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Surface spectroscopic and molecular beam studies of the reactions of trimethylaluminium on Si(100)

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Abstract. The reactions of trimethylaluminium leading to the deposition of Al on Si have been studied using LEED, XPS, AES, TDS and molecular beam scattering. Trimethylaluminium is shown to chemisorb on Si(100) subsequently decomposing to produce $\text{CH}_4(\text{g})$ and contaminated Al layers. Al catalyses the decomposition reaction and opens up a new reaction channel, resulting in the evolution of $\text{C}_2\text{H}_2(\text{g})$.

1. Introduction

The adsorption and reaction of organometallic compounds at semiconductor surfaces is of strategic interest in view of the increasing importance of chemical vapour deposition techniques in the epitaxial growth and metallisation of semiconductor materials [1]. Trimethylaluminium (TMA) is a potentially useful compound as regards the deposition of aluminium [2, 3]. At present almost nothing is known concerning the manner in which species such as TMA bond to surfaces, the nature of the surface species formed and the ways in which the surface modifies the reactivity of the organometallic compound. In order to study such points, we have investigated the adsorption and decomposition of TMA on Si(100) and in this paper we concentrate on the chemical processes involved in the reactions leading to deposition of Al films.

2. Experimental details

All the experiments were performed in two stainless-steel ultra-high-vacuum chambers. The first chamber was equipped with LEED optics, an Ar^+ -ion etching gun, a quadrupole mass spectrometer with a line-of-sight to the sample for thermal desorption studies and a hemispherical electron energy analyser with a Mg $\text{K}\alpha$ x-ray source. The second system was similar to the first except that in the surface analysis we employed RFA-based Auger facilities and the system was also equipped with an effusive molecular beam source permitting the determination of reaction products and probabilities.

The Si(100) sample was cleaned *in situ* by annealing to 1400 K after which the surface displayed a well formed (2×1) reconstruction (LEED) and surface contamination levels (XPS, AES) below 0.01 ML. TMA was admitted to the vacuum chambers by beaming directly

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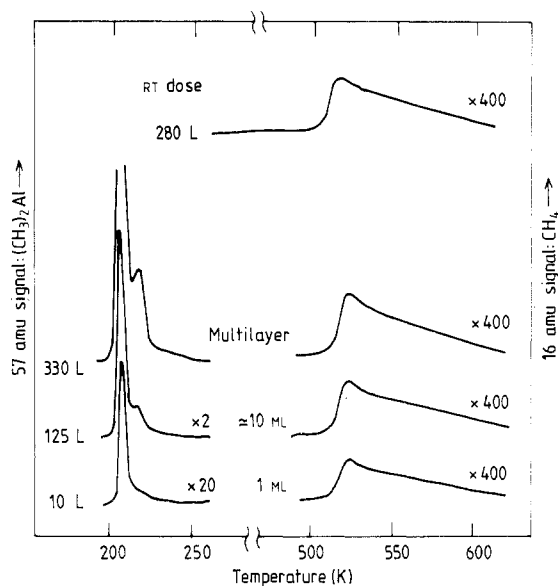


Figure 1. Thermal desorption spectra obtained following TMA adsorption on Si at 77 K. The low-temperature scans are tuned to $\text{Al}(\text{CH}_3)_2$ and the high-temperature scans to CH_4 .

onto the front face of the sample, to prevent reactions with chamber walls, and mass spectral analysis was carried out to verify the purity of the dosing gas.

3. Results

Experiments were performed in which surface phases formed by TMA adsorption at 77 K were analysed by XPS and TDS. Representative TDS data are shown in figure 1. A desorption peak at 210 K (figure 1) produced signals at various masses consistent with the cracking pattern of TMA, indicating desorption of this species. Small quantities of TMA were also found to desorb in the temperature range 300–500 K while methane desorption was seen at higher temperatures (figure 1). Plots of desorption yield versus gas exposure indicated that the low-temperature TMA peak grew in intensity with gas dose whereas the other peaks saturated at approximately monolayer coverage.

XPS measurements were also made as the surface phases formed by adsorption at 77 K were heated. In figure 2 we plot the intensities of Si, Al and C transitions as a function of the temperature to which the surface was heated. For high gas exposures (>100 L) the Si 2p peak cannot be observed at 77 K. However, as the surface is heated above the low-temperature TMA desorption peak, the Si 2p peak intensity grows rapidly as the Al and C peaks decrease. At high temperatures the Al and C peaks decrease further in intensity, ultimately to zero. Measurement of high-resolution spectra showed little variation in the binding energies of the Al and Si 2p transitions during the heating experiments. Marked changes in the Cls binding energy were seen, the peak shifting from 284.8 eV to 283.0 eV on the binding energy scale at temperatures above 700 K.

Molecular beam measurements were performed by exposing the sample to a beam of TMA at an effective pressure at the surface of 10^{-5} mbar. The surface temperature was

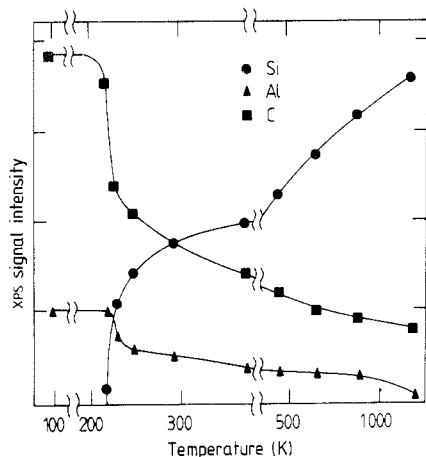


Figure 2. XPS signal intensity variations occurring during heating of a thick layer of TMA on Si.

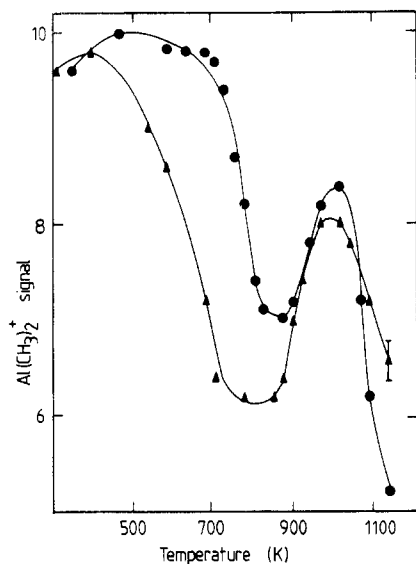


Figure 3. The partial pressure variation of TMA scattered from a sample, as a function of temperature. Triangles: Al-precovered Si substrate; circles: clean Si.

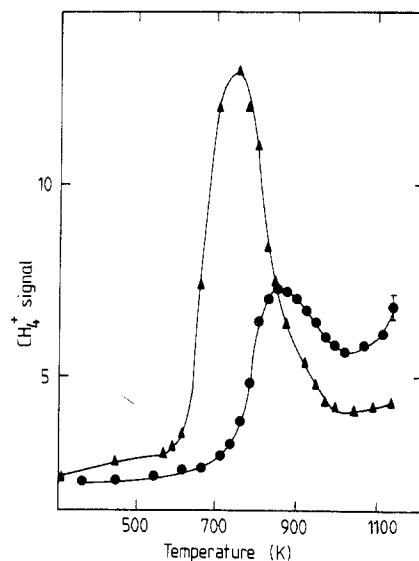


Figure 4. As figure 3, but for methane rather than TMA.

300 K when the beam was switched on and the sample was then heated slowly to determine the scattered products as a function of temperature. Representative data illustrating the variation in measured partial pressures of TMA and CH_4 are presented in figures 3 and 4. The results show that the intensity of back-scattered TMA decreases as the temperature increases with a reversal in this trend in the temperature range 850–1050 K. CH_4 is the main reaction product and the partial-pressure variations are therefore the reverse of what is seen for TMA. Acetylene was another reaction product (data not shown) with partial pressures approximately one fifth of that of methane. Experimental runs were also carried out on surfaces in which thin (≈ 2 ML) of Al were

deposited prior to switching on the molecular beam at a surface temperature of 300 K. The data from such experiments are also shown in figures 3 and 4; it should be noted that the reaction rate increases at significantly lower temperatures than in the case where the experiments commence on clean Si.

4. Discussion

The results provide a useful framework within which to discuss the processes involved in the decomposition of trimethylaluminium on Si(100). The TMA desorption peak at 210 K corresponds to unlimited multilayer growth and is therefore associated with the simple condensation of TMA on the surface, which is completely reversible. In contrast it is apparent from the XPS data that the first layer remains bonded to the surface when the multilayer desorbs, indicating that chemisorption takes place. As the chemisorbed phase is heated this layer decomposes evolving CH_4 into the gas phase and leaving an Al film on the surface contaminated with carbon. The carbon contamination is understandable on the basis of stoichiometry considerations and explains why TMA is an unsuitable precursor for the preparation of pure Al layers on silicon.

The molecular beam results are consistent with the picture described above in the sense that the reaction rate does not increase sharply until the temperature exceeds that for methane desorption, consistent with this being the rate-limiting step in the overall process. However, the strange temperature variation of the reaction (figures 3 and 4) must be explained. It must be borne in mind that Al is deposited during the course of the reaction, whereas AES experiments revealed that Al dissolved into the bulk at around 1000 K, the temperature at which the anomaly in the reaction rate is displayed. The implication of this is that Al catalyses the reaction and this is confirmed by the results shown in figures 3 and 4 for the Al-precovered Si substrate which show enhanced reactivity at lower temperatures. The evolution of acetylene, which was not observed in TDS, only takes place in the presence of Al, indicating that the precise route followed for TMA decomposition depends sensitively on the nature of the reacting surface.

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