

Patterned, photon-driven cryoetching of GaAs and AlGaAs

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We present a high-resolution, damage-free etching technique for GaAs and related compound semiconductors which utilizes surface-specific photochemistry at 193 nm to excite a physisorbed layer of Cl₂ on a cryogenically cooled (~140 K) sample. Etch rates as high as 0.25 Å/pulse (corresponding to 0.09 μm/min) have been achieved. Etching is anisotropic, and etched features of 0.2–0.3 μm linewidth have been routinely obtained. The etch rate has been characterized as a function of several “system” parameters including Cl₂-partial pressure, substrate-temperature, laser repetition rate and fluence, and the addition of rare gases. A phenomenological model of this cryoetching has been developed which agrees well with the experimental data. The etch damage and contamination have been studied with Auger electron spectroscopy, photoluminescence, and Schottky-barrier measurements. All results indicate that there is minimal if any damage induced by the cryoetching process. © 1995 American Vacuum Society.

I. INTRODUCTION

High-resolution, damage-free etching of GaAs and related compound semiconductor materials is an increasingly important requirement in the fabrication of advanced photonic and electronic device structures. For example, both characteristics are crucial for the fabrication of very high speed recessed-gate metal–semiconductor field-effect transistor (MESFET) and heterostructure field-effect transistor (HFET) devices,^{1,2} and especially for the etching of one-dimensional (“wires”) and zero-dimensional (“dots”) quantum-confined structures.^{3,4} The current methods of anisotropic etching rely heavily on reactive ion etching (RIE) or chemically assisted ion-beam etching (CAIBE), in which charged-particle bombardment is utilized to achieve desorption of the reacted products and to provide anisotropic etching along the beam direction. However, etching studies of III–V (and II–VI) materials have demonstrated that ion bombardment can result in damage to the etched surface, thus causing degradation of the electrical properties of patterned material.^{5–9} For example, in the case of etch-defined quantum-confined structures, which is an issue of particular emphasis for the work described in this article, damage may actually render the devices inoperable for feature sizes less than 100 nm and can severely affect performance at even greater sizes.^{5,10,11} In these small structures, the depletion or recombination of carriers due to the surface damage incurred during processing is particularly important and typically causes such an etched microstructure to be electrically nonconductive. In fact, damage may even limit the performance of large-scale devices. For example, recent studies by Thirstrup *et al.*¹² demonstrated that etched waveguide structures in integrated GaInAs/InP electro-optic devices may have their performance degraded by etch-induced damage on the sidewall of the waveguide. Although several methods have been proposed to passivate or remove such damage by application of postprocessing steps such as regrowth or wet-chemical etching,^{13,14} their application adds complexity to the fabrication process.

Photo-induced surface chemistry provides an alternate

route to achieving anisotropic etching, and the application of this technique to both liquid and gas-phase etching has been demonstrated.^{15–19} Typically, the etching chemistry is initiated as a result of direct absorption of a photon by the absorbate molecule in the vicinity of a semiconductor substrate, or in the case of wet etching by the generation of charge carriers from the near-surface region of the semiconductor bulk. Thus, the process generally confines the reaction to the laser illuminated zone. This confinement provides process resolution as well as etching anisotropy. An important advantage of this form of etching, which is purely chemical in origin, is that it does not rely on the bombardment of massive particles to achieve etching and thus damage is not incurred. Moreover, the high flux of atomic species or carriers that is generated by laser irradiation makes it possible to obtain high surface-reaction rates. Etching resolution in such a neutral-atom, laser-assisted method is determined both by the quality of the imaging optics and by the confinement of the reactive species to the illuminated surface area. In the case of laser-assisted gas-phase or wet etching, diffusive motion of the reactive photoactivated species or semiconductor mobile carriers, respectively, can reduce etching resolution.

Recently it has been reported that cryogenic cooling of a substrate during silicon RIE can enhance etching anisotropy^{20,21} by suppressing any thermally initiated etch reactions, particularly on the etched sidewalls. We have described the use of cryogenic-etching technology to enhance process resolution for the case of photon-assisted etching.²² In this etching, a cryogenic (~140 K) physisorbed layer of molecular chlorine is formed on the surface of a GaAs wafer. The use of a continuously formed, then laser-dissociated, physisorbed molecular source contrasts with the use of laser desorption of a chemisorbed chloride layer reported in Ref. 16. Illumination of this physisorbed adlayer by a deep-UV laser, e.g., at 193 nm, generates a surface-localized source of atomic chlorine that, along with the suppression of the etch rate in the nonirradiated area at low temperature, gives rise to an anisotropic etching process with high resolution. Since the etch reaction is purely photochemically initiated and the

etched surface is not subjected to excessive laser heating, etch-induced damage should be minimized. In this article, we present a detailed discussion of this etching, focusing on its etch chemistry and pattern transfer capabilities, its parametric behavior and the modeling of this behavior, the use of this etching in the fabrication of a semiconductor laser, and the results of various measurements, such as Auger electron spectroscopy (AES), photoluminescence, and Schottky-barrier characteristics on etched surfaces.

II. DESCRIPTION OF CRYOETCHING

A. Summary of the relevant etch chemistry

The reaction of molecular and atomic chlorine with various surfaces of GaAs has recently been the subject of several studies. A detailed understanding of the process is made difficult by the fact that multiple sets of etch reactions dominate for different conditions of chlorine adsorbate coverage, extent of reaction, and substrate temperature. While a complete understanding is not yet at hand, a reasonable understanding can be drawn from the common findings of these experiments.

Chlorine in its atomic and molecular forms exhibits very different behavior in so far as its reaction with and sticking to the surface of GaAs is concerned. For example, earlier research has shown clearly that molecular chlorine exhibits a much smaller reactive sticking coefficient than atomic chlorine.^{23,24} Recent molecular-beam experiments have shown strong evidence that when Cl_2 impinges on a GaAs surface it sticks and reacts via two separate mechanisms.²⁵ At low translational energies, i.e., $E_i \leq 0.05$ eV, such as those predominating at temperatures below room temperature, adsorption is via a physisorbed precursor-mediated mechanism. At higher kinetic energies, i.e., $E_i \geq 0.05$ eV, adsorption is via direct chemisorption. Since the reaction barrier to chemisorption from the precursor-mediated state is larger than 0.05 eV, condensed chlorine layers at cryogenic temperatures are expected to remain predominantly in their physisorbed state.

The surface-bound reaction products of chlorine on GaAs depend on the degree of exposure to the reactant flux as well as the form, i.e., atomic or molecular, of the reactant. For example, thermal desorption studies by French, Balch, and Ford²⁶ showed that for GaAs at room temperature, exposure to low dosages of Cl_2 resulted in the formation of only GaCl and free arsenic, while at higher exposures the more volatile triatomic species, AsCl_3 and GaCl_3 , dominated. On the other hand, x-ray photoelectron spectroscopy (XPS) studies by Freedman and Stinespring^{23,24} have shown that surface reaction with atomic chlorine leads to the formation of both gallium and arsenic chlorides—even at the low substrate temperatures of 130 K in that study. Again, higher coverages of chlorine lead to the formation of the di- or trichloride species.

Desorption of product species also plays a key role in determining the etching characteristics. For example, in the molecular-beam studies alluded to above,²⁴ it was found that on a carefully prepared, fully crystalline surface, low volatility reaction products can effectively passivate a surface by

the surface can alleviate this problem by forming the more volatile AsCl_3 or GaCl_3 . However, at lower temperatures, even these species will remain surface bound. In fact, a surface temperature of 175 K is needed to desorb AsCl_3 and 210 K to desorb GaCl_3 .²⁷ It has been suggested separately^{28,29} that the difference in the volatility of these two compounds can lead to surface roughening during etching.

Finally, in many of these prior studies, the specific surface crystallographic orientation of the GaAs substrate has been found to be important to the etching mechanism. For example, while the initial sticking coefficient of chlorine molecules on a bare, well prepared GaAs surface is relatively insensitive to surface orientation, the passivation phenomena mentioned in the previous paragraph is surface-orientation dependent. Note, however, that such passivation appears to be only important in inhibiting reaction for the case of the molecular chlorine.

In addition to the general studies of the surface chemistry of chlorine, there has been prior investigation of the photochemistry of physisorbed chlorine on GaAs; this work, in fact, helped motivate the etching experiments discussed here. In this study, Liberman, Haase, and Osgood²⁷ reported that in the absence of UV irradiation, multilayers of molecular chlorine could be readily physisorbed on a GaAs(110) surface at 85 K. In addition to this physisorbed layer, ~ 1 ML (monolayer) of chlorine was dissociatively chemisorbed. The composition of this chemisorbed species was found to be in agreement with the molecular-beam results discussed above. In particular, temperature programmed desorption (TPD) of this reacted layer suggested that GaCl, As_2 , and As_4 were the predominant desorption products. Irradiation with 193, 248, or 350 nm light was found to induce a much more extensive chlorination of the GaAs(110) surface and, after extended exposure to the UV radiation, AsCl_3 appeared in the thermal desorption spectrum at 175 K. The enhanced chlorination was attributed to the reaction of chlorine atoms which were generated by both direct UV photolysis, and for 248 and 193 nm irradiation, by a UV-induced intermolecular-electron-transfer process in the condensed chlorine film.³⁰ This intermolecular-electron-transfer process is possible only in the condensed film of chlorine and was found to be the dominant dissociation channel only at 193 nm. Further, the time-of-flight (TOF) signatures of the desorbed products in our previous study²⁷ indicated that in the presence of UV illumination, enhanced dissociation of the etch products occurred, thus providing a route for photoactivated desorption. This enhanced dissociation is most probably due to direct or substrate-electron-initiated bond cleavage of the reaction products (see below).

B. Photon-assisted cryoetching

The above results suggest that an etching reaction can be achieved by forming monolayers of physisorbed Cl_2 on a GaAs surface, followed by subsequent irradiation of this surface with a laser wavelength selected so as to excite dominantly the physisorbed layer of chlorine, thus creating a reactive and localized atomic chlorine source on the GaAs surface. This atomic chlorine source allows the multiply

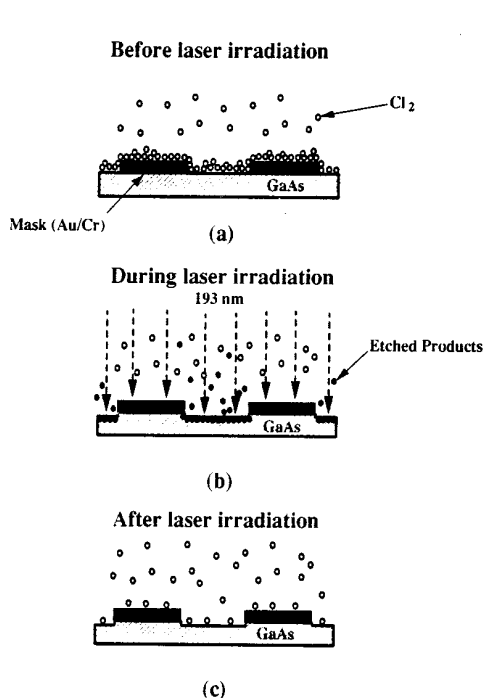


FIG. 1. The laser-assisted cryoetching process. (a) Before laser irradiation, molecular chlorine is physisorbed on the cryogenically cooled substrate. (b) Laser irradiation dissociates the physisorbed chlorine molecules which then react with the surface, and desorbs the chloride reaction products. (c) After laser irradiation, the bare, etched GaAs surface again physisorbs Cl_2 molecules.

semiconductor surface. These may be then desorbed as AsCl_3 and GaCl_x ($x=2,3$) via surface heating or photolysis, thus achieving continuous etching. In such a process, the reactive area is confined to the laser-beam-irradiated zone and the thermal background reaction in the nonirradiated area is suppressed by the low ambient temperature. Further, since the laser fluence is relatively low, the etched surface structure should not be damaged. In effect, the physisorbed molecules act as an atomically thin, $\sim 1\text{--}3$ ML, dry “photoresist” which is continuously replenished between pulses by the low-pressure gas-phase ambient. Finally, note that flood illumination can be used if patterning is accomplished with surface masking.

Figure 1 illustrates the general features of the UV-assisted cryogenic etching process. At the beginning of each etching cycle, a physisorbed layer of molecular chlorine is formed on the cooled GaAs surface by impingement of a flux of molecular chlorine from a gas-phase ambient. Next, a 193 nm laser pulse irradiates the physisorbed layer of chlorine producing a surface-localized source of atomic chlorine; a percentage of these reactive chlorine atoms react with the non-masked GaAs surface to form AsCl_3 and GaCl_x ($x=2,3$), which are nonvolatile at the cryogenic temperatures used here. Also during laser illumination, desorption of the chlorine products occurs at the laser fluence, $15\text{--}20$ mJ/cm^2 , which is typical in our experiments. This process appears to

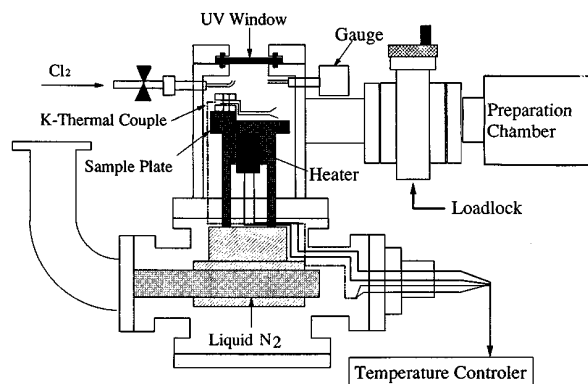


FIG. 2. A sketch of the cryoetching system with sample loadlock. The sample is preheated to 210°C in the preparation chamber to desorb residual moisture.

fects. Finally, after each pulse a new physisorbed layer of Cl_2 forms on the GaAs surface.

III. ETCHING CHAMBER AND EXPERIMENTAL PROCEDURE

Figure 2 presents a sketch of the etching chamber used in our experiment. The chamber is made of stainless steel and can be pumped to a base pressure of $\sim 10^{-7}$ Torr with a turbomolecular pump (pumping speed ~ 600 ℓ/s). The sample is mounted on a molybdenum plate by indium bonding to achieve good thermal contact. Before etching, the sample is heated to 210°C in a preparation chamber to melt the indium foil and to desorb residual moisture on the sample. The molybdenum sample plate is then transferred into the chamber through a loadlock mechanism and fixed on a molybdenum etching platform, which is in contact with a copper heat sink cooled by a liquid-nitrogen dewar. The sample temperature is measured by a K-type thermocouple, spot welded close to the sample, and a digital temperature controller maintains the sample temperature to within 1 K of its set value. During etching, the etching chamber is continuously pumped while chlorine gas (99.999% pure) is introduced through a small tube directed toward the quartz window ~ 2.5 cm above the sample; this gas-flow direction serves to homogenize the condensation of chlorine molecules on the sample. The sample is illuminated with the output from a 15 ns pulse-length excimer laser operating at 193 nm. The light from the laser is collimated and homogenized using a pair of cylindrical lenses, then passed through a square aperture which is projected onto the sample surface such that a uniformly illuminated region is achieved on the sample surface. All samples were chemically cleaned by sequential immersion in trichloroethylene, acetone, methanol, and deionized water. After this cleaning, they were rinsed in a $\text{NH}_4\text{OH}:\text{H}_2\text{O}_2(1:1)$ solution for 10 min to remove any native oxide. Most etching experiments utilized samples of GaAs(100) (n type, 4×10^{17} cm^{-3}); however, a limited number of samples with different crystal orientation, particularly n type, 4×10^{17} cm^{-3} GaAs(110), and different doping type and doping level were used to determine if there were any

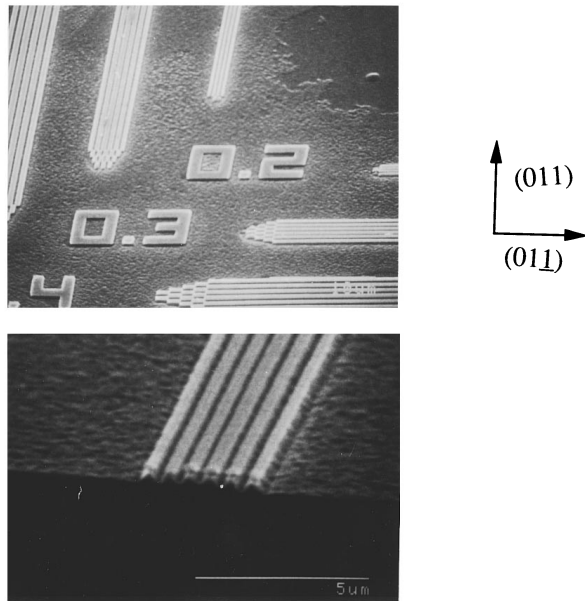


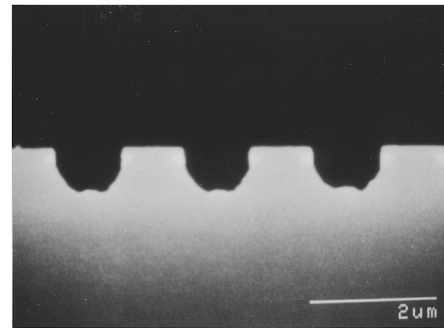
FIG. 3. SEM photos of submicrometer cryoetching of GaAs(100) using an Au surface mask. The etching was done at a fluence of 21 mJ/cm^2 , the exposure time was 30 min at 60-Hz repetition rate, the sample temperature was 140 K, and the chlorine ambient pressure was 5 mTorr.

tivity of etching, samples of molecular-beam epitaxy grown (MBE) $\text{Al}_x\text{Ga}_{1-x}\text{As}$ on GaAs, with differing Al content were also examined.

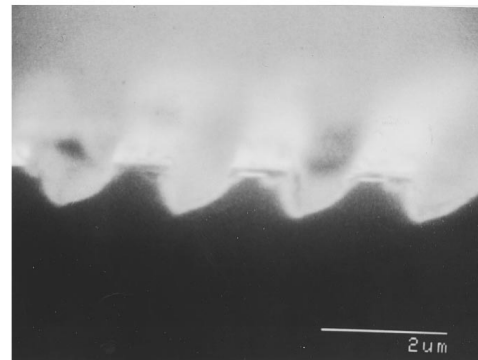
IV. PATTERN TRANSFER

An important requirement of a viable dry etching process is its ability to transfer images of high spatial resolution. Pattern transfer must rely on noncrystallographic etching for the process to be generally applicable as a fabrication technique. In addition, the etching chemistry must be sufficiently controlled that a practical surface-mask material is available and that undercutting of the surface mask does not occur. These properties were investigated using GaAs samples that were patterned with either $1 \mu\text{m}$ scale optical lithography or, for features $< 1 \mu\text{m}$, via electron-beam patterned surface masks formed at Cornell University's National Nanofabrication Facility.

For example, in order to study the resolution limits of this etching process, we investigated the use of various forms of surface masks to pattern features as small as $0.2 \mu\text{m}$. Several different materials were used, including Au/Cr and Si_3N_4 . Both of these mask material systems were suitable for use as surface masks since both were inert to the etching chemistry used here. However, a close examination of the etched features formed at $0.6 \mu\text{m}$ resolution indicated that the Si_3N_4 mask showed a significant near-surface undercut. We attribute this undercutting to the enhanced reactivity of the material just under the nitride mask which we believe to be strained, as has been observed in Ref. 31. When the Au/Cr mask was used, undercutting was significantly reduced and features as small as $0.2 \mu\text{m}$ could be made reproducibly.



(a)



(b)

FIG. 4. Cross sectional SEM photograph showing crystallographic etching. Etched mesa profiles along the $\langle 1\bar{1}0 \rangle$ directions on the GaAs (110) surface are shown. The etching was done at (a) $T_s = 140 \text{ K}$ and (b) $T_s = 300 \text{ K}$, the laser fluence (193 nm) was 21 mJ/cm^2 and the chlorine pressure was 5 mTorr.

patterned and etched GaAs(100) sample with $0.2\text{--}0.3 \mu\text{m}$ pattern features etched to a depth of $0.4 \mu\text{m}$. The etching was done with 20 mJ/cm^2 laser fluence (60 Hz) at 140 K substrate temperature and 5 mTorr chlorine ambient pressure for 30 min. Note that the etched morphology is smooth and exhibits little undercutting.

For some Cl_2 -based plasma etching and for thermal etching of GaAs, the etching rate exhibits crystallographic anisotropy. Typically, in this etching, $k_{\langle 111 \rangle \text{B}} > k_{\langle 110 \rangle} = k_{\langle 100 \rangle} > k_{\langle 111 \rangle \text{A}}$, where $k_{\langle x \rangle}$ is the reaction rate for surface x .^{32–34} However, in our case, no such crystallographic anisotropy of etching was observed. Figure 4 shows two electron micrographs of mesa cross sections which are formed by patterning along the $\langle 1\bar{1}0 \rangle$ direction on a GaAs(110) surface by UV-assisted chlorine etching. In both cases, the same laser fluence and chlorine partial pressure were used. In one case the substrate is at $T = 140 \text{ K}$ and in the other 300 K; thus allowing us to compare photochannel etching from a cryogenic film and from a gas ambient, respectively. We note here that the etching reaction at the higher temperatures is primarily thermally driven.¹⁸ The results show that in contrast to gas-phase Cl etching, the cryoetching is not crystallographic. The lack of crystallographic etching is in agreement with the results of Freedman and Stinespring^{23,24} who showed that there is no preference in Cl-atom chemisorption for particular crystalline surfaces. In contrast to the results

slope of the etched sidewall in our cryoetching is the same for all crystal orientations. There are a number of possible explanations for the origin of the sidewall slope, the most obvious stemming from the fact that the shape of the trench should reflect the local intensity distribution of the etching radiation. Thus as is seen in some photoresist exposure, diffractive effects at the edge of small features would reduce the light intensity at the wall and thus reduce the local etch rate. The fact that in some cases the contour of the etch feature showed features suggesting Fresnel diffraction supports this explanation. Note that once a sloped sidewall is formed, the well known reduction of the flux with incident angle would ensure a continued slower etch rate.

Surface roughness and etch-depth uniformity provide an important measurement of the quality of any device-etching technique, since both influence the fidelity of pattern transfer as well the amount of surface carrier recombination. At low substrate temperatures, the condensation of gas-phase impurities on the surface leads to the blockage of surface sites or possibly even microscopic surface regions if impurity islands are formed. Thus, in our experiments, it was found that the lower the etching temperature, the more the morphology degraded. After installing the loadlock assembly to eliminate any introduction of water vapor, etc., into the etching chamber while loading and unloading the sample, a significant improvement in morphology was achieved. However, an intrinsic roughness of ≤ 50 Å was still detected on etched surfaces upon scanning electron microscopy (SEM) and profilometer examination. This ≤ 50 Å roughness appears to be intrinsic to the process chemistry.

V. PARAMETRIC BEHAVIOR AND MODEL

A. Etch rate measurements

In order to understand the properties of the etching process, sets of experiments were done to characterize its parametric behavior. In these experiments, the excimer-laser beam was patterned by a shadow mask into a narrow rectangle of illumination. After irradiating the sample for a set time, the mask and the laser beam were translated together by a fraction of the length of the rectangle, and a second exposure was made. The etch depths of the various regions were then measured by stylus profilometry, and the etch rate was determined by the slope of a graph of the etch depth versus exposure time. Figure 5 shows the plot of etch depth versus etch time that was done under typical etching conditions. The linear increase of the etched depth with exposure time is consistent with the absence of a buildup of etch-resistant products such as often occurs in plasma-etch techniques.³⁵ Generally, there is a short induction period seen at the beginning of exposure time. Since this induction time was affected by the details of the surface cleaning procedure, for example the time of rinsing in $\text{NH}_4\text{OH}:\text{H}_2\text{O}=1:1$ solution, we believe that the induction time results from the presence of a native oxide layer which is more resistant to the etching chemistry than is the pure semiconductor. If care was taken to remove most of the surface native oxide (*ex situ*),

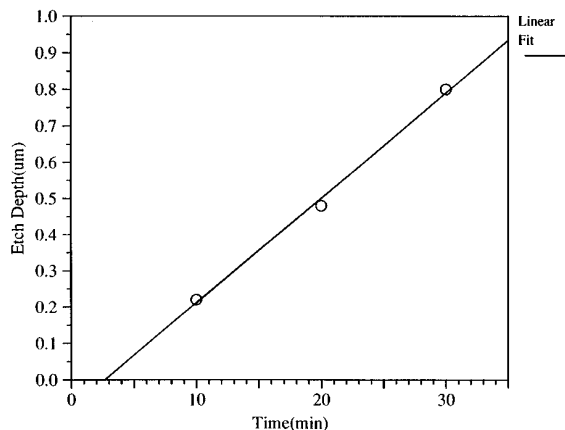


FIG. 5. Etched depth of GaAs(100) vs laser-exposure time. The etching was done at 120 K, 15 mJ/cm² (60 Hz), and 2 mTorr of Cl₂.

In most dry etching systems, the pressure of the reactive gases is an important factor in determining the etch rate. As mentioned above, the chlorine partial pressure determines the coverage of the physisorbed layer of chlorine on the GaAs surface; this layer is then the source for chlorine atoms. Thus for our low-temperature etching, the functional dependence of the etch rate on Cl₂ partial pressure will stem from the variation of the coverage of the physisorption molecules with the partial pressure of the ambient gas. Figure 6 shows the variation of the etch rate with chlorine partial pressure, with the substrate temperature maintained at 150 K and laser fluence at 31.5 mJ/cm². The figure also contains the results of a curve calculated by a model based on multilayer physisorption to be described later. At low pressures, the etch rate increased rapidly with pressure until it reached a plateau at about 10 mTorr. This pressure corresponds to a steady-state coverage of 1 ML as calculated from our model. After this plateau, the etch rate increases more rapidly with pressure, as the physisorbed chlorine begins to exhibit multilayer condensation. A typical etch rate is 0.08 Å/pulse at 1 ML

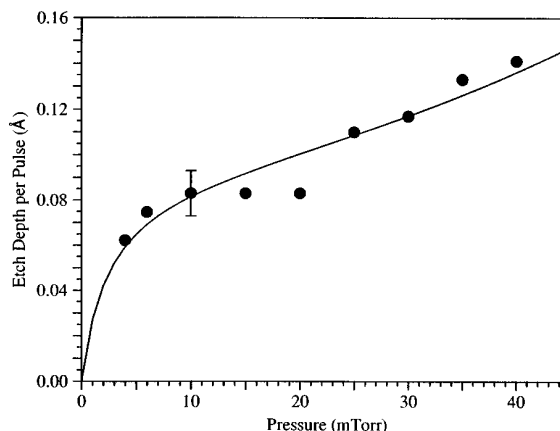


FIG. 6. Etch rate vs chlorine pressure for etching of GaAs(110) at 150 K and 31.5 mJ/cm² (60 Hz). The plateau at 10–25 mTorr is indicative of 1 ML of

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