Chemical Physics Letters 511 (2011) 270–276

Contents lists available at ScienceDirect

Chemical Physics Letters

journal homepage: www.elsevier.com/locate/cplett

Co-adsorption of NH_3 and SO_2 on quartz(0 0 0 1): Formation of a stabilized complex

M.L. Grecea [a,b], M.A. Gleeson [b], W. van Schaik [c], A.W. Kleyn [b,d,e,*], F. Bijkerk [b,f]

[a] Materials Innovation Institute M2i, P.O. Box 5008, 2600 GA Delft, The Netherlands
[b] FOM-Institute for Plasma Physics Rijnhuizen, P.O. Box 1207, 3430 BE Nieuwegein, The Netherlands
[c] ASML B.V., De Run 1110, 5503 LA Veldhoven, The Netherlands
[d] Leiden Institute of Chemistry, Leiden University, P.O. Box 9502, 2300 RA Leiden, The Netherlands
[e] Van 't Hoff Institute for Molecular Sciences, University of Amsterdam, P.O. Box 94157, 1090 GD Amsterdam, The Netherlands
[f] MESA+ Institute for Nanotechnology, University of Twente, P.O. Box 217, 7500 AE Enschede, The Netherlands

ARTICLE INFO

Article history:
Received 22 December 2010
In final form 27 June 2011
Available online 30 June 2011

ABSTRACT

We have investigated the co-adsorption of NH_3 and SO_2 on the quartz(0 0 0 1) surface by TPD and RAIRS. A surface complex is formed as a result of various relative exposures of NH_3 and SO_2, irrespective of dosage order. However, the relative molecular composition of the complex is dependent on the dosage order. Higher desorption temperatures of NH_3 and SO_2 from the co-adsorbed systems, as compared with the isolated adsorbates, demonstrate mutual stabilization in the adlayer. Formation of hydrogen bonds between NH_3 and SO_2 is suggested based on the strong decrease in IR cross-section of the symmetric deformation and asymmetric stretch modes of NH_3 upon co-adsorption of SO_2 and of the symmetric stretch mode of SO_2 upon co-adsorption of NH_3.

1. Introduction

The surface science approach can be used to study surface processes relevant to highly diluted gas molecules in a host gas environment. For instance, impurity levels in the N_2 gas flow of photolithography equipment can be mimicked by an Ultra-High Vacuum (UHV) environment. NH_3 and SO_2, which are present as trace impurities in the flow, are reported to be involved in contamination of optical surfaces in such systems [1–4]. Other fields in which heterogeneous processes between NH_3 and SO_2 molecules are relevant include planetary atmospheres and components of interstellar dust [5,6] and air quality enhancement by destruction via direct reaction [7,8].

Individually, the interactions of NH_3 and SO_2 with metal surfaces have received a great deal of attention. Adsorption of NH_3 has been intensively studied on Ru, Ag, Cu and Ni surfaces [9–14]. Its properties on metals and semiconductors have been recently reviewed [15]. Temperature-Programed Desorption (TPD) spectra from Ru(0 0 0 1) [9], Ru(1 1 $\bar{2}$ 0) [11] and Ag(1 1 1) [12] are characterized by two high temperature features attributed to desorption of NH_3 molecules bound directly to the surface. An additional feature assigned to 2nd layer NH_3 has also been identified in TPDs from Ru [9,11]. Three desorption states corresponding to the few monolayers that precede multilayer formation on Cu(1 1 1) have been reported [13]. Multilayer-like NH_3 condensed on closed-packed transition metal surfaces develops a typical low temperature TPD peak [9–13]. Vibrational studies of NH_3 adsorption on Ru(0 0 0 1) [10], Ni(1 1 0) [14], Ag(1 1 1) [12] and polycrystalline Ag [16] surfaces have been reported. A typical infrared spectrum of NH_3 is characterized by the presence of vibrational bands in the 1050–1150 cm^{-1} (symmetric deformation (‘umbrella’) mode), the 1550–1650 cm^{-1} (asymmetric deformation mode) and the 3200–3400 cm^{-1} (NH symmetric and asymmetric stretch modes) regions. However, complete attenuation of symmetric deformation and asymmetric stretch modes has been observed for certain coverages of NH_3 on Ru(0 0 0 1) [10] and Ni(1 1 0) [14], which was explained by unusually strong hydrogen bonds between the admolecules [10,12].

Adsorption of SO_2 on various metal surfaces has been comprehensively studied [17–23]. TPDs of SO_2 from the different surfaces show many similarities to each other. Desorption temperatures vary with the substrate and its structure. Two main features – assigned to desorption of chemisorbed SO_2 and from multilayer SO_2 – can be identified in the spectra [17,19,20]. These features only were observed from Au(1 1 1) [19] and Pt(1 1 1) [22], whereas an intermediate desorption feature was evident for SO_2 on Ag(1 1 1), Ag(1 1 0), Ag(1 0 0) and Cu(1 1 1) [17,20]. This was assigned to species interacting with both the metal surface and adjacent adsorbates in a compressed monolayer structure [17]. On several surfaces, additional high-temperature desorption features have been assigned to desorption of SO_2 from defects [17,18,20]. Vibrational studies of SO_2 on metal substrates have also been reported

---

* Corresponding author at: FOM-Institute for Plasma Physics Rijnhuizen, P.O. Box 1207, 3430 BE Nieuwegein, The Netherlands. Fax: +31 30 6031204.
E-mail address: A.W.Kleyn@rijnhuizen.nl (A.W. Kleyn).

0009-2614/$ - see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.cplett.2011.06.076

[24–26]. Outka et al. studied SO_2 adsorption on Ag(1 1 0) using HREELS at 100 K [24]. A loss feature at 1005 cm^{-1} was assigned to the 1st layer of SO_2, while the spectra of multilayer SO_2 showed loss features at 1145 cm^{-1} (symmetric SO stretch) and 1320 cm^{-1} (asymmetric SO stretch) [24]. RAIRS studies of solid SO_2 on polycrystalline Au showed a doublet at 1142.8 and 1140.1 cm^{-1} due to symmetric SO stretch of $^{32}SO_2$ and $^{34}SO_2$, as well as two asymmetric SO stretches at 1311 and 1322 cm^{-1} [25,26].

Studies of adsorption of NH_3 or SO_2 on dielectric surfaces are rather scarce. TPD of NH_3 was used to probe acid sites on a series of aluminium fluoride-based solid catalysts prepared by various synthesis pathways [27]. Desorption temperatures and relative intensities of the TPD features depended on the strength and quantitative distribution of Lewis acid sites. Adsorption of SO_2 on the CsF(1 0 0) surface was studied by high-resolution polarization infrared surface (PIRS) spectroscopy [28]. Three adsorption phases were identified as a function of exposure. The first layer converts from phase I to phase II with increasing exposure, while phase III shows the characteristics of physisorbed multilayers.

Co-adsorption of molecules on various surfaces has received much attention with regard to understanding of interaction processes [29]. Studies of co-adsorption on dielectric surfaces benefit from the absence of charge transfer with the substrate. Undisturbed interaction between co-adsorbates can thus be investigated. To our knowledge, no study of $NH_3 + SO_2$ co-adsorption on dielectric surfaces has been reported to date. Unraveling the co-adsorption behavior of NH_3 and SO_2 on the quartz(0 0 0 1) surface may provide valuable information for developing strategies to control gaseous molecular contaminants in semiconductor manufacturing facilities. We study the co-adsorption by means of TPD and Reflection Absorption Infra-Red Spectroscopy (RAIRS). New features appear at higher temperatures in TPD spectra of the co-adsorbed layers, as compared with those of the respective pure layers, irrespective of the dosage order. The effect of co-adsorption on RAIRS spectra is shown. There is a significant reduction of the asymmetric stretch and 'umbrella' modes of NH_3 upon addition of SO_2. Likewise, the symmetric stretch mode of SO_2 is reduced upon addition of NH_3. These effects can be attributed to hydrogen bonding between NH_3 and SO_2 molecules.

2. Experimental

The experiments were performed in an UHV chamber with a base pressure of 4×10^{-10} mbar. A $10 \times 10\ mm^2$, 1 mm thick quartz(0 0 0 1) single-crystal, previously checked by Laue diffraction (Surface Preparation Laboratory), was mounted on a precision Thermionics XY translation stage. It was in direct contact with a liquid nitrogen reservoir for cooling and could be radiatively heated from the rear with a W filament. A ~400 nm thick molybdenum thin film was pre-deposited on the back of the sample. The sample temperature was monitored via a type K thermocouple cemented to the Mo film near the edge of the crystal. Daily surface cleaning before measurements consisted of twice flashing to 450 K followed by twice annealing at 450 K for 1 min. Thermal treatment ensured the removal of adsorbed water, but had little effect on the number of surface hydroxyl groups [30,31]. Surface cleanliness was confirmed by the absence of desorbing species during TPD experiments performed without pre-dosage. No other structural or defect-sensitive tools were utilized.

For TPD experiments, the sample was exposed (at 85 K) to NH_3 (99.98% purity, Messer) and SO_2 (99.98% purity, Linde Gas) using two independent directional dosers. Directional dosing was employed to counter the poor pumping of NH_3 and SO_2. During exposure the dosers were placed ~5 mm in front of the crystal surface. The pressure increase during dosing was 1×10^{-10} mbar with respect to the base value. The gas phase species (NH_3 at $m/z = 17$; SO_2 at $m/z = 64$) were monitored during dosing and TPD via a differentially-pumped Quadrupole Mass Spectrometer (QMS, Balzers QS420/422) axially aligned along the surface normal. The heating rate during TPD was 2 Ks^{-1}.

Coverages of NH_3 and SO_2 were converted to monolayers (ML) based on the total integrated areas of TPDs relative to the integrated area of the saturated NH_3 α_2 and SO_2 β_2 desorption features (see later). We consider the α_2 and β_2 features as corresponding to the first monolayer of NH_3 and SO_2, respectively, based on comparison of our desorption traces with literature [13,32,33]. Molecular sticking probabilities have not been determined for our dosings. However, for adsorption at 85 K the uptake curves of both NH_3 and SO_2 were linear as a function of exposure across the full exposure range studied. For SO_2 adsorption, the uptake curves remained linear for adsorption temperatures up to ~94 K. In contrast, the uptake rate for NH_3 multilayers decreased progressively as the sample temperature was increased from 85 K and only a monolayer coverage could be produced at >91 K.

For the RAIRS experiments (which were performed at a different sample position) background dosing of NH_3 and SO_2 was employed. The resulting exposures are reported in Langmuirs (L). No correction for the gas-dependent ion-gauge sensitivity was applied to these values. RAIR spectra were recorded at a sample temperature of 85 K with an Agilent 670-IR Fourier Transform Infra-Red (FTIR) spectrometer. The IR beam entered the chamber through differentially pumped KBr windows at 85° with respect to the surface normal and was detected by an external liquid nitrogen cooled mercury–cadmium–telluride detector. Typically, 64 scans were averaged at 8 cm^{-1} resolution with triangular apodization. The external optical beam path was purged with dry nitrogen.

3. Results and discussion

TPD spectra of various coverages of NH_3 on quartz(0 0 0 1) are depicted in Figure 1a. For 0.2 ML coverage, a broad feature centered at 160 K (α_1) can be observed. As the coverage increases the α_2 feature emerges, with an earlier leading edge and a peak at 103 K. This can be attributed to increasing repulsion between NH_3 molecular dipoles, with adsorption at surface defects producing the higher temperature feature evident at the lowest coverage. Similar behavior was observed for NH_3 on Ru(0 0 0 1) [9] and Ru(1 1 $\bar{2}$ 0) [11] as well as for H_2S on the LiF(0 0 1) [33]. As mentioned above, we consider saturation of the α_2 feature as corresponding to adsorption of 1 ML of NH_3. All other NH_3 coverages are estimated on the basis of comparison to the integrated area of this trace. Above 1 ML, the NH_3 TPD spectra show characteristics typical of zeroth order desorption of multilayers, namely a common leading edge and a peak temperature that increases with exposure [9,11]. A TPD corresponding to 8.3 ML of NH_3 illustrates the multilayer desorption feature (α_3).

Figure 1b shows TPD spectra obtained following exposure of the quartz(0 0 0 1) surface at 85 K to SO_2. At 0.2 ML coverage, a broad desorption feature (β_1) appeared at 138 K. A β_2 peak with an earlier leading edge emerges at 114 K as SO_2 increases. Similar to NH_3, saturation of the β_2 feature is considered to represent adsorption of 1 ML and this trace is used as the basis for all other SO_2 ML estimations. The emergence of multi-layer desorption (β_3) is evident in the TPD of 1.7 ML of SO_2.

Figure 2 depicts the result of adsorbing 2 ML of SO_2 on a quartz(0 0 0 1) surface that has already been dosed with differing coverages of NH_3. The traces shown are for NH_3 coverages of 0.3 ML (i), 0.7 ML (ii), 1.3 ML (iii) and 6.3 ML (iv). A broad desorption feature (designated γ) with a desorption temperature significantly higher than that of the singly adsorbed species is present