Supplementary Material (ESI) for Chemical Communications

Supplementary Information

Evidence of Carbon-Carbon Bond Formation on GaAs(100) *via* Fischer-Tropsch Methylene Insertion Reaction Mechanism

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Experimental Procedures

1. Preparation of Clean Gallium–rich GaAs(100)–(4×1)

The GaAs samples of approximate dimensions 1 cm × 2 cm were cut from polished semi–insulating GaAs(100) wafers and were mounted (with no prior chemical etching) onto a Ta backing plate spot-welded onto the sample manipulators capable of x-, y- and z- translations and 360^o rotation along the manipulator axis. The sample could be heated to 850K by conduction from the resistively heated Ta backing plate. Following insertion into the chamber and the system bakeout the samples underwent repetitive argon ion bombardment (500 eV Ar^+, 2.5 μA beam current) and annealing cycles at 800K until no C or O could be detected on the surface by Auger electron spectroscopy (AES) or X-ray photoelectron spectroscopy (XPS). Carbon contamination is not a problem with GaAs (as confirmed with AES and XPS) and hence sample cleaning prior to CH_2I_2 dosing and between thermal desorption experiments consisted of one cycle of argon ion bombardment and anneal with conditions noted above.

XPS showed the surface to be gallium-rich with a peak intensity ratio of Ga 3d : As 3d (corrected for the differing X-ray photo-ionization cross-sections) of 1.3 : 1. Low energy electron diffraction (LEED) pattern of a surface prepared in this manner showed the gallium (4×1) reconstruction. All experiments were performed on this gallium rich reconstruction of GaAs(100). The structure of this Ga–rich (4×1) surface is believed to contain three Ga–Ga dimers and one dimer vacancy per unit cell, with imperfect order along the [110] direction[1]. The presence of dimer vacancies mean that arsenic atoms in the second layer are exposed, and so the surface contains both gallium (0.75 ML) and arsenic sites (0.25 ML), although the accessibility of the arsenic sites for adsorption will depend on the size of the adsorbing species.

2. Calibration Experiment: Hydrogen Uptake from the Background by Clean GaAs(100)–(4×1)

The UHV spectrometer (base pressure $<8\text{x}10^{-10}$ mbar) used in the study contains a number of background species, confirmed to be hydrogen radicals, hydrogen, water vapour, carbon monoxide, argon and carbon dioxide, by residual gas analysis using a quadrupole mass spectrometer (UTI 100C, 0–400 amu, operated with 70 eV electron energy). Of the contaminants present only the hydrogen radicals (estimated to have a partial pressure of $2\text{x}10^{-10}$ mbar) were found to adsorb onto the clean surface; molecular hydrogen does not adsorb onto GaAs[2]. Uptake of the hydrogen by the clean GaAs(100)–

(4×1) was monitored by TDS after a fixed 30 minute exposure period, which was the time it took for the sample to cool from the anneal temperature to room temperature (300 K). H_2 (m/z = 2) desorption was detected with a maximum desorption temperature of 500 K, consistent with the value obtained previously[2]. Note that during the cooling period the mass spectrometer was switched off but the ion gauge and the ion pump were left turned on. The same experiment was repeated but with the longer times of 60 and 120 minutes. The effect (if any) of background gases being ionized by the mass spectrometer ion source whilst the sample was cooling was examined with a 60-minute exposure to the background, as before, but with the mass spectrometer left turned on. Typical spectra obtained under the conditions described above are shown in Figure S1.

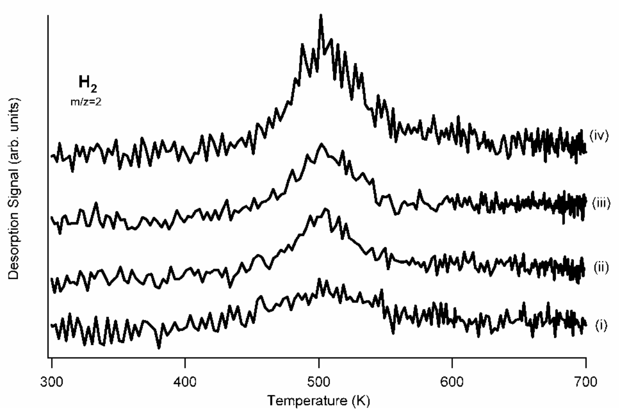

Figure S1: Desorption spectra monitoring H_2^+ (m/z=2) ion currents. Spectra (i), (iii) and (iv) were taken after exposure to the UHV background gases for 30, 60 and 120 minutes respectively, while spectra (ii) was exposed for 60 minutes but with the mass spectrometer filament turned on.

Peak areas under the H_2 desorption traces in Figure S1 plotted against the background exposure time are shown in Figure S2. Note a 10% error in the peak areas was estimated from duplicate runs at the exposure times shown.

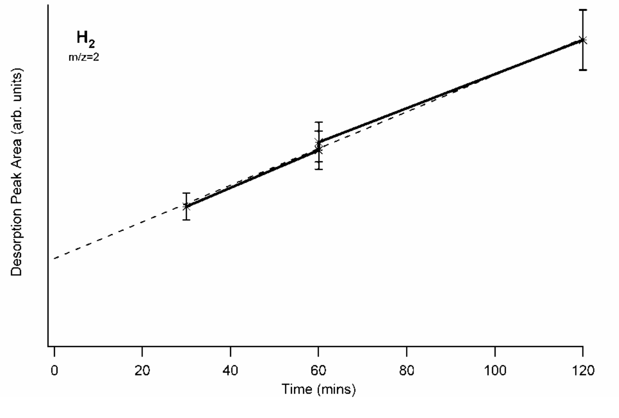

Figure S2: Peak area plotted as a function of time for the H_2 spectra shown in figure S1. The dashed line is a linear fit with extrapolation to time, t = 0 min. The y-axis offset is due to adsorption of hydrogen radicals from the background during cooling of the GaAs sample from annealing temperature to room temperature.

Three points to note from Figure S2: (i) a linear relationship exists between the background exposure times and the H_2 desorption peak areas, (ii) leaving the mass spectra on during background exposure did not increase the hydrogen uptake from the background, suggesting the contribution from ionization of background gases by the mass spectrometer filament did not enhance the hydrogen surface coverage to any appreciable extent, (iii) a constant offset in the calibration plot extrapolated to time, *t*=0 minutes, gives an indication of the hydrogen uptake from the background when the sample was cooling from annealing temperature (800 K) to room temperature (300 K). The uptake of this hydrogen, the majority of which would have occurred between 450 K and 300 K when the hydrogen species becomes stable on the GaAs surface (see Figure S1), was inevitable as hydrogen radicals were always present in the instrument background. The source of these hydrogen radicals is assumed to be the ion pump and possibly the ion gauge, which are always left turned on.

The offset in the calibration plot was further investigated by repeating the calibration experiment described above but by changing the cooling rate of the sample, which in essence reduced the time the clean GaAs surface was exposed to the constant partial pressure of background hydrogen radicals. In another set of experiments the cooling rate of the sample was increased by flowing dry nitrogen gas through the cooling coils (either at room temperature or well below room temperature by using a liquid nitrogen reservoir). Data thus obtained (not shown here) showed that the hydrogen uptake, as determined from the offset value in the calibration curve, was (i) reduced to approximately half the value obtained in Figure S2 when nitrogen gas at room temperature was used, (ii) a negligible amount when the nitrogen gas had been cooled to below room temperature, when the cooling time was reduced to 5 minutes.

The data presented above suggest that by allowing the clean GaAs(100)–(4×1) to cool from 800 K to 300 K, with no dry nitrogen flowing though the cooling coils of the sample manipulator to aid with the cooling process, provided us with a convenient and controlled dosing of the clean surface with a reproducible hydrogen coverage prior to CH_2I_2 dosing. It should be noted that the cooling of the sample in this manner always occurred in 30±2 minutes, and that the partial pressure of the hydrogen radicals in the instrument background remained constant at $\sim 2x10^{-10}$ mbar throughout the duration of the experiments. Hence the surface always attained the same sub-monolayer hydrogen coverage (equivalent of 0.3 L) at 300 K prior to the CH_2I_2 dosing. It should also be noted that the saturation coverage was not reached after 120 minutes of exposure to the background hydrogen radicals. Whilst the exact sub-monolayer hydrogen coverage was not determined (as no other calibration technique for the purpose was available to us) this information was not crucial in the elucidation of the CH_2I_2 reaction mechanism.

3. Effect of Varying Hydrogen Exposure from the Background on the CH_4 Yields

Experiments were conducted to investigate the effect of varying surface hydrogen concentrations adsorbed from the instrument background on the yields of CH_4. The clean surface was prepared as described above, and when the surface had cooled to 300 K (30 minutes exposure of background hydrogen radicals equivalent to 0.3 L exposure) following annealing it was exposed to 0.4 L CH_2I_2, and thermal desorption data monitoring the CH_4^+ (m/z=16) ion current were acquired immediately. The experiment was repeated to monitor the largest fragment of CH_4, the CH_3 radical (CH_3^+, m/z=15) and the spectra are shown in Figure S3. A single peak centred at 550 K for CH_4 and at 560 K for CH_3 is observed in each set. CH_3 is part of the mass spectrometer fragmentation pattern of both CH_4 (85%) and CH_3I (10%) (a product formed by the reaction of adsorbed

CH_3 and iodine[3]) and calculations reveal that the CH_3^+ ion current is entirely made up of contributions from these desorbing species, with no contributions arising from desorbing CH_3 radicals.

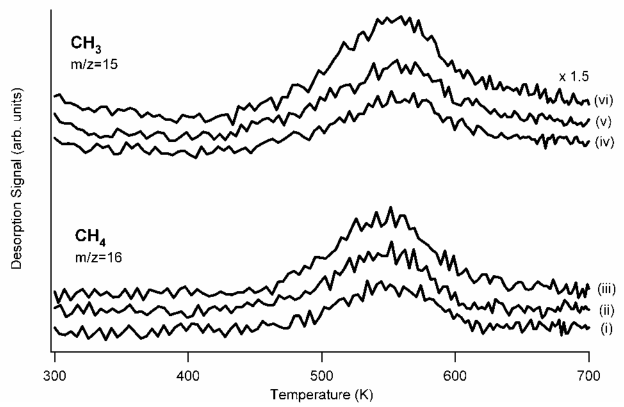

Figure S3: Desorption spectra monitoring CH_4^+ (m/z=16) and CH_3^+ (m/z=15) ion currents following 0.4 L CH_2I_2 exposure at 300 K. Spectra (i) and (iv) were taken immediately after CH_2I_2 dosing, while spectra (ii)/(v) and (iii)/(vi) had a delay of 15 and 45 minutes, respectively, between CH_2I_2 dosing and TDS data acquisition.

The 0.4 L CH_2I_2 exposure was used for three reasons: (i) the pump-down time to the normal base pressure following dosing was very short (a few minutes); (ii) it was comparable to the hydrogen exposure (0.3 L) from the background, (iii) it ensured that surface saturation had not occurred and only sub-monolayer coverages of surface species from CH_2I_2 adsorption were attained (see Figure S3).

The CH_4 and CH_3 spectra were acquired for two other hydrogen exposures with fixed 0.4 L CH_2I_2 exposure and these experiments were conducted as follows: The hydrogen pre-dosed surface at 300 K was dosed with 0.4 L CH_2I_2 and then left in the chamber for additional 15 minutes (contributing an additional hydrogen exposure of ~0.14 L at 300 K) and 45 minutes (contributing an additional ~0.42 L hydrogen exposure) prior to TDS data acquisition tuned to the CH_4^+ (m/z=16) ion current, and the spectrum is presented in Figure S3. Equivalent spectrum was also acquired for the CH_3^+ (m/z=15) ion current, also shown in Figure S3. Since the surface is not saturated following the 0.3 L hydrogen + 0.4 L CH_2I_2 exposure uptake of hydrogen from the background continues to occur if the TDS data acquisition is not conducted immediately and this is confirmed in the spectra shown in Figure S3.

Spectra in Figure S3 show there is a gradual increase in the CH_4 and CH_3 yields with increasing hydrogen exposures (at a fixed CH_2I_2 exposure). However, the desorption maxima remain constant at 550 K for CH_4 and 560 K for CH_3, signaling pseudo-first order desorption kinetics due to the recombination of surface CH_3 with hydrogens being reaction-limited where the process relies on the hydrogens being eliminated from the alkyl species via first-order β-hydride elimination.

There is a linear increase in the CH_4 yields with increasing exposures of hydrogen radicals. This linear increase is mirrored in the CH_3^+ spectra. Since the CH_3 radical is derived predominantly from the mass spectrometer ion source fragmentation of the desorbing CH_4 the linear increase observed in this set of spectra confirms the reproducible surface coverage of hydrogen that can be attained from the background hydrogen radicals, as long as the cooling rate and background hydrogen partial pressure are maintained constant.

4. CH_2I_2 Dosing of Hydrogen Pre-Adsorbed GaAs(100)–(4×1)

Following the calibration of hydrogen uptake from the background at a fixed hydrogen radical partial pressure, this method of hydrogen dosing was used in the study of CH_2I_2 reactions on clean GaAs(100)–(4×1). The surface was cleaned and annealed as described in Section 1 above. During cooling of the sample from the annealing temperature to 300K the surface was exposed to 0.3 L hydrogen radicals from the background over a 30 minute cooling period. The sample was then dosed with 10 L CH_2I_2, an exposure value chosen to ensure the surface was fully saturated[3], such that the monolayer comprised of both the pre-adsorbed hydrogen and the CH_2I_2 products (CH_2 and I species). No hydrogen uptake from the background occurred after the surface had become saturated. The TDS data was subsequently acquired using a heating rate of 12 K s^{-1}.

References

1. D. J. Frankel, C. Yu, J. P. Harbison and H. H. Farrell, *J. Vac. Sci. Technol.*, 1987, **B5**, 1113.
2. J. R. Creighton, J. Vac. Sci. Technol. A 1990, **8**(6), 3984; N. K. Singh, A. Bolzan, J. S. Foord, H. Wright, *Surf. Sci.*, 1998, **409**, 272-282.
3. N. T. Kemp, N. K. Singh, to be submitted to *Surf. Sci.*