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Adsorption, etching and photo-induced reactions at the Si(100)–CCl_4 interface

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Abstract. The adsorption, thermal and photochemical reactions of carbon tetrachloride on Si(100) were investigated using x-ray photoelectron spectroscopy and thermal desorption spectroscopy. Initial CCl_4 adsorption is dissociative at 175 K, with CCl_4 multilayer formation at higher exposures. Silicon chlorides are the only thermal desorption products above 300 K. The influence of UV radiation on the desorption products is discussed.

X-ray photoelectron spectra (XPS) recorded immediately after exposure of Si(100) at 175 K to CCl_4 are shown in figure 1(i)–(vi). There are two distinct chlorine 2p transitions, transition (a) appearing at low exposures and transition (b) growing at higher exposures. Following the highest exposure (vi), the silicon was heated in stages and XPS (vii)–(x) recorded. Chlorine 2p transition (b) and a carbon 1s transition (e) disappear on heating to 210 K. Chlorine 2p transition (a) and the chlorine 2s transition (c) remain to 620 K, and a new carbon 1s transition (d), corresponding to silicon carbide [1], appears.

Thermal desorption spectra (TDS) recorded following exposure of Si(100) at 175 K to CCl_4 show two desorption states α and β with desorption temperatures 470 K (E_a = 111 kJ mol^{-1}) and 810 K (E_a = 204 kJ mol^{-1}) respectively. The desorption products were $SiCl_4$ for the α-state and $SiCl_x$ for the β-state where $x \leqslant 4$. Following saturation of these states at about 25L exposure a third state γ appears at 185 K (E_a = 45 kJ mol^{-1}) corresponding to physisorbed CCl_4. Irradiation of the saturated surface with a 254 nm mercury lamp increases the population of the α-state and decreases the population of the γ-state; the β-state population is unchanged.

Comparison of the XPS and TDS results suggests chlorine 2p transition (b) and carbon 1s transition (e) arise from a physisorbed layer of CCl_4. Chlorine 2p transition (a) therefore arises from chemisorbed chlorine, suggesting initial CCl_4 adsorption is dissociative. The thermal desorption states α and β are similar to those found for the adsorption of Cl_2 on Si(100) [2]; accordingly the β-state is assigned to chlorine chemisorbed on silicon and the α-state to a silicon chloride corrosion phase. The TDS data suggest that UV irradiation enhances the population of this corrosion phase through the dissociation of physisorbed CCl_4. CCl_4 absorbs only weakly at 254 nm and the most likely mechanism involves photogenerated charge carriers created in the underlying Si.

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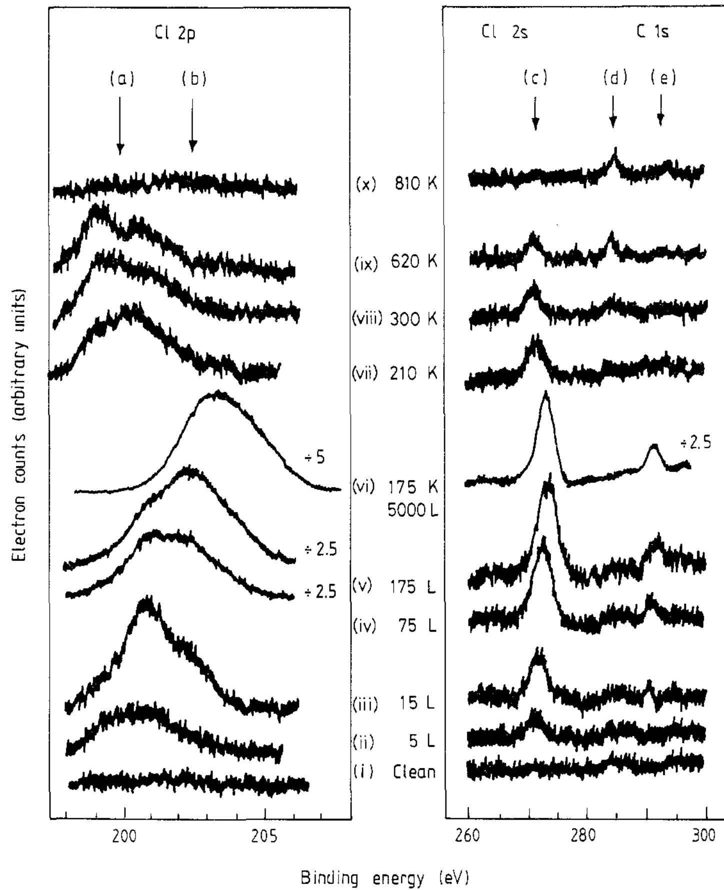

Figure 1. Mg Kα x-ray photoelectron spectra recorded following exposure of Si(100) at 175 K to CCl_4 ((i)–(vi)) and thermal treatment of the saturated surface ((vii)–(x)).

References

[1] Smith K L and Black K M 1984 *J. Vac. Sci. Technol.* A **2** 744–7
[2] Jackman R B, Ebert H and Foord J S 1986 *Surf. Sci.* **176** 183–92