

Adsorption on water-functionalized Si(001)-(2x1) surfaces

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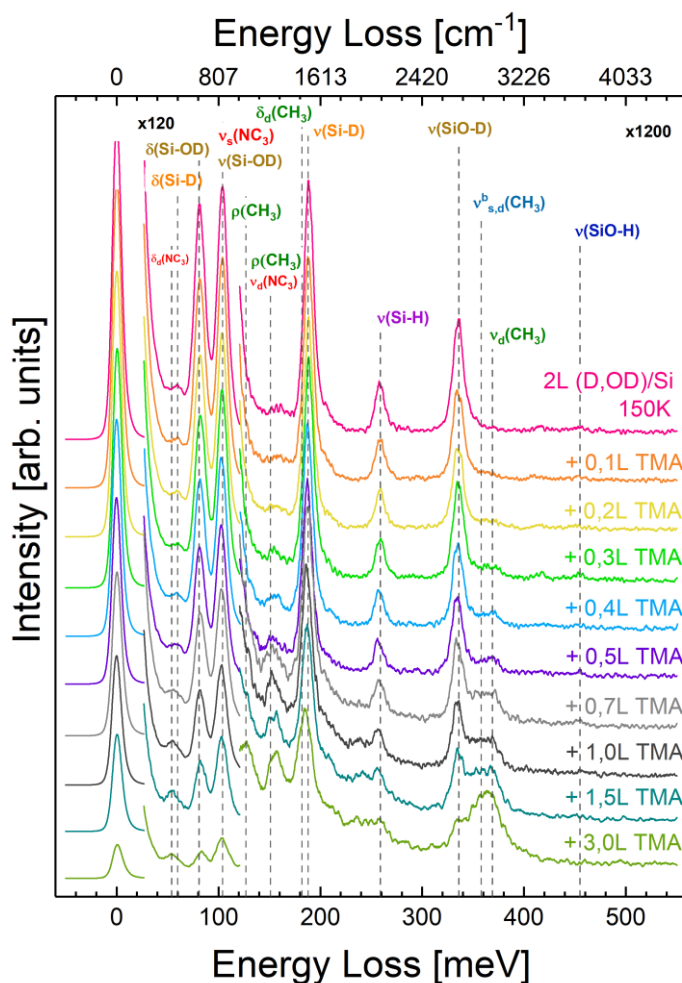
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The functionalization of the Si(001)-(2x1) surface by direct deposition of organic molecules has become an interesting topic for research as this way the surface reactivity can be specifically tuned to facilitate specific applications in the formation of organic/inorganic semiconductor hybrid structures. Here, a main problem is the large variety of possible adsorption geometries on the Si-surface leading to very inhomogeneously bound molecule layers. A possible solution to this problem is the use of an intermediate water layer enabling a better control of the adsorption processes due the reduction of possible adsorption sites and geometries. Surface bound hydroxyl-groups offer special bonding sites. To investigate the binding properties on those silanol-groups (Si-OH) and to examine the chemical reactivity we studied the vibrational modes of ammonia (NH₃) and trimethylamine ((CH₃)₃N) in the temperature range between 100K and 300K at adsorption on a water reacted Si(001)-(2x1) surface using high resolution electron energy loss spectroscopy (HREELS) together with photoemission spectroscopy (XPS) to determine changes in electronic configuration. Despite the similar reaction center (N lone pair electrons) of the amines, these molecules turn out as examples of strong and weak reactivity towards surface silanols, respectively.

NH₃ acts as a Lewis base towards surface silanols. Self-limited adsorption on the silanols in a proton-acceptor geometry (ammonia giving its lone pair to Si-OH) is found below 140K. Taking temperature dependent spectra, the adsorption and desorption kinetics were quantitatively determined and an activation energy for desorption of 0.41eV was found. In addition, there are indications for the growth of a small amount of dissociated ammonia on remaining isolated dangling bonds of the water covered surface.



Trimethylamine (TMA) adsorbs self-limiting and non-dissociative on the water reacted Si surface below 175K affecting only the Si-OH vibrational group. Time, temperature and coverage (see figure) dependent spectra as well as XPS measurements indicate, that the TMA N lone pair electrons are involved in the surface bonding, in either the proton acceptor geometry or the TMA protonation reaction (resulting in SiO⁻(CH₃)₃NH⁺). Compared to ammonia, TMA shows a more ambiguous adsorption behavior which is discussed, considering the intramolecular difference in binding conditions (methyl groups) and the smaller TMA saturation coverage due to the steric hinderance (TMA saturation coverage on clean Si(001)-(2x1) is about 0.25 ML).