

SURFACE SCIENCE LETTERS

Si-O BOND FORMATION ON THE Si(100)-2 × 1 SURFACE AT THE EARLY STAGE OF OXIDATION AS OBSERVED BY AES

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Auger electron spectroscopy is used to follow the initial chemisorption of oxygen on a Si(100)-2 × 1 surface. Careful measurements of the Si L₂₃VV spectra reveal, for the first time, fine structure in the region between 80 and 85 eV. For the clean Si(100) surface a peak at 81 eV has been found. Oxygen chemisorption on the Si(100) surface is associated with the appearance of a new well defined peak at 83 eV in addition to the peak at 81 eV. Since these features are discernible for the (100) crystal face, the 83 eV transition is assigned as due to the Si-O bond.

Surface oxidation studies of silicon using Auger electron spectroscopy (AES) have been numerous. It is well known that in the initial oxidation stage the L₂₃VV Auger spectra reveals the presence of additional chemical states which are not attributable to either Si in SiO₂ or to bulk Si [1-4]. These oxygen induced states have been observed between 60 and 90 eV. Much work has been focussed on a peak around 80-85 eV as indicating the surface condition [1-4]. This peak can be attributed to an intermediate oxidation stage, SiO_x (x ~ 1), which could be the result of Si-O bond formation or also of structural defects in the silicon dioxide [1-3]. However, in most experiments the clean Si L₂₃VV spectrum shows a shoulder in this region. This shoulder has been interpreted as due to mainly L₂₃V₃V₃ transitions [5] although it is at present still not fully understood. Its position is in close proximity to that of the main peak (L₂₃V₁V₁ transition), which, being particularly sensitive to surface conditions, can to a variable degree mask the shoulder. Up to now most experimental L₂₃VV Auger spectra of oxygen covered silicon surfaces have not revealed any distinction between the (possible L₂₃V₃V₃) clean Si peak and the oxygen induced peak between 80-85 eV [1-8]. In view of the above, assignment of the transition around 80-85 eV due to only Si-O bonds [1,2,4] is questionable.

In this letter it will be shown that in the Si L₂₃VV Auger spectrum two peaks can be resolved between 80 and 85 eV upon oxygen exposure of a clean Si(100)-2 × 1 surface. The first peak is already present for the clean Si(100)-2 × 1 surface, the second appears with oxygen exposure.

The experiments were performed in a stainless steel UHV system having a base pressure in the mid 10^{-11} Torr region. The silicon sample ($10 \times 30 \times 0.4$ mm) was made from a 2000 Ω cm, p-type (boron-doped) crystal in the (100) orientation, purchased from Wacker-Chemitronic. Prior to mounting the crystal was ultrasonically cleaned in ethanol. No further chemical treatments were used. The sample could be resistively heated by the passage of a DC current.

A clean surface was obtained by cycles of sputtering (800 eV Ar ions, $2 \mu\text{A cm}^{-2}$, 20 min, angle of incidence 45°) and annealing (800°C , 60 min). During sputtering the crystal was also heated to $\sim 600^\circ\text{C}$ for a few minutes, followed by slow cooling. This procedure yields reproducible sharp (2×1) two domain LEED patterns. In the Auger spectra no elements other than Si could be detected (peak-to-peak ratio C/Si $< 5 \times 10^{-4}$ in the $dN(E)/dE$ mode).

The electron spectrometer was a retarding field four-grid LEED-Auger system with transparent collector (Riber OPR 304). Auger transitions were excited by an electron beam (Riber CER 306 electron gun) at grazing incidence. A Wallis PM2DCP (10–2000 V) high-voltage unit was used to accelerate the primary electrons. Because of the improved signal-to-noise ratio compared with the original set up (Riber ACE 376N power supply with a Bertrand 603-50P (0–5 kV) high-voltage unit built in) low sweep-rates (< 0.5 eV/s) at relatively low modulation voltages (1–2 V ptp) were now possible. The spectra were recorded in the second derivative mode by phase sensitive detection.

Operating conditions: primary beam energy 2 keV; primary current density $\sim 300 \mu\text{A cm}^{-2}$; modulation 2 V ptp; sweep-rate ≤ 0.5 eV per time constant. During all O_2 exposures no filaments were lit in the reaction chamber.

Fig. 1a shows the actual $L_{23}\text{VV}$ Auger spectrum of a clean Si(100)- 2×1 surface between 50 and 90 eV. Note the well-defined peak at 81 eV (negative excursion). Fig. 1 further shows the $L_{23}\text{VV}$ Auger spectra for several stages of the oxygen chemisorption on Si(100) at 300 K ranging from a clean to an almost saturated surface. Each curve (b–f) was obtained after exposing a cleaned surface to the indicated oxygen dose in order to avoid beam assisted effects. In addition to the peak at 81 eV (a–f) a second one is seen to develop at 83 eV (b–f), the magnitude of this oxygen induced peak being proportional to the number of dangling bond surface states which have disappeared [9]. Other peaks emerge at 62 eV (b–f) and ~ 70 eV (f). Fine structure with peaks at 62, 70 and 83 eV was shown to correspond to an unstable silica-like species SiO_x ($x < 2$) [2,3]. So far most O_2 adsorption studies using AES have been performed on the Si(111) crystal face. Apart from a few exceptions [10–13] all $L_{23}\text{VV}$ Auger spectra show a more or less weak shoulder around 80–85 eV for the clean silicon surface (Grant and Haas [10], Chung and Jenkins [11] and Muñoz et al. [13] even find two peaks at ~ 81 and ~ 83 eV for the Si(111)- 7×7 surface). Upon oxygen exposure this shoulder is replaced by a well-defined peak; even the relatively sharp feature at ~ 81 eV in the $L_{23}\text{VV}$ spectra of

Si(111)-2 × 1 completely vanishes [12] and for Si(111)-7 × 7 [13] it almost completely vanishes.

The experimental results of this study show, however, two clearly discernible features at 81 and 83 eV, especially in the early oxygen chemisorption stage (figs. 1b and 1c).

The oxygen induced peak at 83 eV is new and does not originate from a position in the Si L₂₃VV Auger spectrum where a “clean Si” feature is also observed as in case of the L₂₃VV Auger spectra from the Si(111)-7 × 7 surface [10,11,13].

Assignment therefore, of the Si L₂₃VV 83 eV transition due to Si-O bond formation in the early chemisorption stage is less ambiguous. It is suggested [2] that the 83 eV transition has almost pure O_{2p} antibonding character.

In conclusion, the present study demonstrates that careful measurements of the Si L₂₃VV Auger lines reveal fine structure between 80 and 85 eV for the

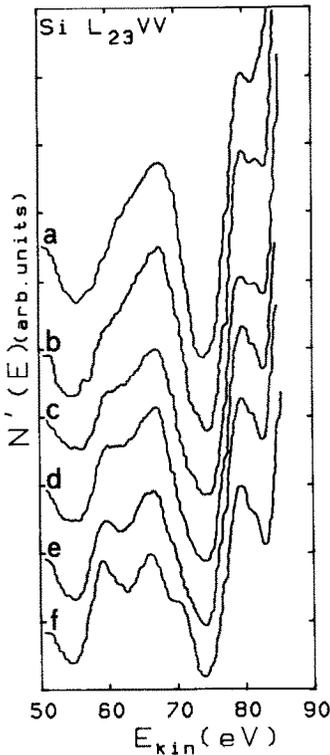


Fig. 1. Si L₂₃VV Auger spectrum for five chemisorption stages of oxygen on Si(100). Minimal beam effects. (a) The clean Si(100)-2 × 1 surface; the surface exposed to O₂; (b) 2 L, (c) 4 L, (d) 8 L, (e) 12 L, (f) 85 L (1 L ≈ 1 × 10⁻⁶ Torr s). For operating conditions, see text.

Si(100) surface. The oxygen induced peak at 83 eV has been shown to be a new feature. Further, the experimental $L_{23}VV$ curve (50–90 eV) for the Si(100)-2 × 1 surface appears to be different from the curve for the (annealed) Si(111)-7 × 7 surface [10,11,13], the $L_{23}VV$ curve for the cleaved (111) surface [10,12] showing, however, close resemblance.

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