RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 44, NUMBER 4 15 JULY 1991-II

NH_3 and NO interaction with Si(100)-(2×1) surfaces

G. Rangelov, J. Stober, B. Eisenhut, and Th. Fauster
Sektion Physik der Universität München, Schellingstrasse 4, D-8000 München 40, Germany

(Received 6 March 1991)

The adsorption of NH_3 and NO on Si(100)-(2×1) surfaces at room temperature and the stepwise nitridation have been studied by high-resolution Si 2*p* core-level photoemission spectroscopy. Both molecules adsorb dissociatively, but only for NO does a reaction occur beyond the first monolayer. For the growth of stoichiometric silicon nitride, annealing to 1200 K is necessary.

The nitridation of silicon surfaces has been studied extensively during the past decade due to the technological importance of silicon nitride as a dielectric layer in metal-insulator-semiconductor devices.[1,2] The interaction of nitrogen-containing molecules such as NH_3 (Refs. 3–15) or NO (Refs. 6 and 16–19) with Si(100) and Si(111) has been investigated under UHV conditions in order to understand the elementary steps of the nitridation reaction. It became clear that the dissociation of the molecules on the surface and the reactant diffusion through the formed nitride layer are the limiting steps for bulk Si_3N_4 formation. Some controversies concerning the NH_3 and NO adsorption on Si(100)-(2×1) surface still exist, however. Several authors[3–6,19] find that NH_3 and NO dissociate to NH+2H and N+O, respectively, on Si(100)-(2×1) surfaces at low temperature and that the dangling bonds play a crucial role in the dissociation process. Nitrogen atoms are assumed to be in subsurface sites and H or O atoms saturate the dangling bonds inhibiting further adsorption.[3–6] The recovery of the dangling bonds by electron irradiation at temperatures as low as 90 K is sufficient for the nitridation to continue and for a thick stoichiometric silicon nitride layer to grow.[3,6] This picture was questioned by several authors,[8,9,12–14] who showed that the dangling bonds are saturated by NH_x [$x=2$ (Refs. 12–14)] and H dissociation products after NH_3 adsorption on Si(100) at room temperature, which puts the N atoms above the Si top layer. Furthermore, N bulk diffusion and stoichiometric nitride formation required annealing to high temperatures.[4,7–9,12–15] The dissociative NO adsorption on Si(100)-(2×1) at room temperatures was ruled out by Auger electron-spectroscopy[18] and stimulated desorption[17] studies.

It is clear that further studies concerning NH_3 and NO adsorption on Si(100)-(2×1) surface are needed. We use high-resolution Si 2*p* core-level photoemission spectroscopy with synchrotron radiation to study the adsorption of NH_3 and NO at room temperature and the thermal nitridation after annealing the adsorbed layers to various temperatures. Repeating the room-temperature adsorption and heating procedure allowed us to study separately both processes governing bulk nitridation of Si(100) surfaces: dissociative adsorption on a clean or reacted surface and Si_3N_4 formation after high-temperature annealing.

The experiments have been performed at the TGM-3 (toroidal grating monochromator) beamline at the Berlin synchrotron facility at BESSY (Berliner-Elektronenspeicherring-Gesellschaft für Synchrotronstrahlung). Angle-integrated high-resolution Si 2*p* core-level photoemission spectra were taken at 130-eV photon energy with a display-type spectrometer.[20] The overall energy resolution of the monochromator and the spectrometer was ~0.4 eV. The sample preparations have been done in a separate chamber described previously.[21] Clean Si(100)-(2×1) surfaces were obtained by repeated cycles of argon-ion bombardment and subsequent annealing to 1100 K in a vacuum. Finally, the sample was heated to 1400 K for 1 min and cooled down slowly from 1200 K to room temperature. This procedure provided us with C and O free samples with a sharp (2×1) low-energy electron-diffraction pattern. The Si(100) crystals were changed after several nitridation experiments to exclude a possible roughening of the surface. The NH_3 and NO exposures were made at room temperature, the chamber being pumped by a liquid-nitrogen-cooled titanium sublimation pump and a turbomolecular pump. Before NO experiments the preparation chamber was passivated by a 2000-L NO exposure.[17]

Figure 1 shows the Si 2*p* core-level spectra from a complete series of NH_3 adsorption and heating cycles. The main part of the figure presents only the Si $2p_{3/2}$ components referenced to the clean surface and normalized to the maximum height. The standard decomposition procedure is illustrated in the inset and consists of a background subtraction (dashed line) followed by a subtraction of the Si $2p_{1/2}$ component.[22] The result of this decomposition procedure is shown as a solid line spectrum and is repeated at the bottom of the main figure. To the right-hand side of the peak the contribution from the surface is seen as a shoulder. This surface peak is attributed to the emission from the outer dimer atoms of the Si(100)-(2×1) surface and their intensity corresponds to 0.5 monolayers (ML) Si atoms.[22,23] An exposure of 40 L of NH_3 was sufficient to saturate the surface and quenched the surface peak (bottom, dotted line). The disappearance of the surface contribution can be understood as a saturation of the free dangling bonds[22,23] by the NH_3 dissociation products. The intensity to the left side of the bulk peak has increased after NH_3 adsorption due to a shifted Si 2*p* component. Such shifts of the Si 2*p* binding energy are due to emission from Si atoms bound to foreign atoms. The amount of the shift depends on the electronegativity difference and the number of the foreign atoms to which the Si atom is bound.[22] In our case we observe only one component shifted by ~0.7 eV which corresponds to one Si—N bond.[1,10,11] From the intensity ra-

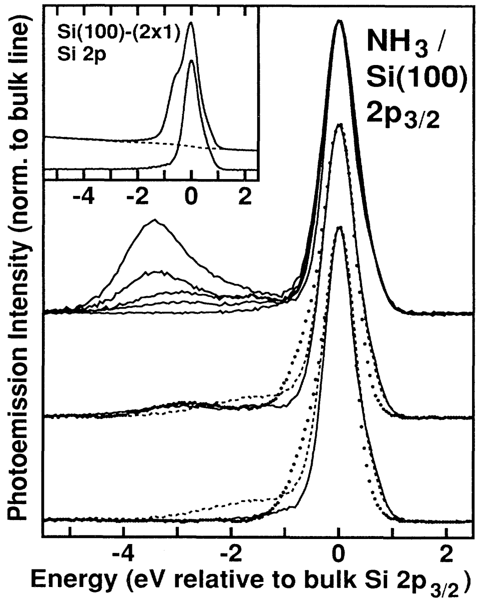

FIG. 1. At the bottom Si $2p_{3/2}$ core-level spectra for the clean surface (solid line), after NH$_3$ saturation (dotted line), and after annealing to 600 K (dashed line) are shown. In the center the last spectrum is repeated, and the result of further annealing to 1200 K (solid line) and subsequent NH$_3$ adsorption (dotted line) is presented. At the top, the spectra demonstrate the growth of the nitride after one, two, four, and eight adsorption and annealing cycles. The inset shows the decomposition of the Si $2p$ doublet for the clean surface.

tio between the main Si $2p$ line and the shifted components conclusions concerning the number of reacted Si atoms can be drawn.[22,23] We estimate that ~0.5-ML Si atoms participate in these bonds. The fact that each reacted Si atom is bound to only one N atom and the disappearance of the dangling bonds after NH$_3$ saturation could be interpreted in terms of NH$_2$ groups saturating one-half of the dangling bonds, the rest being saturated by H in agreement with previous work.[8,12–14] However, our results alone cannot exclude subsurface N and dangling bonds saturation by H only.[3–6]

Heating the sample to ~700 K leads to complete NH$_x$ dissociation and H$_2$ desorption[4,8,12,13] and to pronounced changes in the Si $2p$ peak shape (dashed curves: bottom and center). The dangling bonds are recovered and a tail at higher binding energy appears which we assign to Si atoms bound to one, two, and three N atoms. Further heating to 900 K (not shown) had almost no effect on the spectra, but heating to ~1200 K for 1 min shifted the intensity of the tail to even higher binding energy forming a well separated peak at ~3 eV higher binding energy relative to the main line (center, solid curve). According to existing Si $2p$ core-level experiments[1,9–11,15,16] such an energy shift corresponds to the formation of bulk Si$_3$N$_4$, where every Si atom is bound to four N atoms. This annealing experiment confirms that higher nitridation levels can be reached only after the complete dissociation of NH$_2$ groups.[8,9,13,14] Therefore, one can assume that in the low-temperature nitridation experiments of Bozso and co-workers[3,6] the dissociation of the NH$_2$ groups has taken place simultaneously with hydrogen electron stimulated desorption. However, our data show that the existence of atomic nitrogen on the surface is not enough to produce stoichiometric Si$_3$N$_4$ in agreement with low-temperature N adsorption experiments.[4] The fact that stoichiometric silicon nitride can be formed only after annealing to temperatures well above 900 K proves that the growing of stoichiometric bulk nitride is diffusion dependent.[9]

The further NH$_3$ adsorption on the surface annealed to 1200 K proceeds similarly to the adsorption on the clean surface. The surface emission is quenched again and the Si $2p$ shifted component corresponding to Si atoms bound to only one N atom reappears (dotted curve, center). This finding could be interpreted in the following two ways: formation of silicon nitride islands surrounded by clean Si(100) or the build up of a Si layer on top of the nitride layer. Bischoff, Kubler, and Bolmont[9] concluded from their nitridation experiments that island formation takes place in the low-exposure high-temperature regime (600–800 °C). The existence of a Si overlayer has been suggested by ion scattering experiments.[3,6] Our data cannot decide between both possibilities but the estimated amount of reacted Si (~0.5 ML) is too small to cover the whole surface by stoichiometric nitride.

By repeating the adsorption and heating cycle we obtain Si(100) nitridation in small steps. The top curves in Fig. 1 show the result of one, two, four, and eight cycles. For reference, the spectrum of the clean surface is also included. For the top curve we estimated that ~1.5-ML Si atoms are reacted and most of them are bound to three and four N atoms.

Figure 2 shows the Si $2p_{3/2}$ component as a function of NO exposure. The same decomposition and normalization procedure as in Fig. 1 is used. The clean Si(100) spectrum is also shown (dashed curve). We see that NO adsorption leads to a quenching of the surface emission and the appearance of a Si $2p$ component shifted to higher binding energy. The surface contribution disappears above 0.4 L due to the saturation of the dangling bonds.[6] However, the NO reaction with the surface continues as is obvious from the intensity increase of the shifted Si $2p$ component. The binding energy shift for a Si—O bond is ~0.9 eV (Ref. 22) and for a Si—N bond is ~0.7–0.8 eV.[1,10] At exposures lower than 1 L, Si atoms bound to one ligand dominate. This would be compatible with

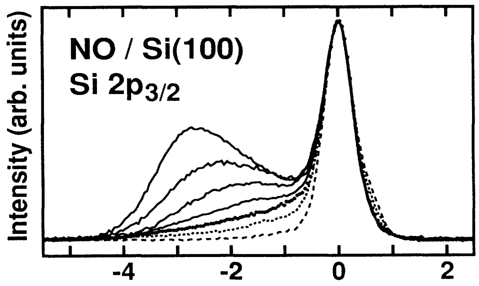

FIG. 2. Si $2p_{3/2}$ core-level spectra after adsorption of 0.0, 0.2, 0.4, 1.0, 3.0, 10, and 40 L of NO (from bottom to top on the left-hand side of the main peak, respectively).

molecular adsorption.[17,18] Since we also find Si atoms bound to more ligands, and Si atoms bound to two or more NO molecules are unlikely, N and O atoms must be on the surface.[19] From our NH_3 experiments and other oxidation studies[23] we know that these atomic species lead to a wide distribution of shifted Si 2*p* components. Therefore, most of the Si atoms bound to one ligand are bound to N or O atoms and not molecules. This is supported by our observation of features in the photoemission spectra of the valence-band characteristic for atomic oxygen. After the saturation of the dangling bonds, Si atoms bound to more than one ligand start to prevail. We suggest that two processes take place: fast adsorption on the dangling bonds and slower diffusion of N or O atoms in the bulk. This suggestion is in accord with ion scattering experiments of Avouris, Bozso, and Hamers[6] who observed subsurface N diffusion even at low temperatures. For the highest exposure (40 L) we obtain a broad shifted Si 2*p* component with a maximum around −2.7 eV. The majority of the reacted Si atoms are bound to more than one ligand and ∼3.5 ML of Si atoms are reacted with N or O atoms, seven times more than for the case of NH_3 saturation.

Heating above 1200 K removes the oxygen from the surface.[6,16] The corresponding Si $2p_{3/2}$ spectrum is presented in Fig. 3 (dotted line, bottom). The spectrum for Si(100) exposed to 40 L of NO at room temperature is also shown for comparison (solid line, bottom). We see that the heating has recovered the surface emission similar to the NH_3 case and has reduced the intensity of the shifted Si 2*p* component due to O removal. From the shape and the binding-energy shift (∼3 eV) of the dotted curve it is clear that we have formed a nearly stoichiometric nitride as in the case of NH_3 nitridation, the amount of the reacted Si, however, is three times as large. By NO adsorption and subsequent annealing the nitridation proceeds further. This process is illustrated in Fig. 3 which shows the spectra for the first, third, fifth, and seventh cycle from bottom to top. Solid curves are taken after NO exposure (40 L) and the dotted spectra after annealing to 1200 K for 1 min. The comparison to the NH_3 case shows that after annealing a fully reacted nitride is formed with increasing thickness after each cycle. After annealing the surface emission recovers which means that dangling bonds exist on the reacted surface as well. A Si overlayer on top of the nitride was proposed by Avouris, Bozso, and Hamers[6] and Taguchi *et al.*[19] The room-temperature NO adsorption on the reacted Si(100) surface proceeds similar to the clean surface. The surface emission disappears illustrating the saturation of the dangling bonds. NO continues to adsorb dissociatively according to the increase of the shifted peak intensity in the region where emission from Si atoms bound to more than one ligand is expected. The obvious shift of the reacted peak to lower binding energy after NO exposure can be explained by a superposition of peaks owing to Si atoms reacted with two and three ligands.

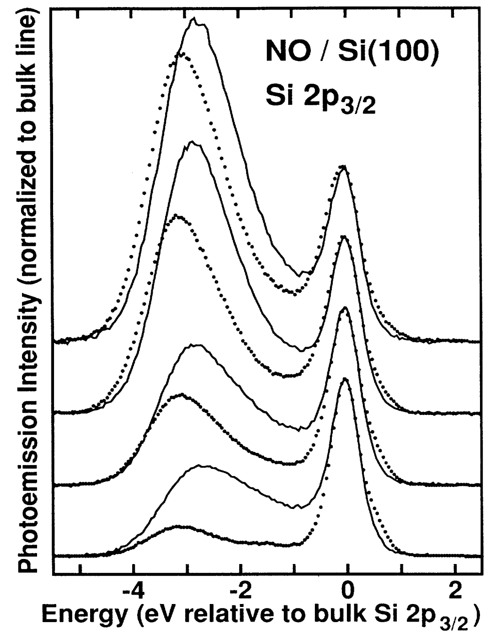

FIG. 3. Si $2p_{3/2}$ core-level spectra after adsorption of NO (solid lines) and after subsequent annealing to 1200 K (dotted curves). The results after one, three, five, and seven adsorptions are shown from bottom to top.

In summary, our Si 2*p* core-level measurements show conclusively that NH_3 and NO adsorb dissociatively on Si(100)-(2×1) surfaces. The dangling bonds play an important role in this process. Their saturation inhibits further NH_3 adsorption but not NO adsorption. This is due to the incomplete dissociation of NH_3 at room temperature. However, even the complete dissociation of the N containing molecules is not enough to produce a stoichiometric Si_3N_4 layer. The diffusion of the reactants taking place at temperatures around 1200 K is necessary for the growth of a stoichiometric nitride. The comparison between NH_3 and NO nitridation after room-temperature adsorption shows that the basic processes are the same, but the efficiency of the NO nitridation is higher.

We acknowledge stimulating discussions with Professor W. Steinmann and the continuous support by the staff of BESSY. This work has been supported by the German Federal Minister of Research and Technology under Contract No. 05 464 AAB 2.

---

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

[2] B.-R. Zhang, Z. Yu, G. J. Collins, T. Hwang, and W. H. Ritchie, J. Vac. Sci. Technol. A **7**, 176 (1989), and references therein.

[3] F. Bozso and Ph. Avouris, Phys. Rev. Lett. **57**, 1185 (1986).

[4] F. Bozso and Ph. Avouris, Phys. Rev. B **38**, 3937 (1988).

[5] R. J. Hamers, Ph. Avouris, and F. Bozso, Phys. Rev. Lett. **59**,

2071 (1987).

[6] Ph. Avouris, F. Bozso, and R. J. Hamers, J. Vac. Sci. Technol. B **5**, 1387 (1987).

[7] L. Kubler, E. K. Hlil, D. Bolmont, and G. Gewinner, Surf. Sci. **183**, 503 (1987).

[8] E. K. Hlil, L. Kubler, J. L. Bischoff, and D. Bolmont, Phys. Rev. B **35**, 5913 (1987).

[9] J. L. Bischoff, L. Kubler, and D. Bolmont, Surf. Sci. **209**, 115 (1989).

[10] F. Cerrina, B. Lai, G. M. Wells, J. R. Wiley, D. G. Kilday, and G. Margaritondo, Appl. Phys. Lett. **50**, 533 (1987).

[11] B. Lai, R. Nachman, A. K. Ray-Chaudhuri, and F. Cerrina, Solid State Commun. **71**, 721 (1989).

[12] M. J. Dresser, P. A. Taylor, R. M. Wallace, W. J. Choyke, and J. T. Yates, Jr., Surf. Sci. **218**, 75 (1989).

[13] M. Fujisawa, Y. Taguchi, Y. Kuwahara, M. Onchi, and M. Nishijima Phys. Rev. B **39**, 12918 (1989).

[14] C. U. S. Larsson and A. S. Flodström, Surf. Sci. **241**, 353 (1991).

[15] C. Maillot, H. Roulet, and G. Dufour, J. Vac. Technol. B **2**, 316 (1984).

[16] M. D. Wiggins, R. J. Baird, and P. Wynblatt, J. Vac. Sci. Technol. **18**, 965 (1981).

[17] E. C. Ekwelundu and A. Ignatiev, Surf. Sci. **179**, 119 (1987); **215**, 91 (1989).

[18] A. G. B. M. Sasse and A. van Silfhout, Phys. Rev. B **40**, 1773 (1989); H. Wormeester, A. van Silfhout, E. G. Keim, and A. G. B. M. Sasse, Surf. Sci. **233**, L249 (1990).

[19] Y. Taguchi, M. Fujisawa, Y. Kuwahara, M. Onchi, and M. Nishijima, Surf. Sci. **217**, L413 (1989); Y. Taguchi, M. Fujisawa, and M. Nishijima, *ibid.* **233**, L251 (1990).

[20] F. Rieger, R. D. Schnell, W. Steinmann, and V. Saile, Nucl. Instrum. Methods **208**, 777 (1983).

[21] C. A. Schug, B. Konrad, B. Eisenhut, E. Bertel, and W. Steinmann, Surf. Sci. **225**, 58 (1990).

[22] F. J. Himpsel, B. S. Meyerson, F. R. McFeely, J. F. Morar, A. Taleb-Ibrahimi, and J. A. Yarmoff, in *Photoemission and Absorption Spectroscopy of Solids and Interfaces with Synchrotron Radiation,* Proceedings of the International School of Physics "Enrico Fermi," Course CVIII, Varenna, Italy, 1988, edited by M. Campagna and L. Rosei (North-Holland, Amsterdam, 1989).

[23] F. J. Himpsel, F. R. McFeely, A. Taleb-Ibrahimi, J. A. Yarmoff, and G. Hollinger, Phys. Rev. B **38**, 6084 (1988).