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Fundamental Surface Chemistry of GaAs OMVPE

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Organometallic and hydride compounds are widely used as precursors for the epitaxial growth of GaAs and other compound semiconductors. These precursors are most commonly used to perform organometallic vapor phase epitaxy (OMVPE) and also in related deposition techniques such as atomic layer epitaxy (ALE) and metalorganic molecular beam epitaxy (MOMBE). We have investigated the surface chemical properties of these precursors on GaAs(100) using a variety of surface science diagnostics. Results of these experiments have shed light on the mechanisms of precursor decomposition which lead to film growth and carbon doping. For instance, the kinetics of trimethylgallium (TMGa) decomposition on the Ga-rich and As-rich surfaces, measured by TPD, are in semiquantitative agreement with ALE results. This indicates that the dominant growth mechanism during ALE is heterogeneous in nature. Furthermore, there is no compelling evidence for the production of methane (CH_4) on the GaAs surface when TMGa and arsine (AsH_3) are coadsorbed.

We have also investigated the mechanism of carbon incorporation arising from TMGa decomposition. Normally, a small fraction of adsorbed methyl (CH_3) groups dehydrogenate into methylene (CH_2) groups, which are a likely precursor to carbon incorporation. This adsorbate

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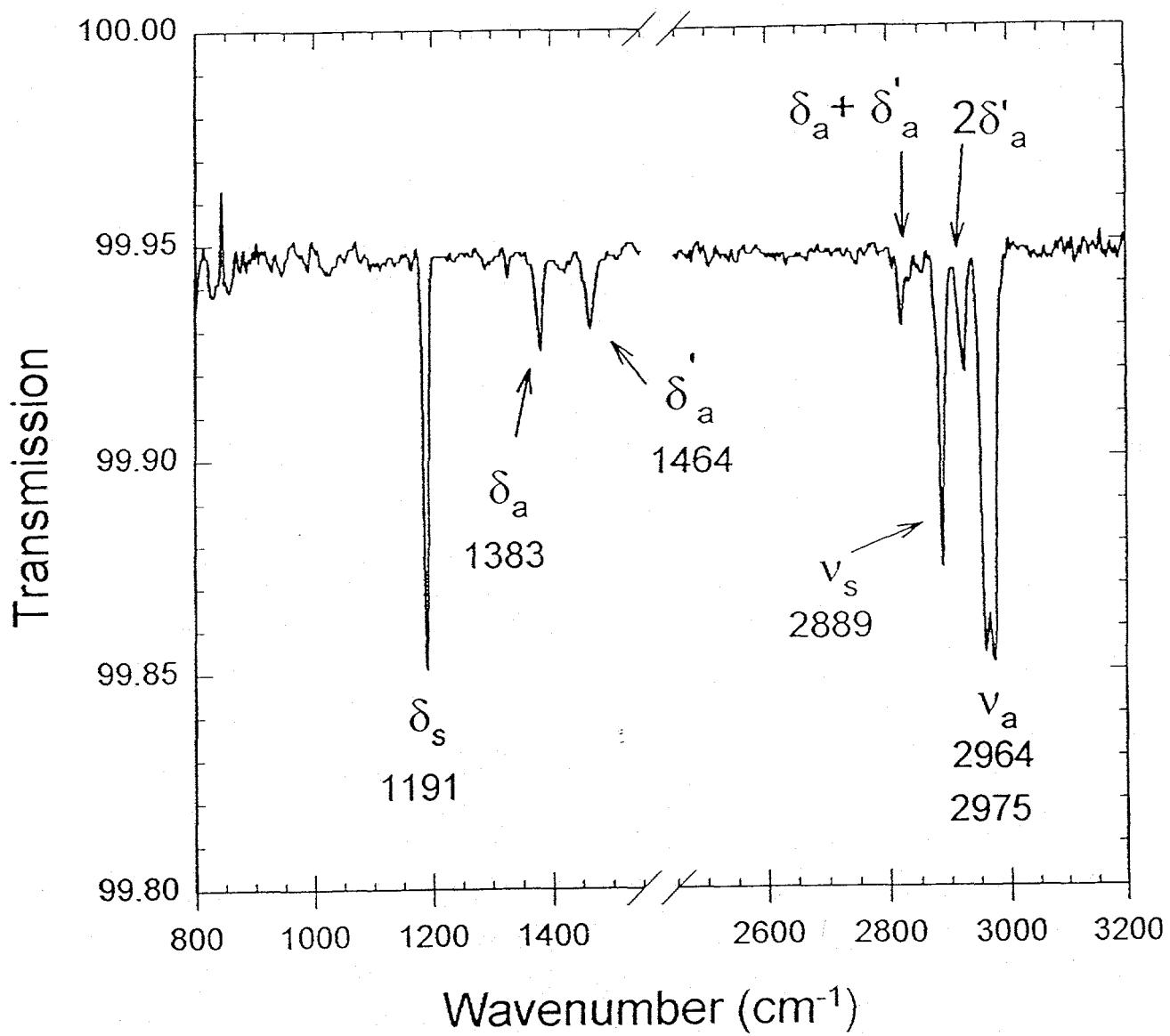
was characterized with vibrational spectroscopies and static SIMS. The rate of CH_3 dehydrogenation is consistent with the carbon doping levels obtained during ALE and MOMBE.

We have focused recent efforts towards elucidating the structure of the adsorbate covered GaAs(100) surfaces using LEED and multiple internal reflection infrared spectroscopy (MIRIRS). Generally, by examining the polarization and azimuthal dependence of the adsorbate vibrational modes, it is possible to determine the bonding geometry of the adsorbate with respect to the surface. The reaction of trimethylgallium (TMGa) with the GaAs(100) surface at 300-400°C creates an ordered CH_3 adlayer that exhibits a (1 X 2) LEED pattern. We refer to this surface condition as the monomethylgallium (MMGa) state. At typical GaAs ALE conditions the GaAs surface should exist in the MMGa state at the end of the TMGa exposure cycle. The CH_3 adsorbate in the MMGa state exhibits relatively sharp ($\text{FWHM} < 10 \text{ cm}^{-1}$) vibrational modes at 1191 and 2889 cm^{-1} , corresponding to the symmetric C-H bending (δ_s) and stretching modes (ν_s), respectively (see figure). Polarization measurements indicate that the carbon-surface bond lies exclusively in the [-1,1,0] plane, indicating that the CH_3 adsorbate is bonded to surface gallium (rather than arsenic) atoms. The Ga- CH_3 bond is tilted away from the surface normal by $50 \pm 10^\circ$, in good agreement with the expected bond angle for a tetrahedral geometry. Using these results we propose a structure of the (1 X 2) CH_3 -covered surface that consists of 1/2 ML of CH_3 groups bonded to a complete monolayer of Ga atoms. The proposed structure is consistent with the CH_3 bond orientation obtained by MIRIRS, the observed LEED pattern, and the electron counting scheme for compound semiconductors.

In order to explain the crystallographic dependence exhibited for GaAs OMVPE and ALE, we have investigated the chemisorption properties of TMGa and arsine on GaAs (111) and (110). The behavior of TMGa on the GaAs(111)A surface is similar to the behavior on the (100) surface. Both the (100) and (111)A surfaces reconstruct to create a sizable number of atom vacancies, and both surfaces decompose TMGa irreversibly. However, the (110) surface is stoichiometric (i.e. no vacancies) and TMGa chemisorption on this surface is reversible. These results have provided insights to the structure-reactivity relationship for GaAs surfaces.

In addition to the group III precursors, we have also investigated the surface chemistry of the common group V precursors, e.g. arsine and tertiarybutylarsine (TBAs). Due to safety concerns, there has been considerable interest in alternative group V precursors, and TBAs has emerged as the most promising candidate. On the "(4 X 6)" Ga-rich surface TBAs chemisorption reaches a saturation coverage of 0.34 ML at 130 K. Approximately 0.08 ML of the adsorbed TBAs-derived species completely decompose during the heating to higher temperatures, depositing As as well as liberating isobutene and isobutyl radicals in the 370-660 K temperature range, and H₂ in the 320-520 K range. In comparison with arsine (AsH₃), TBAs clearly exhibits stronger reactivities on both the Ga-rich "(4x6)" and the As-rich c(2x8)/(2x4) surfaces.

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Unpolarized IR spectrum (recorded at 120 K) of the Ga-rich GaAs(100)-(1 X 2)-CH₃ surface prepared by TMGa adsorption at 350°C.

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