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# Thermal and photochemical decomposition pathways of $AsH_3$ on GaAs(100): Implication for atomic layer epitaxy

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We report spectroscopic evidence for the thermal and photochemical decomposition pathways of arsine ($AsH_3$) adsorbed on Ga-rich GaAs(100). Arsine adsorbs molecularly on the Ga-rich GaAs surface at 120 K and dissociates upon either heating to above 200 K or irradiation with 6.4 eV photons. The dissociation of arsine is accompanied by the formation of surface Ga-H species, which is both thermally and photochemically more stable than surface $AsH_x$. This implies that the removal of hydrogen from Ga is the rate-limiting step in the initial stage of As deposition from $AsH_3$ in the thermal or photoassisted atomic-layer epitaxy of GaAs.

$AsH_3$ is the most widely used As precursor molecule for the organometallic chemical vapor deposition (OMCVD) of GaAs. It is believed that surface-catalyzed decomposition of $AsH_3$ plays a dominant role in GaAs OMCVD and atomic-layer epitaxy (ALE).[1–5] For example, in GaAs OMCVD from trimethylgallium and arsine, it has been suggested that $AsH_3$ decomposes heterogeneously by adsorption and loss of hydrogen to the GaAs surface.[2] However, the surface chemistry of $AsH_3$ in these epitaxial processes, is not understood. We report a high-resolution electron energy loss spectroscopy (HREELS) study of the thermal and photodissociation of arsine adsorbed on Ga-rich GaAs(100)-(4×6) in ultrahigh vacuum (UHV). Arsine adsorbs molecularly on the Ga-rich GaAs surface at 120 K. Dissociation is evidenced by the formation of a H—Ga bond in HREELS when the surface is either heated to above 200 K or irradiated with 6.4 eV photons. The surface Ga-H species is stable until 500 K, above which temperature $H_2$ desorbs.

All experiments were conducted in a UHV chamber, pumped by ion, turbomolecular, and Ti sublimation pumps, with a base pressure of $2\times10^{-10}$ Torr.[6] It houses a high-resolution electron energy loss spectrometer (HREELS), a quadrupole-mass spectrometer (QMS) for temperature-programmed desorption (TPD) and residual gas analysis (RGA), a hemispherical energy analyzer and an x-ray source for x-ray photoelectron spectroscopy (XPS), a low-energy electron diffraction (LEED) apparatus, an ion gun for sputter cleaning, and a 2-$\mu$m pinhole collimated molecular doser. The UV light used in photochemical studies was pulsed (11 ns) 193 nm ($h\nu = 6.4$ eV) light from an ArF excimer laser. After passing through a series of prisms and apertures, the UV light entered the chamber through a $CaF_2$ window, uniformly illuminating the whole sample along the surface normal. To prevent desorption due to thermal heating, the laser pulse energy was kept below 0.5 mJ/cm$^2$. This assured that the transient surface temperature rise during irradiation was below a few Kelvin; no temperature rise was detected by the thermocouple. The reflected light exited the UHV chamber through the same $CaF_2$ window.

The sample was a rectangular slice (15×10×1 mm) of a semi-insulating GaAs(100) wafer ($10^{15}$/cm$^3$ Si doped). It was held on the edges by two Ta clips which were spot welded to the Mo leads of the sample holder. The back of the sample was covered with a 3000-Å-thick Ta film, which served as the predominant electrical pathway for resistive heating. The sample could be cooled by liquid nitrogen to ~115 K and heated to 900 K. The temperature was measured by a chromel-alumel thermocouple spot welded to a small Ta clip which was glued to the bottom edge of the sample with a high-temperature cement (Aremco-516). Cleaning the sample was achieved by Ar-ion sputtering, annealing (773 K), and flashing (900 K) cycles. Surface cleanliness was verified by XPS and LEED. The latter showed a (4×6) LEED pattern, which has been discussed previously.[7–9] Arsine was dosed through the pinhole doser at 120 K with the doser tube terminated at about 1 mm from the GaAs surface. This procedure minimizes adsorption on surfaces other than the center portion of the front face (~60% of the crystal).

The left panel in Fig. 1 shows a series of HREELS spectra taken after the GaAs(100)-(4×6) surface was saturated with $AsH_3$ at 120 K and annealed to the indicated temperatures. The HREELS spectra of both clean and arsine-covered GaAs(100) are dominated by losses below 1000 cm$^{-1}$ due to the surface optical phonons of GaAs. The peaks at 287, 575, 861, and −287 cm$^{-1}$ are the single, double, and triple phonon loss, and phonon gain peaks, respectively.[10,11] The adsorption of $AsH_3$ at 120 K is characterized by the H-As stretch loss peak at 2100 cm$^{-1}$ (bottom spectrum). This frequency is very close to the As-H stretch of isolated gas-phase $AsH_3$ (symmetric and asymmetric stretches at 2116 and 2123 cm$^{-1}$, respectively[12]) and adsorbed hydrogen on GaAs(100) [2105–2110 cm$^{-1}$ (Refs. 11 and 13)]. While annealing to 200 K did not change the position of the H-As stretch, its intensity decreased significantly. This decrease corresponds to molecular arsine desorption (Fig. 2).

A new loss peak at 1870 cm$^{-1}$, the H-Ga stretch,[11,13,14] appears when the surface is heated to 300 K,

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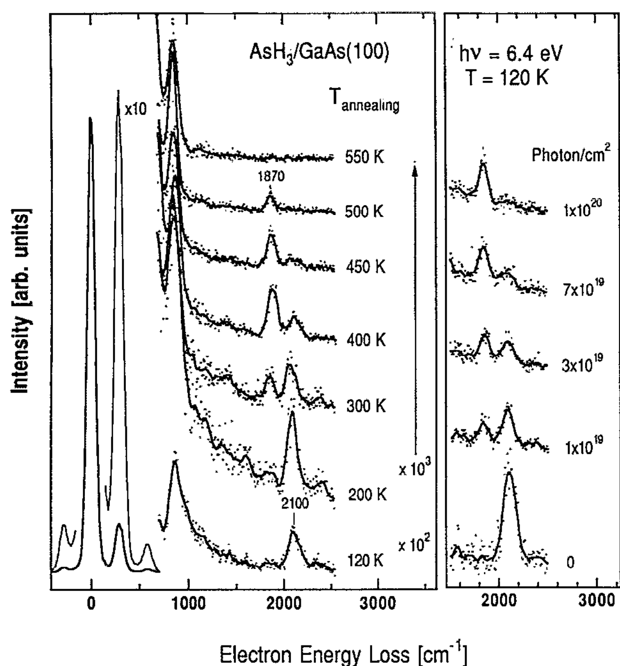


FIG. 1. Left panel: High-resolution electron energy loss spectra of $AsH_3$ on GaAs(100)-(4×6). Saturation amount of $AsH_3$ was dosed onto the GaAs surface at 120 K. The spectra were taken at 120 K after the surface was annealed at the indicated temperatures. Each spectrum was normalized to its elastic peak. The loss region (>700 $cm^{-1}$) of the bottom spectrum was multiplied by a factor of $10^2$ while those of other spectra were multiplied by a factor of $10^3$. The solid curves in the loss region (>700 $cm^{-1}$) are smoothed versions of the experimental data (dots). The primary electron energy was 3.5 eV and the resolution (FWHM) was 80 $cm^{-1}$. Right panel: HREEL spectra taken after the $AsH_3$-saturated GaAs(100)-(4×6) surface was irradiated with the indicated number of 6.4 eV photons at 120 K. The light source was a pulsed ArF excimer laser with a pulse duration of 11 ns. The pulse energy was kept below 0.5 $mJ/cm^2$ to avoid transient surface heating.

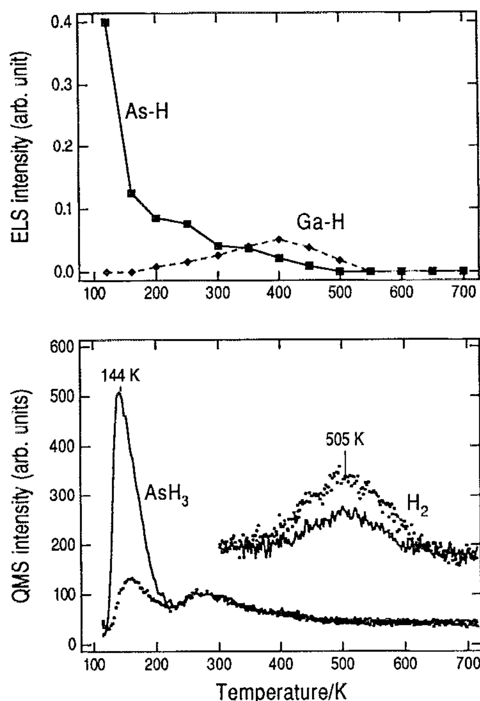


FIG. 2. Upper panel: HREELS intensities (solid squares for As-H and diamonds for Ga-H) of a 120 K $AsH_3$ saturated surface as a function of annealing temperatures. The data points were obtained from HREEL spectra, such as those shown in the left panel of Fig. 1. Lower panel: Temperature-programmed desorption (TPD) spectra ($m/e = 78$ for $AsH_3$ and $m/e = 2$ for $H_2$) taken after the GaAs(100)-(4×6) surface was dosed with saturation amounts of $AsH_3$ at 120 K (solid spectra) and irradiated with $1 \times 10^{18}$ photons/$cm^2$ (dotted spectra). The heating rate used in TPD was 5 K/s.

indicating the dissociation of adsorbed $AsH_3$ and the formation of H-Ga bonds. Upon annealing to 400 K, the As-H intensity decreases while Ga-H grows. Above 450 K, the HREELS spectra are dominated by the H-Ga stretch. Finally, when the surface is heated to above 550 K, no hydrogen remains and the HREELS spectrum is indistinguishable from the clean GaAs(100)-(4×6) surface.

The intensities of the H-As and H-Ga loss peaks are plotted as a function of annealing temperature in the upper panel of Fig. 2. The H-As intensity decreases monotonically with annealing temperature above 120 K, but the H-Ga loss is observed only after the surface is heated above 200 K. Since, for a Ga-rich surface, we expect the dissociation of $AsH_3$ to be accompanied by the formation of H-Ga species, the appearance of H-Ga loss at 250 K is taken to indicate the onset temperature of arsine decomposition. Between 250 and 400 K, the transfer of hydrogen from As to Ga proceeds monotonically, as evidenced by the smooth increase in H-Ga and decrease in H-As (upper panel in Fig. 2). This is most probably due to a stepwise dissociation of $AsH_x$($x = 1$–3) to atomic As. Above 400 K, both H-As and H-Ga decrease monotonically with increasing annealing temperature, indicating the desorption of hydrogen-containing species in this temperature region.

The desorption products, detected by QMS in temperature-programmed desorption, are shown as solid lines in the bottom panel of Fig. 2. The dotted curves will be discussed below. For an arsine-saturated GaAs(100)-(4×6) surface at 120 K, $AsH_3$ and $H_2$ are the only two products observed in TPD. Molecular $AsH_3$ desorbs in two peaks, an intense peak at 144 K and a broad peak between 200 and 450 K. The exact origin of this broad arsine desorption is not understood. Since HREELS results presented above show that $AsH_3$ decomposition starts above 200 K, the molecular arsine desorption peak between 200 and 450 K might originate from the recombinative desorption of $AsH_x$ species and surface hydrogen (on either Ga or As). We estimate from TPD that this desorption state accounts for ~33% of total $AsH_3$ desorption. Since the HREELS data indicate that Ga-H dominates between 400 and 550 K, the $H_2$ thermal desorption peak originates mainly from the recombinative desorption of hydrogen derived from surface Ga-H.

In the atomic-layer epitaxy (ALE) of GaAs(100), the initial stage of As deposition from arsine involves the thermal decomposition of $AsH_3$ on Ga-rich or Ga-terminated GaAs(100) surfaces.[1-5] Our study shows that, on Ga-rich GaAs(100), while surface $AsH_3$ decomposes as low as 250 K, Ga-H is thermally more stable than $AsH_x$ surface spe-

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cies, and dissociates between 400 and 600 K. This implies that removal of H from surface Ga is the rate-limiting step in the initial stages of As deposition from arsine in GaAs ALE.

One commonly encountered problem in GaAs epitaxy is poor control of surface morphology and deviation from 1:1 stoichiometry, particularly in the near-surface region. The increasing requirements for better spatial and morphological control of GaAs crystals have inspired several studies of laser-assisted low-temperature ALE and OMCVD.[15–18] In order to elucidate the surface photochemical mechanism in these ALE or OMCVD processes, we have studied the photochemical pathway of adsorbed arsine on GaAs(100)-(4×6) under 6.4 eV photon irradiation.

The right panel in Fig. 1 shows a series of HREEL spectra (H-Ga and H-As region) taken after the arsine-covered surface was irradiated at 120 K by the indicated photon fluences ($1\times10^{19}$–$1\times10^{20}$ photons/cm$^2$). Clearly, the photochemical pathway of adsorbed arsine at 120 K is very similar to the thermal decomposition pathway shown in the left panel. Irradiation of the arsine saturated surface with $1\times10^{19}$ photons/cm$^2$ results in the formation of surface H-Ga. With increasing photon fluence, the surface $AsH_x$ species further dissociates and a continuing transfer of hydrogen from As to Ga is observed. At $1\times10^{20}$ photons/cm$^2$, surface H-Ga dominates. For photon fluences lower than $10^{18}$ photons/cm$^2$ (not shown), we observed no evidence of H-Ga above the noise level. These results suggest that the first step of arsine photodissociation probably proceeds through the desorption of hydrogen and retention of $AsH_x(x=1,2)$, while the subsequent photodissociation steps mainly involve the transfer of hydrogen from As to Ga. Further support for this interpretation comes from post-irradiation TPD measurements, shown as the dotted spectra in the lower panel of Fig. 2 taken after the arsine-saturated surface was irradiated with $10^{18}$ photons/cm$^2$ at 120 K. Compared to the arsine-saturated surface with no illumination, we observed a significant decrease in the 144 K $AsH_3$ desorption peak area and an increase in the $H_2$ desorption area at 505 K. This can be easily explained by the formation of $AsH_x$ ($x=1,2$) species during irradiation. These $AsH_x$ ($x=1,2$) species dissociate during the temperature ramp and lead to increased $H_2$ thermal desorption. Interestingly, we found that the high-temperature thermal desorption state is much less photoactive than the 144 K arsine state. A significant decrease in the area of the former is only observed when the surface is irradiated with $>1\times10^{20}$ photons/cm$^2$.

A quantitative assessment of the photochemical pathway is under way and will be published later. Based on post-irradiation TPD areas, we estimate an initial arsine photodissociation cross section of $10^{-17}$ cm$^2$ at 193 nm. The H-Ga species is also photoactive, but with a much lower photolysis cross section, on the order of $10^{-21}$ cm$^2$. This implies that the removal of hydrogen from Ga is also the rate-limiting step in the initial stage of As deposition from $AsH_3$ in photochemical ALE of GaAs. While the low cross section for total hydrogen removal makes photochemical ALE practically impossible within a reasonable time scale, i.e., a few seconds, the relatively high initial photodissociation cross section might result in an enhanced dissociative sticking of $AsH_3$, thus increasing the rate of GaAs OMCVD or shortening the time scale for the $AsH_3$ cycle in ALE. This may explain the observed enhancement in laser-assisted GaAs OMCVD and ALE.[15,16]

To summarize, from HREELS measurements, we find that arsine adsorbs molecularly on the Ga-rich GaAs(100) surface at 120 K and dissociates upon either heating to above 200 K or irradiation with 6.4 eV photons. The dissociated arsine leads to As deposition and molecular hydrogen desorption. On Ga-rich GaAs(100), the dissociation of arsine is accompanied by the formation of surface Ga-H species, which is both thermally and photochemically more stable than surface $AsH_x$. These results suggest that the removal of hydrogen from Ga is the *rate-limiting step* in the initial stage of As deposition from $AsH_3$ in the thermal or photochemical atomic-layer epitaxy (ALE) of GaAs.

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