The only surface nitrogen detected is that from condensed NH_3 . The hydrogen from NH_3 shadows the Si atoms and gives rise, because of its smaller mass, to the inelastic background at small E/E_0 . However, the facts that after NH_3 desorption the Si ISS signal has only half of its original intensity and that there is still significant inelastic background indicate the presence of surface hydrogen directly bonded to silicon. Since reactions between closed-shell species have high activation energies,⁸ this surface hydrogen, by tying up the dangling bonds of the silicon surface, may inhibit further NH_3 dissociation and, thus, lead to the observed self-limiting behavior. Strong support for this hypothesis is provided by the data shown in Fig. 2. Figure 2(a) shows the TD spectrum of H_2 from the NH_3 -exposed $Si(100)$ surface, while Fig. 2(b) shows the $N(1s)$ XPS intensities observed after 12-L NH_3 exposures of the $Si(100)$ surface at temperatures between 90 and 1075

K. From 90 up to ~ 650 K, i.e., at temperatures below the threshold for H_2 desorption, exposure to NH_3 does not lead to any further increase in the intensity of the silicon nitride $N(1s)$ 397.7-eV peak beyond that observed at 90 K [Fig. 1(a)]. At 725 K and higher temperatures, however, the increase in $N(1s)$ XPS signal indicates a greatly enhanced reactivity towards NH_3 dissociation and nitride formation. In addition, if the hydrogen is desorbed at high temperatures and the sample is cooled back down to 90 K, the surface exhibits very similar reactivity towards NH_3 as the original clean Si(100) surface. This is true even in the case where XPS indicates the presence of more than a monolayer of nitride.

The above experiments clearly show that hydrogen produced by the dissociation of NH_3 ties up the Si surface dangling bonds and blocks the reaction $Si(100) + NH_3$ at low temperatures. High temperatures are necessary to desorb hydrogen, produce surface dangling bonds, and restore surface reactivity. The nitrogen, on the other hand, is found to reside in subsurface sites and does not affect significantly the reactivity of the surface.

Having understood the reason for the surface passivation, we sought to enhance the film growth process by nonthermal means. In the following, we present results showing that silicon nitride film growth can be achieved even at 90 K provided that the surface hydrogen is continuously removed by electron-stimulated desorption (ESD). In our ESD studies we find that the minimum electron-beam energy needed to desorb H^+ from the NH_3 -exposed Si surface is ~ 21 eV. In subsequent studies, higher (300–1200-eV) electron energies were utilized so as to optimize the electron-beam current and desorption yield. XPS studies clearly indicate the growth of the $N(1s)$ signal when the Si(100) surface at 90 K is simultaneously exposed to a flux of NH_3 and to the electron beam. However, to avoid artifacts due to the mismatch of the electron-beam and x-ray-beam sizes at the surface, we used the same electron beam both to stimulate hydrogen desorption and to monitor the nitride-layer growth by electron-excited Auger spectroscopy. In Fig. 3(a) we show the $Si(LVV)$ and $N(KLL)$ Auger spectra of a portion of the Si surface exposed at 90 K to 10^{-7} Torr of NH_3 for 10 min, without electron irradiation during exposure (solid lines), and the corresponding spectra from the region of the surface exposed, simultaneously, to NH_3 and a $30\text{-}\mu A$, 1.2-keV electron beam (dashed lines). We see that the exposure to the electron beam leads to an approximately tenfold increase in the $N(KLL)$ Auger signal. Similarly, the LVV signal of clean Si is eliminated by the electron-beam irradiation and is replaced by the $Si(LVV)$ signal characteristic of silicon in silicon nitride. Assuming a layer-by-layer growth mechanism we estimate¹² a thickness

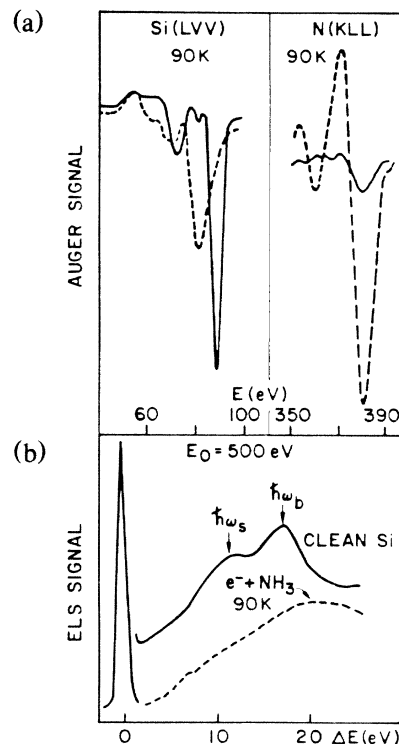


FIG. 3. (a) $Si(LVV)$ and $N(KLL)$ Auger spectra of the $Si(100)$ surface after exposure to $900 \text{ sec} \times 10^{-7}$ Torr of NH_3 at 90 K (solid lines), and after a simultaneous exposure to the same NH_3 dose and a $30\text{-}\mu A$, 1200-eV electron beam at 90 K (dashed lines). Area of surface exposed to the electron beam: $\sim 4 \text{ mm}^2$. (b) Electron energy loss spectra of the clean $Si(100)$ - (2×1) surface (solid line) and of the surface produced by simultaneous exposure to NH_3 and the electron beam as in (a) (dashed line). The spectra show the characteristic surface and bulk plasmon losses of silicon and bulk plasmon losses of silicon nitride, respectively.

of $20 \pm 5 \text{ \AA}$ for the nitride film grown at 90 K [Fig. 3(a)] with the help of electron-beam irradiation. Our results suggest that the main role of the electron irradiation is to help maintain a hydrogen-free Si surface which can then dissociate NH_3 . In addition, the electron beam can probably further enhance the film growth rate by dissociating molecularly adsorbed NH_3 . In that respect, however, we find no significant growth rate enhancement as the electron-beam energy is scanned (at constant current) from energies below to energies above the nitrogen K edge.

Further characterization of the nitride layer formed at 90 K is provided by electron-energy-loss spectroscopy (EELS) with use, again, of the same electron beam for characterization and reaction. In Fig. 3(b) we show the EELS spectrum of the clean Si(100) surface showing peaks at ~ 11 and ~ 17 eV which are due to Si surface and bulk plasmon excitations, respectively. After electron irradiation, as in Fig. 3(a), the resulting EELS spectrum shows no plasmon losses

characteristic of clean Si but instead a new broad plasmon loss is observed at ~ 21 eV. This loss is in agreement with published values for stoichiometric Si_3N_4 , which are in the range of 20–22 eV,^{13–15} and with our own observations on thermally grown nitrides.

In conclusion, we find that there is no significant activation barrier for the dissociative adsorption of NH_3 on Si(100). The surface dangling bonds can readily dissociate NH_3 even at 90 K. However, while the N atoms occupy subsurface sites, the hydrogen produced by the dissociation of NH_3 ties up the Si surface dangling bonds and thus passivates the Si surface. The high temperatures found to be essential for thin-film growth simply reflect the need to thermally desorb the hydrogen, regenerate surface dangling bonds, and thus allow sustained surface reaction. We have also shown that electron-stimulated hydrogen desorption can be used instead of thermal desorption to produce surface dangling bonds and to allow a sustained reaction even at 90 K. These results also demonstrate that bulk \leftrightarrow surface diffusion is not the rate-limiting step in this thin-film growth process. Our findings suggest an appealing approach to low-temperature film growth by the reaction of molecular hydrides with the appropriate substrate, with the help of electron-beam irradiation. Multivalent small atoms, such as N or C, tend to occupy subsurface sites, while surface H has a large electron-stimulated-desorption cross section¹⁶ and can be effectively removed. As a further test of these ideas, we investigated the reaction of Si(100) with C_2H_4 to give SiC.¹⁷ We found a completely analogous behavior, i.e., subsurface C, and surface H which leads to a self-limiting reaction. Again, sustained reaction at 90 K could be achieved with the help of electron-beam irradiation. The use of an electron beam for the activation of the reaction should allow good spatial control of the reaction, a characteristic particularly desirable in applications to microelectronics.¹⁸

We would like to thank Dr. R. Walkup for a critical reading of the manuscript and useful suggestions.

¹For reviews see A. Atkinson, *Rev. Mod. Phys.* **57**, 437 (1985); R. H. Williams and I. T. McGovern, in *The Chemical Physics of Solid Surfaces and Heterogeneous Catalysis Vol. 3*, edited by D. A. King and D. P. Woodruff (Elsevier, New York, 1984); B. A. Joyce and C. T. Foxon, in *Simple Processes at the Gas-Solid Interface*, *Comprehensive Chemical Kinetics* Vol. 19, edited by C. H. Bamford, C. F. H. Tipper, and R. G. Compton (Elsevier, Amsterdam, 1984).

²M. M. Moslehi and K. C. Saraswat, *IEEE J. Solid-State Circuits* **20**, 26 (1985).

³J. A. Nemetz and R. E. Tressler, *Solid State Technol.* **79**, xx (1983).

⁴S. Nishino, J. A. Powell, and H. A. Will, *Appl. Phys. Lett.* **42**, 4606 (1983).

⁵F. Bozso, J. T. Yates, J. W. Choyke, and L. Muelhoff, *J. Appl. Phys.* **57**, 2771 (1985).

⁶J. D. Levine, *Surf. Sci.* **34**, 91 (1973).

⁷R. M. Tromp, R. J. Hamers, and J. E. Demuth, *Phys. Rev. Lett.* **55**, 1303 (1985).

⁸S. W. Benson, *Thermochemical Kinetics* (Wiley, New York, 1976).

⁹J. A. Taylor, G. M. Lanchester, A. Ignatiev, and J. W. Rabalais, *J. Chem. Phys.* **68**, 1776 (1978).

¹⁰C. Maillot, H. Roules, and G. Dufour, *J. Vac. Sci. Technol. B* **2**, 316 (1984).

¹¹D. Hackleman, Y. G. Vlasov, and R. B. Buck, *J. Electrochem. Soc.* **125**, 1875 (1978).

¹²T. A. Gallon, *Surf. Sci.* **17**, 486 (1969).

¹³R. Kärcher, L. Ley, and R. L. Johnson, *Phys. Rev. B* **30**, 1896 (1984).

¹⁴N. Lieske and R. Hezel, *Thin Solid Films* **61**, 217 (1979).

¹⁵M. Nishijima and K. Fujiwara, *Solid State Commun.* **24**, 101 (1977).

¹⁶M. L. Knotek, *Rep. Prog. Phys.* **47**, 1499 (1984).

¹⁷F. Bozso and Ph. Avouris, to be published.

¹⁸*Nanometer Structure Electronics: An Investigation of the Future of Microelectronics*, edited by Y. Yamamura, T. Fujiwara, and S. Namba (North-Holland, Amsterdam, 1985).