Laser probing of the kinetics and dynamics of III-V semiconductor growth

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Work is carried out on the dynamics of Ga, In, and As scattering, sticking, and desorption from silicon single crystals using laser induced fluorescence and laser ionization probing of the Ga and In atoms and As atoms, dimers, and tetramers in the gas phase. Desorption kinetics are used to probe the InAs and GaAs heterostructures on silicon and the islanding behavior that occurs for the mixed systems. It is observed that islands form readily when In or Ga are grown on a prelayer of As on Si(100). State-resolved detection of As$_2$ species is demonstrated by laser-induced fluorescence probing for the first time. Laser single photon ionization detection of III-V semiconductor species is also demonstrated with high sensitivity and species specific detection. These results are relevant to the epitaxial growth of GaAs and InAs on silicon.

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A. L. Alstrin, R. V. Smilgys, P. G. Strupp, and S. R. Leone, "Vibrational distributions of As₂ in the cracking of As₄ on Si(100) and Si(111)," J. Chem Phys. 97, 6864 (1992).


Apparatus

The apparatus for these studies consists of a home-built molecular beam epitaxy (MBE) machine with commercial Ga, In, and As$_2$, As$_4$ sources, LEED, Auger, RHEED, sputter gun, load lock, azimuthal sample rotation, optical ports for introduction of laser beams and for collection of laser-induced fluorescence light with a photomultiplier, a frequency tripling cell to produce 118 nm laser light for pulsed ionization of the gaseous species, and a time-of-flight (TOF) mass spectrometer. The 118 nm laser ionization technique is an extremely general, highly sensitive new way of detecting the fluxes and compositions of the gas phase MBE species. It may be applied to both source fluxes or scattered and desorbed species. It is an *in situ*, real time, noninvasive probe, which can be arranged in a geometry compatible with conventional MBE growth chambers. Table I shows a detailed list of species that are amenable to the single photon ionization technique.

Table I Species Potentially Ionized by a 118 nm Photon (10.5 eV)

<table>
<thead>
<tr>
<th>Species</th>
<th>Ionization Potential (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>6.0</td>
</tr>
<tr>
<td>Ga</td>
<td>6.0</td>
</tr>
<tr>
<td>In</td>
<td>5.8</td>
</tr>
<tr>
<td>As</td>
<td>9.8</td>
</tr>
<tr>
<td>As$_2$</td>
<td>9.7</td>
</tr>
<tr>
<td>As$_4$</td>
<td>8.5</td>
</tr>
<tr>
<td>P$_4$</td>
<td>9.7</td>
</tr>
<tr>
<td>GaAs</td>
<td>7.2</td>
</tr>
<tr>
<td>AsH$_3$</td>
<td>10.0</td>
</tr>
<tr>
<td>PH$_3$</td>
<td>10.0</td>
</tr>
<tr>
<td>Al(CH$_3$)$_3$</td>
<td>9.1</td>
</tr>
<tr>
<td>Zn</td>
<td>9.4</td>
</tr>
<tr>
<td>Cd</td>
<td>9.0</td>
</tr>
<tr>
<td>Hg</td>
<td>10.4</td>
</tr>
<tr>
<td>Se</td>
<td>9.8</td>
</tr>
<tr>
<td>Te</td>
<td>9.0</td>
</tr>
<tr>
<td>Zn(CH$_3$)$_2$</td>
<td>9.0</td>
</tr>
<tr>
<td>Cd(CH$_3$)$_2$</td>
<td>8.6</td>
</tr>
<tr>
<td>Sn</td>
<td>7.3</td>
</tr>
<tr>
<td>Sn(CH$_3$)$_2$</td>
<td>8.0</td>
</tr>
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</table>
Ga and In interactions with As on Si(100)

It is known that an As prelayer on Si(100) leads to a particularly stable 2x1 dimer structure. The electronic configuration and stable bonding of this layer dramatically reduce the reactivity with Ga and In. Our studies of Ga overlayers on silicon demonstrate that the Ga terminated Si(100) surface is also stable and involves well-ordered overlayers of the same structure. When Ga impinges on a surface that has been pre-covered by one ML of Ga, there is a strong tendency to form islands on top of the well-ordered monolayer structure. Our work found this tendency to be very dependent on the temperature and on impurities. At low temperatures, e.g. 300 K, Ga can grow on a Ga prelayer in a layer-by-layer fashion (Frank-van der Merwe growth), whereas at higher temperatures a Stranski-Krastanov growth mechanism (islands on top of a layer) is always observed in our measurements. In the presence of contaminants, there is evidence that islands of Ga may start to grow on the bare Si substrate (Volmer-Weber growth mode).

In recent experiments in our laboratory, we used thermal desorption techniques together with laser-induced fluorescence detection of Ga and In atoms and As₂ dimers in order to investigate the energetics and structures of the GaAs-Si(100) and InAs-Si(100) interfaces. At the temperatures used to induce desorption, the activation energy needed for surface diffusion is amply available. Desorption from three dimensional islands typically displays either zero order or fractional order kinetics. Desorption of atoms from noninteracting sites in a two-dimensional (2D) layer typically obeys first order kinetics. Therefore, by measuring the coverage at which the kinetic order undergoes a transition, it is possible to determine the fraction of Ga, for instance, that is bound in a 2D layer or in islands. Based on the resulting data, we have been able to propose models for the growth process.

The data for temperature programmed desorption of Ga from pure Si(100) exhibit two peaks. A higher temperature peak occurs at the lowest coverages and increases in amplitude up to one monolayer of coverage (1 ML = 6.8 x 10¹⁴ cm⁻²). This higher temperature peak is correlated with the 2D layer growth of Ga directly bonded to silicon and the desorption kinetics of this feature is first order. For deposition of >1 ML Ga, an additional lower temperature peak occurs, signifying the onset of island formation on top of the prelayer of Ga. The material in this feature
desorbs by a zero order kinetic process.

In the presence of As, the single feature for Ga at 0.9 ML coverage is split into a lower and higher temperature component, immediately signifying a substantial amount of Ga in islands. The higher temperature desorption peak is shifted by 25 K to higher temperature in the presence of As. Isothermal desorption measurements reveal that the higher temperature peak desorbs by a first order kinetic mechanism, but the kinetic parameters change in the presence of As.

In order to account quantitatively for the amount of Ga residing in islands and in the 2D layer, it is recognized that As and Ga desorb in the same approximate temperature range. The $\text{As}_2$ desorption is also measured directly with laser-induced fluorescence. When this effect is taken into account, we find that essentially all of the Ga atoms initially form islands on top of the As prelayer. When some of the As desorbs during the temperature ramp, this vacates sites on the silicon, allowing some Ga to fill these sites and bind to both the underlying silicon and to neighboring As atoms. Nearly half of the As can vacate sites before the temperature ramp reaches its final value, explaining why the higher temperature Ga desorption feature saturates at $0.55 \pm 0.1$ ML. The stronger bond to As $\cdot$ in the mixed 2D layer accounts for the increased temperature of desorption observed in the high temperature peak. The results suggest certain conclusions. At equilibrium, an excess of As will displace Ga from Si bonding sites to form As-terminated Si(100). The Ga atoms form islands on this surface. During the desorption process, Ga interacts strongly with the underlying silicon and the remaining As, causing a higher temperature desorption process.

On bare Si(100), In atoms have qualitatively the same temperature programmed desorption spectra as Ga. There is a high temperature peak due to desorption from a 2D layer bound to Si, but this peak saturates at 0.5 ML, instead of 1 ML in the case of Ga, most likely because of the larger size of the In atom. There is also a low temperature peak which is due to desorption from islands. Both of these peaks occur at an overall lower temperature than do those of Ga because In interacts less strongly with Si. Thus for the required temperature ramp to desorb In, the desorption of arsenic is much less probable. When As is present, the In desorption peaks occur at the same temperatures as on bare Si, but the higher temperature peak
is almost completely removed and all of the In desorbs from the lower temperature (island) feature. There does not appear to be as strong an interaction between the In and As in the 2D layer on Si, because even when the As is introduced at lower coverages, the higher temperature feature is not shifted. Thus, the In may be segregated into 2D islands in the presence of As. Measurements of the desorption kinetics suggest a 2/3 order desorption from the islands of In on top of the As prelayer. Thus, the results reveal that In grows three dimensionally in islands on a fully terminated As prelayer. For partial coverage of As on Si(100), In may grow in segregated 2D domains. The results suggest that in the initial stages of epitaxial growth of InAs on Si(100) with an arsenic prelayer, islanding of In takes place immediately. Then in subsequent InAs growth, independent microcrystallites form.

Laser Desorption of Ga and In on Si(100)

In and Ga are commonly used as dopants in Si, and the MBE growth of In and Ga-doped devices is complicated by low dopant incorporation probabilities and strong tendencies for the dopants to segregate on the surface. In addition, the growth of III-V materials on Si is affected by the energetics and clustering behavior of In and Ga on Si. Increasingly, lasers are being used to address these semiconductor fabrication problems. For example, laser-assisted doping of In and Ga into Si has been successfully employed in the production of p-n junctions and ohmic contacts. The laser desorption method has also been used extensively to probe concentrations of species on the surface as a function of time during a chemical process. Given the proliferation of laser-processing techniques, it is important to investigate the effects of rapid pulsed laser heating on desorption and incorporation. A resulting goal of our studies in this area was to determine how pulsed laser desorption of In and Ga from Si(100) differs from more traditional thermal heating methods.

In these studies, the 532 nm frequency-doubled output of a 2 or 6 ns pulsed Nd:YAG laser is focused onto an In or Ga-dosed Si(100) substrate to induce desorption by rapid transient heating of the silicon. Computer modeling of the surface heating rate shows that the transient heating can drive the system up to the melting point of the Si (depending on laser energy and focusing) and that the hottest
part of the heating pulse is over in 30-40 ns. In our work, the laser energy density is adjusted to remain below the melting point, however, as will be shown below, the incorporation of In or Ga into the Si can alter these conditions dramatically. The rapid heating rate allows the possibility to distinguish kinetic processes that require longer timescales than 30-40 ns. Here, a second tunable dye laser detects the density of gas phase atoms that are desorbed after a short time delay. The quantity of desorbed material is determined with each laser pulse and as a function of the number of laser pulses and initial coverage. From the time delay information, the velocity of the desorbed atoms is also obtained. The sensitivity of detection of small In or Ga coverages in these experiments is extremely good, $\approx 10^{-3}$ of a monolayer. The results discussed below are consistent with a desorption mechanism where the atoms desorb predominantly from the two-dimensional (2D) atomic adlayer which is directly in contact with the Si. Little or no desorption occurs from the adsorbate islands on the timescale of the rapid heating pulse.

Only a small amount of In or Ga is removed with each laser pulse. Signals are obtained by laser-induced fluorescence of the gas phase atoms at a time delay (15 $\mu s$), set to probe the maximum of the flux after the desorption laser pulse. For In, the amplitude reaches a maximum at 0.5 ML of initial coverage, and for Ga it reaches a maximum at 1.0 ML of initial coverage. These coverages correspond identically to the coverages for both In and Ga at which the 2D layer is saturated and islands start to grow. Data is also taken as a function of the number of desorbing pulses. At coverages greater than 0.5 and 1.0 ML for In and Ga, respectively, the signals are unchanging even after thousands of laser pulses. However, for lower coverages, the signals decay away as the material in the 2D adlayer is depleted.

The results are explained by a model in which the rapid heating pulse predominantly desorbs atoms from the 2D layer, and the 2D layer is replenished from the islands on the longer timescale between laser pulses. The poorer thermal conductivity between the heated silicon surface and the atoms in the islands kinetically separates the response of the 2D layer from that of the island material. The important consequence of this result is that the pulsed laser desorption can be used to probe directly the 2D adlayer. We were also able to show that the desorption parameters as measured by the laser heating for the 2D layer are in excellent
agreement with values from temperature programmed desorption and isothermal desorption.

We also observed a significant enhancement of the effect of laser-induced damage to the silicon substrate in the presence of adatoms of In or Ga. Hot spots in the laser beam create significant damage in only a few thousand laser pulses (3 minutes at 10 Hz) in the presence of In or Ga (0.18 ML), whereas on clean silicon it requires $6 \times 10^4$ laser pulses (97 minutes at 10 Hz) to observe any damage. As the coverage is increased, the severity of damage also increases dramatically. Our earlier studies determined that gallium and indium adsorb and desorb on silicon (100) in a reversible manner, provided the temperature does not exceed ≈1000 K. However, the mechanism of the laser damage most likely involves incorporation of In or Ga into the solid at temperatures near to the melting point of silicon (1683 K). Incorporation is observed directly by In and Ga Auger signals on the laser-heated samples after thorough thermal heating to remove any excess desorbate. Incorporation of the material when the silicon is heated near to its melting point is a familiar mechanism for laser-induced doping. However, the incorporated material increases the optical absorption coefficient of the silicon, and on subsequent laser pulses, the laser energy is more strongly absorbed, producing the damage. In our work we explored the limits of the laser melting and incorporation with computer models of the pulsed heating. The observed sensitivity of damage to small changes in In or Ga coverage and laser energy is important for attempts to fabricate reliable devices by laser-induced doping.

**Single Photon Ionization Detection**

The laser-induced fluorescence method is applicable to study Ga and In atoms and As$_2$ dimers. However, many other species are not amenable to fluorescence methods. These include the clustered species, such as As$_4$, P$_4$, S$_n$, and most metal organic molecules. It therefore is highly desirable to develop a more general laser detection method which is applicable to all of the III-V and II-VI species of interest. This method is single photon laser ionization time-of-flight mass spectrometry.

In Table I we showed a large list of species which are amenable to study by single photon ionization with 10.5 eV photons (118 nm). This wavelength can be
generated reliably by nonlinear frequency tripling of the output of a standard third harmonic of a Nd:YAG laser at 355 nm in Xe or a Xe/Ar mixture. In most cases, the photon energy is sufficient to ionize the molecule, but insufficient to both ionize and fragment the molecule. Thus, selective ionization detection is possible without mass spectral cracking. In a first attempt to use multiphoton ionization detection at 266 nm, we observed substantial cracking of a pure beam of As$_4$, whereas with 118 nm we observe only As$_4^+$ and a trace (<1%) of fragment ions such as As$_2^+$ and As$_3^+$.

In experiments described below, we discuss the use of laser ionization to determine a much more complete picture of the dynamics. For example, even simple questions, such as which species is desorbed, i.e. As$_4$, As$_2$, or As, have not been answered reliably because of mass spectral cracking or the invisibility of certain species to the laser fluorescence method. The most exciting new aspect of the laser ionization technique is the potential to use it as a complete, real time diagnostic for all relevant species in MBE processing. Below we give more detail about the laser ionization method and present data on some of the first measurements we have been able to carry out.

Our laser/time-of-flight (TOF) mass spectrometer is based on the Wiley-McClaren design. However, the time-of-flight mass spectrometer had to be designed to fit around the substrate sample and its manipulator, in a manner so that a laser beam travelling parallel to the substrate can ionize the incident, scattered, or desorbed fluxes, and, at the same time, so that the epitaxial beams can access the substrate without interference. In addition, our time-of-flight mass spectrometer is arranged in a unique geometry which allows for simultaneous RHEED measurements. A custom RHEED phosphor screen, which has a region removed, allows transmission of the laser beam. The voltage applied to the TOF mass spectrometer deflects the RHEED electron beam such that the RHEED diffraction pattern is visible on the remaining segment of the RHEED screen rather than propagating to where the screen has been cut away.

The 118 nm laser light is generated by focusing the 355 nm output of a pulsed Nd:YAG laser (5 ns pulse, 10 Hz) with a lens into a Xe or Xe/Ar gas mixture in the frequency tripling cell. The 118 nm light is coherent with the 355 nm light and continues to propagate in the same direction. Both beams pass through a lithium
fluoride (LiF) lens mounted inside the gas cell. Because of the different indices of refraction of the LiF material at 118 nm versus 355 nm, the lens can be positioned such that the 118 nm light is collimated while the 355 nm light is diverging. After the lens, the light propagates through a LiF window which serves as both the output window of the tripling cell and the input window of the MBE chamber. The 118 nm light passes through the cutaway opening in the RHEED phosphor screen and approximately 1 cm in front of the growth substrate.

The substrate is mounted within the extraction region of the TOF mass spectrometer in the MBE chamber. Gas phase species in front of the growing substrate are ionized by the laser pulses and are accelerated up the flight tube toward a focused mesh electron multiplier where they are detected. Resulting voltages from the electron multiplier occur at various delay times relative to the laser pulse, characteristic of the flight time and therefore of the mass of the detected species. Thus, signals corresponding to the density (relative or absolute) of individual species can be monitored simultaneously at a high repetition rate (typically 10 Hz or greater). Thus far, we have detected As$_4$, As$_2$, As, Ga, In, and GaAs species by the single photon ionization method.

The mass spectrum for a pure beam of As$_4$ is obtained from the MBE source without heating the cracker oven. The mass spectrum shows only one peak, at 300 u, due to the tetramer ion As$_4^+$. More careful examination of this spectrum under higher signal-to-noise reveals a trace component of As$_2^+$ at the 0.4% level. These ions most likely come about due to further fragmentation of As$_4^+$. Yoo, Ruscic, and Berkowitz have studied the ionization and fragmentation of As$_n$ species in detail. According to that work, the energy of a single photon at 118 nm is insufficient to fragment As$_4$ or As$_4^+$. Therefore it is possible that the fragment ions come from additional absorption of a portion of the 10 mJ of unfocused 355 nm light that also enters the MBE chamber in our experiment. The 118 nm intensity is most likely too small to produce multiphoton events (typically $<10^{-5}$ conversion efficiency). We also recorded the mass spectrum of As$_4$ and As$_2$ when the cracker oven is heated. Partial dissociation of As$_4$ to As$_2$ occurs in the cracker, and both mass peaks are observed in the spectrum (300 and 150). There is no signal from atomic As, once again indicating the selectivity of the ionization with a photon of
energy 10.5 eV.

It has been assumed that the desorption of arsenic from Si produces exclusively \( \text{As}_2 \) and therefore it is expected that the kinetics will exhibit the second order (recombination) process. Our results show that in fact both \( \text{As}_2 \) and As atoms desorb. The substrate is covered initially with 1 ML of arsenic. The predominant desorbed species is \( \text{As}_2 \), especially at the lower temperatures, which is reasonable since the \( \text{As}_2 \) bond is very strong, 4.3 eV. However, as the arsenic coverage becomes lower, the second order recombination rate decreases, and desorption of atomic As begins to compete with the dimer formation at the higher temperature. In addition, the fraction of atoms desorbing is increased at the higher silicon temperatures. We have also been able to map the catalytic cracking of an incident beam of \( \text{As}_4 \) on a heated silicon surface by detecting each laser-ionized species (tetramer, trimer, dimer, and atoms) as a function of surface temperature (note, the trimer comes from a secondary photolysis process at the higher laser power used here). We have also observed the desorption of the GaAs diatomic when Ga and As are present simultaneously.

We have now calibrated the ionization efficiencies of each \( \text{As}_n \), Ga, In species, so that the signals can be put on a quantitative scale. These results indicate the powerful capability of the single photon ionization method to interrogate the complex processes involved in MBE growth.

**Cracking of \( \text{As}_4 \) on Heated Silicon**

Using the single photon ionization method of detection, the scattered flux of arsenic species from a heated Si(100) substrate is probed to determine what species are produced during the adsorption and desorption processes. Here, the incoming beam is a skimmed, pure beam of \( \text{As}_4 \). The cracker stage in the arsenic oven is turned off for these experiments. The ionization probe laser is positioned to intercept primarily the scattered fluxes. Thus, the scattered species \( \text{As}_4, \text{As}_3, \text{As}_2, \) and As are detected by the time-of-flight mass spectrometer and as a function of surface temperature. The \( \text{As}_4 \) species decreases, and the \( \text{As}_2 \) species dramatically increases as the temperature of the Si(100) is increased. At the highest temperatures, above 1000 K, abundant As atoms are also produced. Thus \( \text{As}_4 \) is catalytically cracked on the
heated Si(100) substrate, producing both As₂ dimers and As atoms, depending on temperature.

A model for the catalytic cracking has been developed, including the rate processes for sticking and scattering of the As₄, chemisorption of the As₄ and its dissociation to atoms on the Si(100) substrate, reassociation to form As₂, followed by desorption of As₂, and desorption of As atoms at the higher temperatures. There may also be direct cracking of the tetramer to dimers on the heated substrate without adsorption. Additional accurate flux data was measured for As₂ by laser-induced fluorescence. These results show that, at the lowest temperatures, the desorption flux of As₂ is limited by the rates of recombination of As atoms and desorption as As₂ from the surface. At higher temperatures, the As₂ desorption flux is limited by the incoming flux of As₄. In this region, a doubling of the incident As₄ flux also doubles the desorbing As₂ flux. Finally, at the highest temperatures, the decrease in the As₂ flux nicely correlates with the desorption of a significant number of As atoms. A complete picture of the catalytic cracking has been developed and from an analysis of the results, various rate processes, sticking coefficients, and desorption probabilities have been estimated.

Finally, the dynamics of the desorption of As₂ from Si(100) and Si(111) have been probed by laser-induced fluorescence measurements of the As₂ vibrational population distributions. A motivation for these experiments was to determine whether the surface geometry plays a significant role in the dynamics of the recombination and desorption. On Si(100), the As atoms are bonded to two Si dangling bonds and tend to form dimerized species on the substrate. On Si(111), the Si atoms occupy three-fold hollow sites with three bonds to underlying Si atoms. Thus, if there would be an observed difference in the vibrational distributions of the desorbing As₂, it may reflect this difference in the structure. Laser-induced fluorescence detection of the gas phase As₂ is carried out on several vibrational states, v''=0, 1, 2, 3 → v'=5 of the A¹Σ⁺-X¹Σ⁺ transition at λ=240 nm.

Approximate Boltzmann distributions of 790±100 K and 730±100 K fit the vibrational data for desorption of As₂ from Si(100) and Si(111), respectively. The results show that the vibrational distributions on both substrates are very similar, but that both are much colder than the surface temperature. The lack of
accommodation to the surface temperature is attributed to dynamical aspects of the desorption, but the similarity of the results on the two substrates suggests that the surface structure does not play a major role in the mechanism of desorption. One model which can explain the results of the desorption considers the use of vibrational energy from the As-As bond in the final step to desorb the molecule from the surface. Here, the last step of the desorption might involve an As$_2$ species bound by only one bond to a silicon atom. Vibrational energy in the As-As species would be used to break this last bond to the surface, resulting in a colder vibrational excitation in the gas phase As$_2$. Other models are also considered in detail in our publication.

Kinetics of As$_2$ Desorption from Si(100)

In previous studies, we attempted to measure the desorption kinetics and energetics of arsenic removal from Si(100) by the method of laser-induced fluorescence detection of As$_2$. Such results could be used to determine how strongly bound to silicon the arsenic species is, compared to Ga and In. The observed large laser-induced fluorescence signals arising specifically from As$_2$ were convincing evidence that the desorbing species was the dimer. However, our observed kinetics were not unambiguous; both second order and first order kinetic fits to the data were equally imprecise. In a study at AT&T, the desorption of arsenic from Si(111) was measured; it was assumed that As$_2$ is the predominant desorbing species, and a pre-exponential factor and activation energy were obtained.

It is now certain that the desorption of arsenic involves a mixture of kinetic processes and product species. Starting with 1 ML of arsenic coverage on Si(100), both arsenic dimers and arsenic atoms are observed during the temperature programmed desorption ramp. Isothermal desorption measurements starting at higher initial temperatures reveal that a large percentage of atoms can be desorbed and the ratio of desorbing atoms/dimers depends on the surface temperature and are highly dependent on coverage. Thus, both the temperature of the silicon substrate and the heating rate are important variables that will influence which species desorbs. In addition, when the initial coverage of arsenic is greater than 1 ML, we observe As$_4$ desorption first, until ≈1 ML coverage is reached, at which point
dimers start to desorb.

Finally, it is worth mentioning that the catalytic formation of As atoms at high temperatures on Si substrates might be used as a source of As atoms for epitaxial growth. The temperatures at which substantial atom production is observed are far lower than required for thermal dissociation to atoms. A two stage effusion cell could easily be developed in which a beam of $\text{As}_4$ or $\text{As}_2$ impinges first on a heated silicon substrate to convert a substantial fraction of the beam to atoms.