

## Aluminium Film Growth by Chemical Vapour Deposition of $\text{AlH}_3(\text{NMe}_3)_2$

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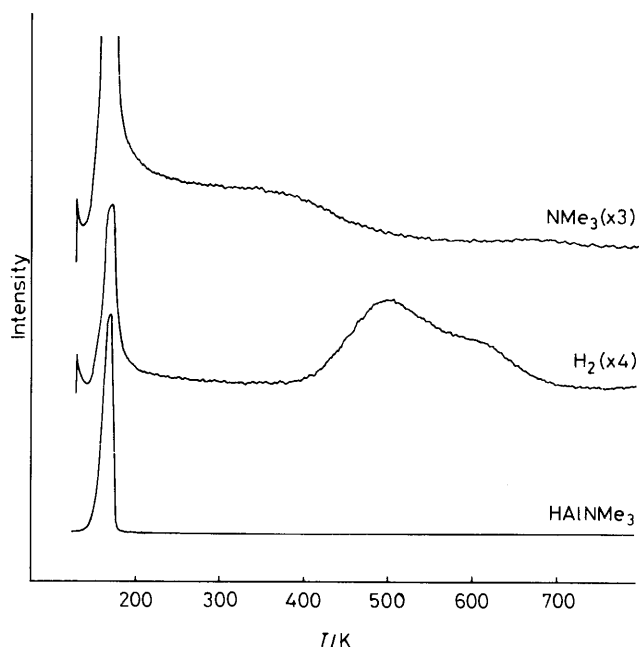
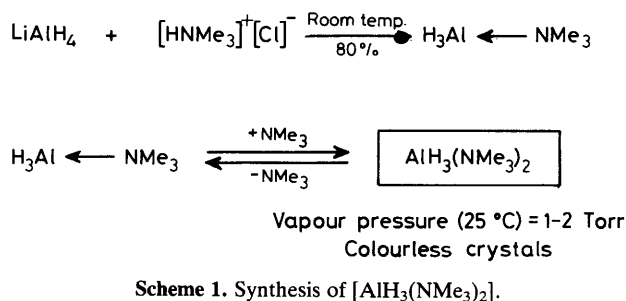
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The surface thermal decomposition mechanism of bistrimethylamine alane [ $\text{AlH}_3(\text{Me}_3\text{N})_2$ ] on the Ga rich ( $4 \times 1$ ) GaAs(100) surface was studied by thermal desorption spectroscopy (TDS), high resolution electron energy loss spectroscopy (HREELS), and XPS and was found to result in the deposition of carbon free aluminium films.

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The deposition of aluminium from gas phase precursors is of importance for both the growth of GaAlAs and the metallisation of semiconductor devices. The advantages of volatile organometallic precursors over metallic evaporation sources<sup>1</sup> have led to adsorption studies of simple organometallics such as trimethylaluminium (TMA) on semiconductors.<sup>2,3</sup>

Although limited success can be achieved using TMA, the strength of the Al-C bond and the lack of a hydride elimination reaction for the removal of methyl radicals is such that heavily carbon contaminated films result. We have therefore investigated the surface reaction mechanisms of alternative aluminium precursor species and in this paper

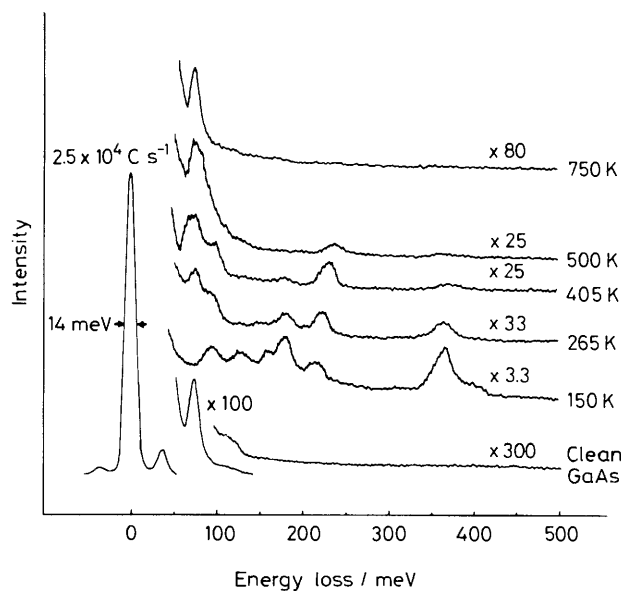


**Figure 1.** Thermal desorption spectra after exposure of GaAs(100) at 150 K to 20 L (1 L =  $10^{-6}$  mbar s)  $[\text{AlH}_3(\text{NMe}_3)_2]$ , with quadrupole mass spectrometer (QMS) tuned separately to  $\text{HAlNMe}_3$ ,  $\text{NMe}_3$ , and  $\text{H}_2$  species.

report results of the thermal decomposition of bistrimethylamine aluminium hydride on GaAs(100) studied by thermal desorption spectroscopy (TDS), high resolution electron energy loss spectroscopy (HREELS), and X-ray photoelectron spectroscopy (XPS).

$[\text{AlH}_3(\text{NMe}_3)_2]$  has been prepared as described previously<sup>4</sup> (Scheme 1). Reaction of  $\text{LiAlH}_4$  with  $[\text{HNMe}_3]^+\text{Cl}^-$  in diethyl ether gives after sublimation *in vacuo* white crystals of  $\text{AlH}_3\text{NMe}_3$  in 80% yield. Subsequent reaction of  $\text{AlH}_3\text{NMe}_3$  with an excess of  $\text{NMe}_3$  gives a quantitative yield of the 2:1 adduct  $[\text{AlH}_3(\text{NMe}_3)_2]$ . The 2:1 adduct is in equilibrium with the 1:1 adduct, so purification is required in the presence of an excess of  $\text{NMe}_3$  to prevent dissociation.

A typical thermal desorption spectrum for bistrimethylamine alane adsorbed at 150 K on GaAs(100) is shown in Figure 1. At this temperature the complex forms a multi-layer, most of which desorbs molecularly at 170 K as seen by  $\text{AlH}_3\text{NMe}_3$  TDS. The fractional order desorption kinetics shown in this peak are characteristic of a nondissociatively adsorbed, physisorbed state of multi-layer dimensions. Using the Redhead equation<sup>5</sup> with  $T_p = 170$  K, heating rate  $\beta = 11$  K  $\text{s}^{-1}$  and pre-exponential =  $10^{11}$   $\text{s}^{-1}$ , we obtain a desorption activation energy for the physisorbed state of 34.5 kJ  $\text{mol}^{-1}$ .



**Figure 2.** HREELS spectra recorded after 80 L exposure of  $[\text{AlH}_3(\text{NMe}_3)_2]$  on GaAs(100) at 150 K and subsequent thermal treatment.

This can be taken as an estimate of the desorption energy of the physisorbed precursor even though the desorption kinetics are not first order. In addition to this peak, desorption features are observed at 300–400 K in the  $\text{NMe}_3$  TDS and at 500–600 K in the  $\text{H}_2$  TDS. These indicate that the remaining bistrimethylamine aluminium hydride cracks on the surface producing volatile products that all desorb below 600 K.

HREELS was used to help identify the intermediates in the above decomposition (Figure 2). Adsorption of  $[\text{AlH}_3(\text{NMe}_3)_2]$  on the surface at 150 K yielded a spectrum with intense loss peaks that are assignable from gas phase IR spectroscopic data to  $\text{NMe}_3$ <sup>6</sup> and its Al complexes.<sup>4</sup> Using data determined from gas phase spectra, the IR absorbances at 100, 135, 160, 185, and 370  $\text{meV}$  ( $1 \text{ cm}^{-1} = 8.067 \text{ meV}$ ) are assigned to the C–N deformation, the C–N stretch and Me  $A_1$  rock, the Me E rock, the Me deformation and the Me stretch, respectively. Figure 2 also shows spectra after brief annealing of this surface at a series of temperatures. On annealing to 265 K all these peaks show a substantial drop in intensity and disappear entirely by 500 K. This is consistent with the desorption of the physisorbed state below room temperature and subsequent desorption of  $\text{NMe}_3$  observed in the TDS data.

On warming to 265 K, the Al–H deformation is also apparent at about 95  $\text{meV}$  but the Al–H stretch has sharpened and shifted up to 225  $\text{meV}$ , indicating further cracking of the complex. On heating to 405 K it shifts further to about 232  $\text{meV}$ , and on heating to 500 K both the stretch and deformation peaks fall in intensity leaving only a small peak centred at 238  $\text{meV}$ . Adsorption of atomic hydrogen on the clean GaAs surface and an Al covered surface yielded peaks due to Ga–H and Al–H stretches at 237 and 233  $\text{meV}$  respectively. While the similarity of these frequencies makes it hard to distinguish them, they do indicate that by 405 K the only remaining hydrogen on the surface is bound either to elemental Al or surface Ga. The small shift to 238  $\text{meV}$  and loss of the Al–H deformation peak by 500 K suggest that while the main peak in the  $\text{H}_2$  spectrum, centred on 500 K, is associated with hydrogen bonded to Al on the surface, the high temperature shoulder may be associated with hydrogen bonded to surface Ga.

The C:N:Al stoichiometry of the adsorbed layer at 150 K can be estimated from the XPS data. The observed stoichiometry is 6.0:2.0:0.8, which is in good agreement with that calculated for  $[\text{AlH}_3(\text{NMe}_3)_2]$  (6:2:1), the largest error (20%) probably being due to the Al 2p peak which is the weakest signal. When the surface was heated to 250 K, this stoichiometry changes to become relatively Al rich corresponding to the onset of  $\text{NMe}_3$  desorption. Furthermore, the Ga 2p peak becomes observable and the average adsorbate thickness is estimated to be about 4 Å, confirming that the physisorbed state has desorbed. Further heating to 620 K causes a gradual increase in the Ga 2p and As 3d signal intensities, and a decrease in the C 1s and N 1s signal intensities to below the XPS detection limit occurs by 490 K.

In conclusion we can say that  $[\text{AlH}_3(\text{NMe}_3)_2]$  physisorbs molecularly at low temperatures but dissociation takes place as the temperature is raised resulting in  $\text{NMe}_3$  desorption without further fragmentation and formation of metal-carbon bonds. This key feature results in the deposition of pure Al films, in marked contrast to the results obtained with conventional Al organometallic precursors where heavy carbon contamination generally results. It is therefore the case

that  $[\text{AlH}_3(\text{NMe}_3)_2]$  offers great possibilities as a new precursor for the contaminant free deposition of Al species at solid surfaces.

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