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HREELS studies of C₂H₄ adsorption on III-V semiconductor surfaces

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Abstract. The adsorption and decomposition of C₂H₄ on GaAs(100) and Al-GaAs(100) has been studied using TDS, AES and HREELS techniques. Ethene is adsorbed non-dissociatively between 150 and 650 K on both surfaces. On heating to 650 K approximately 60% of the adsorbed C₂H₄ is desorbed intact. The remainder is decomposed to CH₂ and CH species which remain at the surface for temperatures up to 800 K. Above 800 K dehydrogenation occurs to give the corresponding carbide. This results in significant contamination of the substrate surface. The effect is most significant on an Al-covered surface.

1. Introduction

The decomposition of organometallic compounds at solid surfaces provides the basis for a wide range of processes for the deposition of thin films. Unfortunately carbon incorporation from the volatilizing ligands and reaction products tends to limit the quality of the films produced. Ethene is an important byproduct in the decomposition of common group III metal alkyl precursors such as TEG (triethylgallium) and TEA (triethylaluminium) which are used to deposit Ga and Al. The characteristics of C₂H₄ adsorption and decomposition on III-V semiconductor surfaces are therefore of importance in understanding mechanisms of carbon incorporation during the preparation of ternary alloys such as Al_{1-x}Ga_xAs. These observations are fully investigated in this paper.

2. Results

All experiments were carried out on the surface of an n-type Si-doped ($\sim 2 \times 10^{18} \text{ cm}^{-3}$) GaAs(100) wafer. The surface was cleaned by cycles of argon ion bombardment and annealing at 850 K until no carbon or oxygen could be detected by AES and LEED showed a (4 × 1) reconstructed surface consistent with a Ga stabilized surface [1]. Al was evaporated in controlled amounts onto the GaAs(100) surface from an ultra high purity evaporation source prior to dosing with TEG.

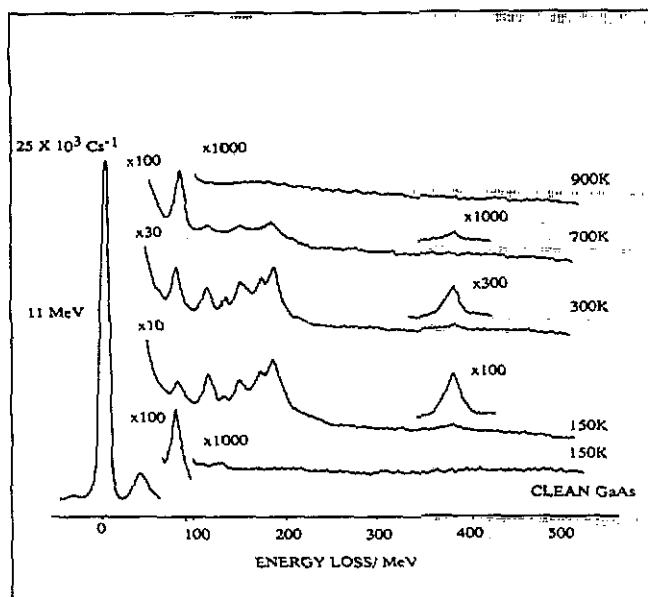


Figure 1. HREEL spectra obtained after dosing GaAs(100) with 55 L of C_2H_4 at 150 K. The substrate was then annealed to the temperatures indicated.

2.1. C_2H_4 adsorption at 150 K

The HREEL spectra obtained after dosing clean and Al covered GaAs(100) held at 150 K with 55 L of C_2H_4 are presented in figures 1 and 2. The additional losses observed after C_2H_4 adsorption at 150 K are summarized in table 1.

Using gas phase IR data it is possible to assign both spectra to non-dissociated C_2H_4 resident on the semiconductor surface [2]. The presence of Al is found to increase the amount of C_2H_4 adsorption. The $C=C$ stretching mode is shifted from its $C_2H_4(g)$ value of 203 meV to around 140 to 150 meV after adsorption onto the semiconductor substrate. This implies significant weakening of the $C=C$ bond in the chemisorbed state. The bond-weakening effect is most significant in the presence of Al. The intensity of the CH_2 symmetric stretch is very weak relative to the rest of the spectrum. Off-specular studies have shown that the loss is dominated by a predominantly dipole mechanism. These observations are consistent with an almost completely planar structure for the C_2H_4 molecule lying parallel to the semiconductor surface. The CH_2 symmetric stretching mode occurs in the range 374 to 377 meV. This is in contrast to the Si(100)/ C_2H_4 system which has a mode 368 meV. Characteristic stretching energies of CH_2 groups in sp^2 and sp^3 hybridized gas phase hydrocarbons occur at 381 and 370 meV respectively [5]. This implies predominantly sp^2 hybridization for C_2H_4 adsorbed on both clean and Al covered GaAs(100). The extent of rehybridization may be calculated in terms of the Madix and Stuve $\pi\sigma$ parameter [6] where

$$\pi\sigma(C_2H_4) = \frac{203 - (\text{Band I})}{203} + \frac{168 - (\text{Band II})}{68} / 0.366.$$

Band I refers to the higher frequency and band II to the lower frequency of the $\nu(C=C)-\delta(CH_2)$ pair. The numbers 203 and 168 correspond to $\nu(C=C)$ and $\delta(CH_2)$ frequencies in meV for gaseous C_2H_4 .

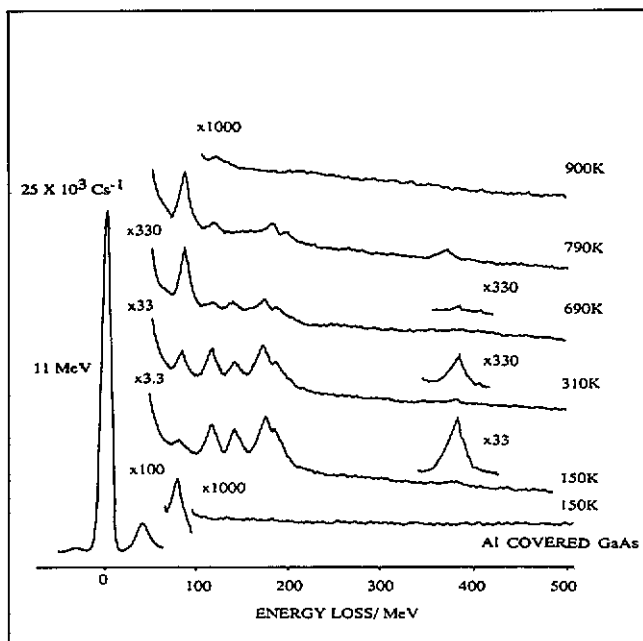


Figure 2. HREEL spectra obtained after dosing GaAs(100) covered with approximately 1 ML Al (as measured by Auger) with 55 L C_2H_4 at 150 K. The substrate was then annealed to the temperatures indicated.

Table 1. Summary of additional losses observed after C_2H_4 adsorption at 150 K. Loss of energies are quoted in meV.

	$C_2H_4(g)$ [2]	$C_2H_4/Si(100)$ (150 K) [3]	$C_2H_4/GaAs(100)^a$ (150 K)	$C_2H_4/AlGaAs^a$ (150 K)	AlC_2H_4 (14 K) [4]
CH_2 rock	103	—	—	—	98
CH_2 wag	118	117	116	116	117
CH_2 twist	128	—	131	—	—
CH_2 rock	154	—	—	—	—
CH_2 scissors	168	—	165	168	173
	181	178	185	183	—
CH_2 as stretch	374	368	—	374	373
	378	—	377	—	—
CH_2 as stretch	388	—	—	—	—
C=C stretch	203	132	150	142	150

^a This refers to the work described in this article.

The values of $\pi\sigma$ calculated for the systems Si(100)/ C_2H_4 , AlGaAs(100) and GaAs(100)/ C_2H_4 correspond to 0.8, 0.68 and 0.53 respectively ($\pi\sigma(C_2H_4(g)) = 0$ and $\pi\sigma(C_2H_4Br_2) = 1$). It can be seen that the values calculated for $\pi\sigma$ correlate directly with the trends in C=C bond weakening observed previously.

2.2. Thermal decomposition

On heating to 650 K approximately 60% of the adsorbed C_2H_4 is desorbed intact from four different states at 185, 230, 390, and 560 K. A species of mass 55 amu was found to desorb from an Al-covered surface. This is thought to arise from the etching of Al-

C_2H_4 from the substrate. Further heating to 900 K induced H_2 desorption between 650 and 800 K. Auger analysis indicated significant contamination of the substrate surface with carbon. The carbon levels for the Al-covered surface were an order of magnitude higher than for clean GaAs.

HREELS was used to identify any intermediates in this decomposition process. On heating to 300 K a drop in intensity consistent with desorption is observed. The energy and relative intensities of the losses remain unchanged up to temperatures of approximately 700 K. At 790 K the removal of the losses attributed to C=C stretching modes implies C=C bond scission. The losses remaining at 116, 177 and 189 meV may all be attributed to CH_2 and CH species resident at the surface [7]. Annealing to 900 K removes all remaining features.

3. Conclusions

Ethene is found to adsorb non-dissociatively between 150 and 650 K on GaAs(100) and AlGaAs(100). On heating to 650 K approximately 60% of the adsorbed C_2H_4 is desorbed intact, the remainder is decomposed to CH_2 and CH species. Above 700 K dehydrogenation occurs to give the corresponding carbide. This results in significant carbon contamination of the substrate surface.

Previous work investigating the decomposition of TEG and TEA on GaAs(100) has shown that the major decomposition pathway involves β hydride elimination of surface ethyl groups to give C_2H_4 and H_2 between 460 and 560 K [8, 9]. This means that ethene is both created at the surface and is also present in significant quantities in the growth reactor. The work presented here then implies that subsequent reactions of ethene with the growing surface presents a pathway for C incorporation in the growing film.

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