

SURFACE SCIENCE LETTERS

**COMMENT ON 'NITRIC OXIDE ADSORPTION ON THE Si(100)(2 × 1) SURFACE
– A VIBRATIONAL STUDY, BY Y. TAGUCHI, M. FUJISAWA, Y. KUWAHARA, M. ONCHI
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Both molecular and dissociative adsorption behaviour of NO on the Si(001)(2 × 1) surface at room temperature have been reported. This contradicting difference in adsorption behaviour was obtained from the application of different experimental methods. The attention must be focused on the various sample preparation techniques used and on the influence of primary excitation sources of the different experimental techniques applied on this adsorbed system.

The complex adsorption behaviour of simple gaseous molecules like O₂ and NO on the Si surface is still subject of discussion [1–4]. The attention in these discussions is focused as to whether the adsorption is molecular, dissociative or even a combination [1–3] and, more recently, if a stable molecular precursor state is involved [4]. From the reported differences in adsorption behaviour of the adsorbates on the surface it may be argued that the experiments are influenced to a varying degree by sample preparation conditions and/or the interaction of electrons, ions or photons of the applied analytical techniques with the adsorbed layer.

Recently, some contradictory results with regard to the adsorption behaviour of NO on the Si(001)(2 × 1) surface have been reported. From their X-ray photoelectron spectroscopy (XPS) and ion-scattering spectroscopy (ISS) experiments, Avouris et al. [2] arrived at the conclusion that NO exists on the Si(001) surface at 90 K in both a dissociated and in a weakly adsorbed molecular form. Their sample was cleaned by Ar⁺ bombardment at 2 keV followed by annealing at 1150 K. Ekwelundu and Ignatiev [5] performed photodesorption experiments on a clean Si(001) surface prepared by Ar⁺ bombardment at 2.5 keV followed by annealing at 800 K. They found that at

300 K the photodesorption only showed NO species, indicating molecular adsorption of NO. Recently, Sasse and van Silfhout [3], reported also molecular adsorption at 300 K as derived from their spectroscopic differential reflectometry (SDR), Auger electron spectroscopy (AES) and low energy electron diffraction (LEED) measurements. Their clean Si(001) surface was prepared by Ar⁺ bombardment at 800 eV followed by annealing at 1100 K. The latter two experimental results [3,5] are in contrast with those reported by Taguchi et al. [1] who, applying high resolution electron energy loss spectroscopy (HREELS), did not find any indication of molecular adsorption at 300 K. Their Si(001) surface was cleaned by cycles of Ar⁺ bombardment and flash annealing. Although they did not mention the annealing temperature, it is well known that flashing cycles may lead to a drastic increase in the number of defects [6]. In general, the reconstruction of the Si(001) surface is sensitive to the cleaning procedure, especially the anneal procedure [7,8]. The most obvious difference in NO adsorption behaviour can be seen from LEED observations at saturation; whereas Sasse and van Silfhout [3] report a virtually unchanged 2 × 1 two domain reconstruction at a saturation coverage of 7% N and 7% O, Taguchi and coworkers [1] report a complete dis-

appearance of the ordered LEED image at saturation. The fractional N/O coverage at this stage is however, not provided by their paper. The LEED results of Taguchi et al. [1] compare favourably with the change of the LEED pattern upon exposing the Si(001) surface to N₂O up to saturation (0.85 ± 0.15 monolayer atomic oxygen) [9], in which case the oxygen atoms go into bridging positions, as confirmed by recent calculations [10]. The observations with HREELS by Taguchi et al. [1] clearly indicate an identical bridge bonding position for the dissociated N and O atoms. Since the LEED pattern at saturation observed by Taguchi and coworkers [1] is so much different from the one obtained by Sasse and van Silfhout [3], one must conclude that both groups have studied a different system. Upon surveying the reports [1,3] one difference in the experimental procedure is obvious without doubt, that is the sample surface cleaning. The sensitivity of the adsorption kinetics towards the sample cleaning procedure is supported by the results of Ekwelundu and Ignatiev [5], who also found evidence of purely molecular adsorption of NO with a cleaning procedure comparable to the one used by Sasse and van Silfhout [3].

Additional evidence of molecular NO adsorption at the Si(001)(2 × 1) surface at room temperature is given by cluster calculations of Sasse and van Silfhout [3]. They have shown that dissociative adsorption of NO at 300 K is thermodynamically unfavourable, leading only to molecularly adsorbed NO at a relatively low saturation coverage which is in agreement with their experimental findings. Their calculations also show that the energy barrier for dissociation is relatively low as evidenced by their experimental results; dissociative adsorption was found to occur already at 550 K. They also found a significant influence of the primary electron beam in AES on the adsorbed layer. The AES spectra were found to alter in shape after a few minutes of exposing the surface to the electron beam. Similar effects have been

reported by Bermudez et al. [11] by analysing the NO adsorbate on GaAs(110) using photoemission spectroscopy. This "primary beam" artefact may also explain the contradictory reports in literature on the adsorption behaviour of NO on Si(001) [1–3,5].

In order to investigate the adsorbed state of a molecule, the application of experimental techniques which probe the surface region using high energy fluxes or heavy particles like ions (ISS), electrons (EELS, AES, LEED) and photons (XPS, UPS) should be considered with great care. The influence of these primary excitation sources on the adsorbed system may be severe, leading, e.g., to dissociation of the molecularly adsorbed species. Even if only dissociated species are found molecular adsorption of simple molecules, in particular in the initial stage, cannot be excluded. The use of techniques having an essentially non-perturbing nature like SDR and photodesorption, that can be employed during exposure, are therefore more appropriate candidates to study whether gas adsorption is molecular or not.

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