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THE ADSORPTION OF NITRIC OXIDE ON A SILICON (100) 2×1 SURFACE STUDIED WITH AUGER ELECTRON SPECTROSCOPY

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We present an Auger electron spectroscopy (AES) study of the adsorption of nitric oxide (NO) on a clean Si(100)2×1 surface at 300 and 550 K. Accurate measurements reveal well resolved fine structure at Auger Si $L_{2,3}VV$ transitions at 62 and 83 eV. These peaks can be attributed to Si–O and Si–N bonds. Furthermore, it is argued that the broadening in the Si $Li_{2,3}VV$ Auger transition at 83 eV at 300 K may be composed of two nearby peaks, which could be attributed to two different kinds of chemical bonding, Si–N and Si–O. The absence of a peak at 69 eV at room temperature strongly suggests the NO adsorption on a Si(100)2×1 surface to be molecular. Dissociation of NO on the Si(100)2×1 surface is observed at 550 K.

In the last decade substantial research has been devoted to the nitridation of the clean Si(111) surface be means of adsorption with nitrogen containing gas molecules (NO, N_2O, NH_3, etc.) [1–3,5–9]. The adsorption behaviour of these molecules on Si(100) is investigated with considerably less intensity [2,4,10]. To our knowledge only two AES investigations of NO adsorbed on the Si(100) surface were published before: He and Smith [2] ($T > 1200$ K), and Boszo and Avouris [4] ($T = 90$ K).

The aim of this study is to give a description of the NO adsorption mechanism on the Si(100)2 × 1 surface at 300 and 550 K, by using Auger electron spectroscopy (AES). The adsorption of NO on the Si(100)2 × 1 surface at 300 K is of particular interest, because of its unique adsorption mechanism. In ref. [10] it has been argued that NO is predominantly molecularly adsorbed at missing dimer defects.

A semi-quantitative analysis of the coverage of the different types of atoms in the surface region is made from the KLL Auger spectra. From the Si $L_{2,3}VV$ Auger spectra site specific chemical information can be obtained [11,12]. The gas–solid reactions were studied in ultrahigh vacuum (UHV) at a sample temperature of 330 and 550 K. The experimental setup, surface cleaning, and gas handling are described in detail elsewhere [9,10]. The pressure during the exposures is 2.5×10^{-6} Torr in all our experiments. The static background pressure is about 6.0×10^{-11} Torr.

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AES can be used to measure the relative concentration of oxygen and nitrogen absorbed on the clean Si(100)2 × 1 surface. The amount of adsorbed oxygen and nitrogen is proportional to the ratio of the oxygen and nitrogen KLL, 510 and 381 eV with respect to the silicon KLL (1619 eV) peak to peak (p–p) height in the first derivative ($\mathrm{d}N(E)/\mathrm{d}E$) of the energy distribution, i.e., $I_{O,N}/I_{Si}$. The information depth is of the order of 3 atomic layers which corresponds to an escape depth of about 9 Å. The Auger spectra were recorded using a primary beam energy of 3 keV, primary current density of ~ 200 μA/cm^{-2}, modulation voltage of the energy analyzer of 9 V_{p-p}, a sweep rate of 1.0 eV/s and a lock-in time constant ≤ 1 s. The angle of incidence of the primary electron beam on the silicon surface was 79° for the performed Auger experiments.

The signal ratio $I_{O,N}/I_{Si}$ was converted into a relative oxygen and nitrogen surface concentration using the equation,

$$C_x[\%] = \frac{I_x/S_x}{\Sigma_n(I_n/S_n)} \times 100, \qquad (1)$$

where C_x is the relative surface concentration of element x in percent, I_x is the p–p height of the element x, and S_x is the respective relative elemental sensitivity factor. The relative elemental sensitivity factors used in eq. (1) were O_{KLL}: 0.50, N_{KLL}: 0.30, and Si_{KLL}: 0.022 [13]. We estimate that the experimental accuracy in the determination of the surface concentration of the element x is about 15%.

Relevant information concerning the chemical bonding can be extracted from the Si $L_{2,3}VV$ Auger spectra in the range of 40–85 eV. In this range of emerging electrons the information depth is about 1.5 atomic layers [12]. Recently it has been shown that careful measurements of the Si $L_{2,3}VV$ Auger spectrum in this energy range can lead to more definite conclusions about the binding state of an element adsorbed on the silicon surface [9,11,12]. The Si $L_{2,3}VV$ Auger spectra were recorded under the following operating conditions: primary beam energy 2 keV; primary current density of ~ 140 μA/cm^{-2}; modulation 2 V_{p-p}: sweep rate = 0.5 eV/s and a lock-in time constant ≤ 1 s.

The Si $L_{2,3}VV$ Auger spectra between 40 and 85 eV of the several adsorption experiments are shown in fig. 1. The Si $L_{2,3}VV$ spectrum of a freshly cleaned silicon surface is shown in fig. 1a. We could resolve peaks at 43, 54, 74, 81, and 91 eV. The 91 eV is not shown in fig. 1. The peaks at 81 and 91 eV are associated with real Si $L_{2,3}VV$ Auger transitions [14]. The 91 eV peak is called the Si main peak for the Si–Si bond. The peak at 74 eV is the first plasmon loss peak of the main peak [15–17]. It is suggested that the 54 eV peak is the second order plasmon loss peak of the main peak [14,17], but this is not generally accepted [15]. The Coster–Kronig transition ($L_1L_{2,3}V$) can be attributed to the peak of 43 eV [14].

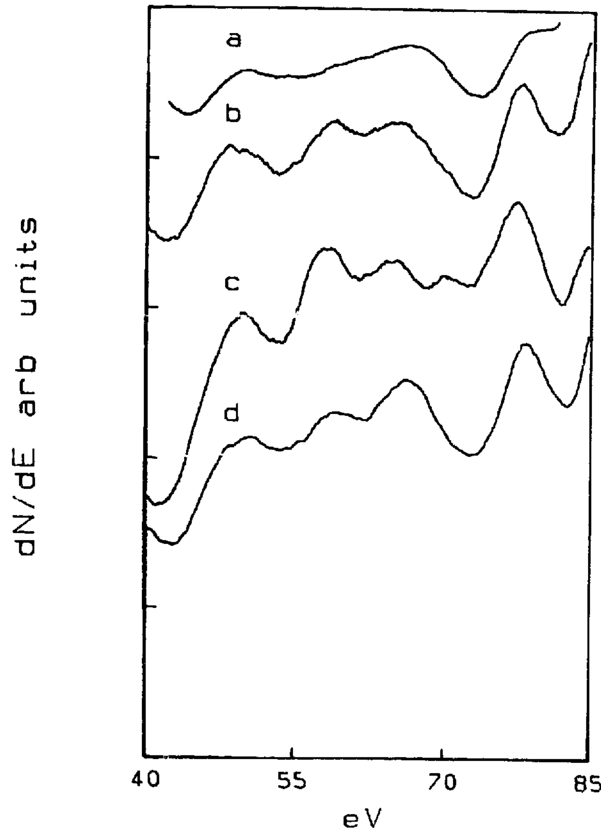

Fig. 1. Si $L_{2,3}VV$ spectra of (a) clean Si(100); (b) Si(100) exposed to 2.0×10^3 L NO at 300 K; (c) Si(100) exposed to 2.0×10^3 L NO at 550 K; (d) Si(100) surface in (c) heated to 1050 K after finishing the exposure.

Fig. 1b shows the spectrum for NO adsorption at 300 K on Si(100). When the pressure is kept constant (2.5×10^{-6} Torr) we obtained equal Si $L_{2,3}VV$ Auger spectra for exposures between 2.0×10^2 and 2.0×10^4 L. The main peak at 91 eV is shifted downwards by 1 eV. Due to adsorption of NO at a silicon surface new peaks are observed at 62 and 83 eV. The 83 eV peak as well as the 62 eV peak are well known in $L_{2,3}VV$ Auger measurements of nitridation on the Si(111) surface [7,18–20], however the Si $L_{2,3}VV$ Auger transition at 83 and 62 eV can also be assigned to the Si–O bond [9]. The broadening of the Auger transition at 83 eV in fig. 1b, relative to that of fig. 1c, suggests that two adjacent peaks are involved, which are due to a slight degeneration of the strength of the Si–N and the Si–O bond. This observation is consistent with the KLL Auger measurements, which yield a concentration of $7 \pm 1\%$ nitrogen and $6 \pm 1\%$ oxygen on the silicon surface at all performed exposures. Therefore, we believe that at 300 K these bonds contribute both to the 62 eV peak and the 83 eV peak.

When the sample, heated at 550 K, was exposed to 2.0×10^3 L NO (fig. 1c) the same peaks were observed as in fig. 1b, but also a new peak emerges at 69 eV. In ref. [9] and references therein it is concluded that this peak can be associated with the forming of more bulk-like oxide. This bulk-like oxide can be formed, after dissociation of the NO molecule, by allowing diffusion of atomic oxygen through the surface layer [21,22]. The absence of the Auger transition at 69 eV in the Si $L_{2,3}VV$ spectrum at 300 K (fig. 1b) suggests therefore molecular adsorption of NO. That dissociation may occur is also consistent with the KLL Auger measurements, which yield a concentration of $12 \pm 1\%$ nitrogen and $7 \pm 1\%$ oxygen on the silicon surface. These percentages agree with the results of Wiggins et al. [1] for the Si(111) surface. The difference in the amount of the oxygen and nitrogen concentration on the surface can be explained by the increase of the activation energy through heating of the silicon sample and new adsorption sites become available due to desorption of SiO [1].

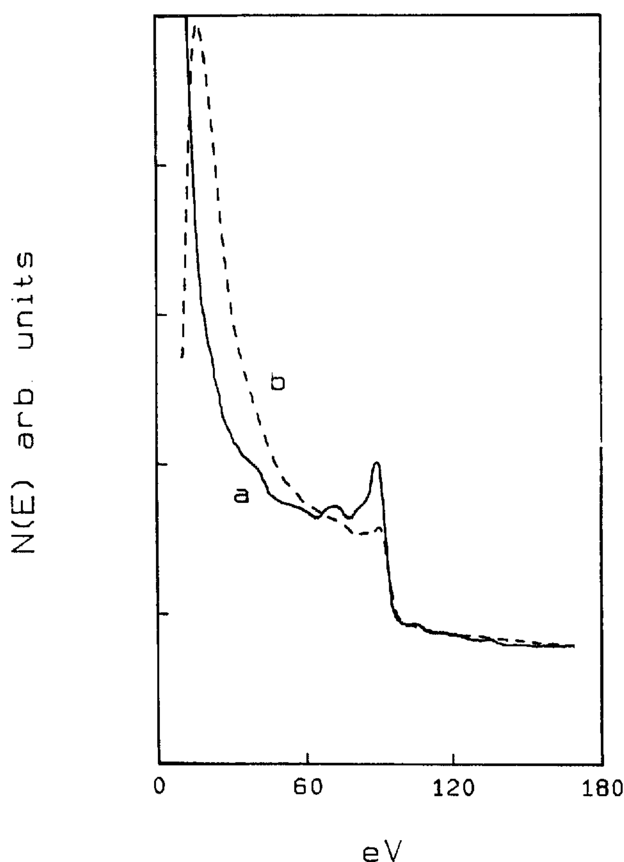

Fig. 2. The shape of the background in the $N(E)$ Auger spectrum between 10 and 180 eV of (a) clean Si(100) surface (solid line); (b) Si(100) surface exposed to 2.0×10^3 L NO at 300 K (dashed line).

After exposing the sample to NO at 550 K, the sample was heated to 1050 K. The Auger transition at 69 eV disappeared, but other peaks still could be observed (fig. 1d). No oxygen could be detected with Auger KLL measurements. The amount of nitrogen (12%) remained the same. These peaks can be fully attributed to the Si–N bonds, because of the desorption of oxygen as SiO [1]. The broadening of the 83 eV peak in fig. 1d became significantly smaller as has been observed in fig. 1b and supports the suggestion of the occurrence of two adjacent peaks at 83 eV at 300 K. The slope of the curve, in the lower energy part of the Si $L_{2,3}VV$ Auger spectra after adsorption of NO is increased. An enlargement of the background is responsible for this phenomenon (fig. 2). The difference in the background after adsorption of NO can be explained by the change in the potential of the surface due to chemisorbed NO molecules on the Si(100) surface, and caused a difference in the energy distribution of the secondary electrons [17].

The Auger transition at 54 and 74 eV which appear in all spectra of fig. 1 is not well understood yet. The 74 eV peak can be associated with the first order plasmon loss, but the difference in its shape could be an indication that the Si–N bonds as well as the Si–O bonds are involved too in this transition.

In summary, we conclude that at room temperature NO is adsorbed as a molecule at the Si(100)2 × 1 surface. Furthermore, it is argued that the broadening in the Auger transition at 83 eV at 300 K is composed of two nearby peaks. These two peaks could be attributed two different kinds of chemical bonding, Si–N and Si–O. Dissociation of the NO molecule is observed during adsorption when the sample is heated at 550 K.

We also want to emphasize, that careful measurements of the $L_{2,3}VV$ Auger spectra can lead to a more definite conclusion about the binding state of an element adsorbed on a silicon surface.

References

[1] M.D. Wiggins, R.J. Baird and P. Wynblatt, J. Vacuum Sci. Technol. 18 (1981) 965.
[2] D.R. He and F.W. Smith, Surface Sci. 154 (1985) 347.
[3] M. Miyamura, Y. Sakisaka, M. Nishijima and M. Onchi, Proc. 7th Intern. Congr. and 3rd Intern. Conf. on Solid Surfaces, Vienna, 1977.
[4] F. Boszo and Ph. Avouris, Abstract SS1-We A2 in the "final program" of the 10th Intern. Conf. on Solid Surface and 33rd Natl. Symp. of the American Vacuum Society.
[5] T. Isu and K. Fujiwara, Solid State Commun. 42 (1977) 477.
[6] M. Nishijima and K. Fujiwara, Solid State Commun. 24 (1977) 101.
[7] M. Nishijima, H. Kobayashi, K. Edamota and M. Onchi, Surface Sci. 137 (1984) 437.
[8] M. Nishijima, K. Edamoto, Y. Kubota, H. Kobayashi and M. Onchi, Surface Sci. 158 (1985) 422.
[9] E.G. Keim, L. Wolterbeek and A. van Silfhout, Surface Sci. 180 (1987) 565.
[10] A.G.B.M. Sasse, P.M. Kleinherenbrink and A. van Silfhout, Surface Sci., to be submitted.
[11] D.E. Ramaker, in: Spectroscopy as a Probe of Valence Bonds and Bands, Vol. 4 of Chemistry and Physics of Solid Surfaces, Eds. R. Vanselow and R. Howe (Springer, Berlin, 1982) p. 19.

[12] R. Weissmann and K. Muller, Surface Sci. Rept. 1 (1981) 251.
[13] L.E. Davis, N.C. MacDonald, P.W. Palmberg, G.E. Riach and R.E. Weber, Handbook of Auger Electron Spectroscopy, 2nd ed. (Perkin-Elmer, Eden Prairie, MN, 1976).
[14] J.T. Grant and T.W. Haas, Surface Sci. 23 (1970) 347.
[15] H.G. Maguire and P.D. Augustus, J. Phys. C4 (1971) 283.
[16] R. Weissmann, W. Schnellhammer, R. Koshatzky and K. Muller, Appl. Phys. 14 (1977) 283.
[17] W.M. Mularie and T.W. Rusch, Surface Sci. 19 (1970) 469.
[18] A.G. Schrott, Q.X. Su and S.C. Fain, Jr., Surface Sci. 123 (1982) 223.
[19] A.G. Schrott and S.C. Fain, Jr., Surface Sci. 123 (1982) 204.
[20] R. Hezel and N. Lieske, J. Appl. Phys. 51 (1980) 2566.
[21] B. Lang, P. Scholler and B. Carriere, Surface Sci. 99 (1980) 103.
[22] C.M. Garner, I. Lindau, C.Y. Su, P. Pianetta and W.E. Spicer, Phys. Rev. B19 (1979) 3944.