

Pattern transfer and photoluminescence damage assessment of deep-submicrometer features etched by photon-induced cryoetching

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Abstract. We present a study of pattern-transfer and etchinduced damage in photon-induced cryoetching. Features with effective radii as small as ≈ 100 nm have been formed in both bulk and layered GaAs/AlGaAs materials. A measurement of the photoluminescence of etch-defined deep-submicrometer structures material suggests that this form of etching results in minimal process-induced damage. Modeling of the luminescence vs feature size for these features shows that the luminescence is limited only by carrier diffusion and non-radiative surface recombination.

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Photoinduced surface chemistry provides an alternate route to plasma and ion-induced reactions for achieving anisotropic etching of semiconductor materials, and the application of this technique to both liquid- and gas-phase etching has been demonstrated [1-5]. Generally lightinduced chemistry occurs within the laser-illuminated zone; this phenomenon thus 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 reactive atomic or radical species that are readily obtained by laser irradiation make it possible to obtain high photon-induced surface-reaction rates. Etching resolution in such a neutral-atom, laserassisted method is determined both by the quality of the imaging optics and by the confinement of the reactive species to the illuminated surface area.

It has been reported that cryogenic cooling of a substrate during silicon reactive-ion etching (RIE) can enhance etching anisotropy [6, 7] by suppressing any

thermally- initiated etch reactions, particularly on the etched sidewalls. These results plus recent ultraviolet mechanistic studies [8] led us to consider the use of cryogenic-etching technology to enhance process resolution for the case of photon-assisted etching. In this etching, described in [9], 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 [4]. 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 non-irradiated 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 bulk or near-surface damage should be minimized. In this paper, we report on the use of cryoetching for etching of features with deep-submicrometer lateral resolution in GaAs/AlGaAs quantum well as well as in bulk GaAs crystals, and on the use of photoluminescence to study the properties of the resulting features. To the authors' knowledge, this is the first report of the application of a plasmafree, "dry" etching technique to the etching of high-resolution features in quantum wells. The results show that this technique is suited for etching of deep-submicrometerlateral-resolution features because it has the high-feature resolution of ion-based techniques and the non-damaging attributes of wet etching, i.e., the luminescence efficiency of these features is not limited by damage induced by the etching technique.

1 Brief description of photon-assisted cryoetching

Figure 1 illustrates the general features of the UV-assisted cryogenic-etching process described in [9]. 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

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Fig. 1a–c. 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 into low-energy atoms 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

gas-phase ambient. Next, a 193 nm laser pulse irradiates the physisorbed layer of chlorine producing a surfacelocalized source of atomic chlorine; a percentage of these reactive chlorine atoms react with the non-masked GaAs surface to form AsCl₃ and GaCl_x (x = 2, 3), which are non-volatile at the cryogenic temperatures used here. Also during laser illumination, desorption of the chloride products occurs at the laser fluence, 15–20 mJ/cm², that is typical in our experiments. This process appears to occur primarily through low-temperature photochemical effects. Finally, after each pulse a new physisorbed layer of Cl₂ forms on the GaAs surface.

In the etch process, the reactive area is confined to the laser-beam-irradiated zone and the thermal background reaction in the non-irradiated area is suppressed by the low ambient temperature. Further, since the laser fluence is relatively low, the etched surface structure should not be damaged (this point is examined extensively in Sect. 5). In effect, the physisorbed molecules act as an atomically thin, \sim 1–3 ML, dry reactive source which is continuously replenished between pulses by the low-pressure gas-phase ambient. Finally, note that in these experiments flood illumination is used since patterning is accomplished with surface masking.

2 Experimental procedure

Figure 2 presents a schematic diagram of the etching chamber used in our experiment; the chamber was evacuable to a base pressure of $\sim 10^{-7}$ Torr. Prior to its mounting on the sample plate, all samples were chemically cleaned by sequential immersion in trichloroethylene, acetone, methanol and deionized water. After this cleaning, they were rinsed in a $NH_4OH : H_2O(1:1)$ solution for 10 min to remove any native oxide. The sample was then indium-bonded to a molybdenum plate to achieve good thermal contact. Before its introduction to the etch chamber, the sample was heated in a preparation chamber to \sim 200 °C in order to melt the indium foil and to desorb residual moisture on the sample. Subsequently, the sample was transferred into the etch chamber via a loadlock and fixed onto a liquid-nitrogen cooled molybdenum etching platform. In this chamber, the sample temperature was measured and controlled by a temperature controller. During etching, the etching chamber was continuously pumped while chlorine gas was introduced through a small tube directed toward the quartz beam-entrance window, ~ 2.5 cm above the sample; this gas-flow direction serves to homogenize the physisorption of chlorine molecules on the sample. A chemically cleaned sample was illuminated with the output from a 15 ns-pulse-length excimer laser operating at 193 nm. The light from the laser

LOAD LOCK SYSTEM



Fig. 2. (a) A sketch of the cryoetching system with sample loadlock. The sample is preheated to $210 \,^{\circ}$ C to desorb residual moisture. (b) A more detailed sketch of the structure of the etching chamber including a molybdenum-block resistive heater

was collimated and homogenized using a pair of cylindrical lenses and then passed through a square aperture which was projected onto the sample surface so as to achieve a uniformly illuminated region.

Etching has been examined for various types of bulk and epigrown III–V materials. Most etching experiments utilized samples of GaAs(100); 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 strong dopant-dependent effects. In order to reveal the chemical selectivity in etching different material composition, samples of MBE-grown Al_xGa_{1-x}As on GaAs, with differing Al content were also examined, as well as a variety of GaSb, InAs, InGaAs epilayers, which are useful for a variety of resonant tunnelling devices. Experiments on materials other than GaAs/AlGaAs are discussed in a separate publication [9].

The etch-rate dependence on laser energy density, gas pressure, pulse-repetition rate and substrate temperature has been previously examined and is reported in detail elsewhere [9]. Briefly, these studies showed that the etch depth per pulse is determined by physisorbed chlorine-layer coverage and photon-flux. Thus the etch rate increases with gas pressure and laser fluence, and decreases with temperature. The etch rate varies linearly with fluence for values below $\sim 30-40 \text{ mJ/cm}^2$. The etch-rate dependence on gas pressure and temperature are those expected on the basis of the pressure and temperature dependence of a physisorbed gas precursor species. At low repetition rates (below 10 Hz) the etch depth per pulse is insensitive to the rate, and decreases at higher repetition rates [9].

3 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 non-crystallographic 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 both bulk GaAs samples and MOCVD GaAs/Al-GaAs layered or MQW samples that were patterned with either 1- μ m scale optical lithography or, for features < 1 μ m, via electron-beam-patterned surface masks.

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 with radii as small as 95 nm. Several different materials were used, including Au/Cr and Si₃N₄. Both of these thin film 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 600 nm resolution indicated that the Si₃N₄ 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 other forms of etchings



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

[10]. When the Au/Cr mask was used, undercutting was significantly reduced and 100 nm features could be made reproducibly.

Figure 3 shows electron micrographs, containing both a surface and an edge-on view of a typical etched GaAs(100) sample which was patterned with an Au/Cr surface mask. The cleaved profile shows that it contains 200–300 nm features etched to a depth of 400 nm. The etching was done with 20 mJ/cm² laser fluence (60 Hz) at 140 K substrate temperature and 5 m Torr-chlorine-ambient pressure for 30 min. In addition, in this particular experiment, a small ~4 m Torr partial-pressure xenon buffer gas was added to the mixture. As discussed in [9] (second paper cited), the xenon additive was sometimes helpful in improving surface morphology. Note that the etched morphology is smooth and exhibits little undercutting.

In our etched samples, non crystallographic anisotropy of etching was observed. This behaviour contrasts with the crystallographic behaviour sometimes observed for Cl₂-based plasma etching and for thermal etching of GaAs, a result which derives from a crystallographicsensitive etching rate [11–13]. Figure 4 illustrates this point by showing two electron micrographs of mesa crosssections which are formed by patterning along the $\langle 1\overline{10} \rangle$



Fig. 4a,b. Cross sectional SEM photograph showing crystallographic etching. Etched mesa profiles are along the $\langle 1 \bar{1} 0 \rangle$ directions on the GaAs (1 1 0) surface are shown. The etching was done at (a) $T_s = 140$ K and (b) $T_s = 300$ K, the laser fluence (193 nm) was 21 mJ/cm² and the chlorine pressure was 5 mTorr. The etch profile in (a) does not exhibit crystallographic etching as the thermal component has been suppressed at $T_s = 140$ K

direction on a GaAs(110) surface by UV-assisted chlorine etching. In both cases, the same laser fluence and chlorine partial pressure were used. However, for the result shown in Fig. 4a, the substrate was at T = 140 K while in Fig. 4b the substrate temperature T = 300 K; this allows us to compare photochemical etching from a cryogenic film and from an ambient-temperature film. Also note here that the etching reaction at 300 K is primarily thermally driven [4]. The micrograph result shows clearly that in contrast to gas-phase-Cl etching, the cryoetching is not crystallographic. In contrast to the results seen for thermally activated etching of GaAs by Cl₂, the 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 near-field 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 on that slope.

Surface roughness and etch-depth uniformity provide an important measurement of the quality of any deviceetching technique, since both influence the fidelity of pattern transfer as well as the amount of surface-carrier recombination. After installation of the loadlock assembly to eliminate any introduction of water vapor, etc. into the etching chamber while loading and unloading the sample, the intrinsic roughness was found to be ≤ 50 Å based on SEM and profilometer examination. This roughness appears to be intrinsic to the process chemistry, and possibly attributable to statistical, local blockage of surface sites by small adsorbate islands.

4 Characterization of the etched material

One of the motivations for investigating neutral atom or "beam" etching, a class which includes the chemical-etch mechanisms in photon-assisted cryoetching, is that, in principle, it should not cause the bulk or near-surface damage which normally results from the momentum transfer of massive particles. Thus it is important to measure the amount of the bulk damage and compare it against an undamaged sample. In addition, clearly the condition of the etched surface itself, i.e., the last 1-2 rows of surface atoms can also play a role in controlling surface recombination. Since, in general, most of the studies described in this paper involved ex situ measurements, we would expect the untreated sample surface to be at best comparable to other (100) surfaces with a thin nativeoxide layer. However, obviously any additional layers of certain forms of impurities imparted during the etch process could further degrade the surface. In order to determine the existence of damage and of contamination as a result of etching, we performed experiments to characterize both the surface and bulk (really a near-surface region) of the etched material. In the case of the latter, we utilized epilayers containing a quantum well as a diagnostic of the etch process. This approach has been used by others in the study of ion damage in plasma or ion etching [14]. Our experiments are described below.

4.1 Surface analytical studies

Auger-electron spectroscopy was used to provide elemental identification of any surface-bound species and an Auger spectrum on two typical uniformly etched samples is given in Fig. 5. The samples were chemically cleaned GaAs(100) (as described earlier); and then etched with 30 mJ/cm^2 at 60 Hz, 5 m Torr Cl₂ and 140 K substrate temperature. These *ex situ* measurements show that etching leaves a stoichiometric surface, if the sample is not subsequently exposed to chlorine during the warm-up of the molybdenum block. For example, heating the sample in a reaction chamber, immediately after dosage, can cause excess chlorine which is condensed on the liquid nitrogen dewar to be released and react with the GaAs surface; this process then typically results in additional



Fig. 5. Auger spectra of GaAs (100) prepared under various conditions. (a) Chemically cleaned reference sample (b) Cryoetched sample heated at room temperature in the etch chamber: (c) Cryoetched sample heated to room temperature in the preparation chamber so as to avoid additional chlorination a = ---; c = ----

chlorination of the sample surface as is shown in Fig. 5b. Such a surface is Ga rich when heated to 300 K, as is shown in Fig. 5b, since AsCl₃ desorbs at room temperature [15], while GaCl₃ remains on the GaAs surface. If, on the other hand, spurious chlorination is eliminated first by irradiating the sample with the excimer laser immediately after etching (but with no chlorine in the chamber), then immediately removing the sample to the sample preparation chamber, a stoichiometric surface is obtained (Fig. 5). Note that the trace amounts of chlorine, carbon, and oxygen on the etched surface result from air exposure and the presence of some residual etch products; postirradiation heating of the sample surface prior to removing the sample from the preparation chamber resulted in a partial removal of even this residual surface chlorination.

4.2 Photoluminescence

Photoluminescence (PL) is used extensively as a process diagnostic for etch damage [14]. While the use of any technique has its limitations, PL is a particularly convenient method, with certain important advantages. Specifically, it is non-invasive and thus does not alter the etched material, and can be easily used to examine different regions on the surface. Its spectral output is useful in probing a variety of phenomena on etched surfaces. Finally, luminescence is particularly suited as a process diagnostic for light-emitting devices since it is, in fact, a direct measurement of light-emitting properties.

4.2.1 Bulk material. Any change in the photoluminescence as a result of our chemical etching process will probe changes in the near-surface bulk radiative properties of the semiconductor. In particular, in the presence of

a near-surface damage layer, the non-radiative recombination rate will increase, thus decreasing the integrated photoluminescence intensity from the sample. We have performed ex situ photoluminescence measurements at room temperature in air and in situ PL at 140 K with the sample in vacuum. While the room-temperature photoluminescence lineshape is broad, total luminescence efficiency (measured here by the peak intensity) is sensitive to this damage [16, 17]. In the measurements reported here, the luminescence was excited by using a 20 mW, 488 nm (absorption depth 810 Å) Ar^+ laser focused to a 20 μ m spot size. Laser excitation and luminescence collection were both normal to the sample surface. The luminescence radiation was detected by a photomultiplier tube in a photon-counting configuration after being dispersed by a 0.85 m double spectrometer. In these experiments as well as in the case of the experiments described in Sect. 1 below, the laser power was varied by ~ 2 and the PL signal was found to respond linearly.

In these experiments, the peak intensity of room-temperature photoluminescence was plotted as a function of etch depth for samples etched both by cryoetching and reactive-ion etching. These measurements were taken by measuring the PL signal when the spectrometer was set at the peak luminescence wavelength at 7870 Å. For each etch depth, the luminescence signal was measured at five different spatial locations on the etched surface in order to check for variations in the signal (represented by the error bars in the graph). As seen in Fig. 6, the luminescence intensity for the cryoetched sample was independent of etch depth and comparable to that of a chemically cleaned unetched sample, suggesting that photon-driven cryoetching does not produce near-surface bulk damage. In contrast, for samples etched by a commercial reactive ion etcher under the conditions of 20 sccm $CCl_2F_2/10$ sccm Ar (50 mTorr chamber pressure) at 50 W RF power, the luminescence efficiency decreased as the samples were etched. This decrease is due to the formation of a damage layer in the underlying material, which increases as the etching progresses [18].

One possible drawback of the above results was that the cryoetched sample was transferred out of the etching system in order to perform the luminescence measurements. In order to determine the importance of the ex situ exposure, in situ photoluminescence measurements were also performed. The measurements consisted of measuring the photoluminescence of a GaAs sample held in situ at a typical etching temperature (140 K), performing cryoetching and then measuring the luminescence efficiency after the etching. Again it was found that the luminescence signal did not change due to the etching. Note that since this measurement was performed only at high vacuum ($\sim 10^{-7}$ Torr) conditions, at the time of the post-etch PL measurement, the surface did contain some surface oxide [19, 20]. The photoluminescence peak intensity was also studied as a function of laser fluence in the range $20-35 \text{ mJ/cm}^2$. No change was found, indicating that the absence of near-surface bulk damage is not sensitive to laser energy density in this range of fluences. Surface damage would be expected at fluences well beyond our operating range, under conditions such that the surface is melted or ablated $\lceil 20 \rceil$.



Fig. 6. Peak room-temperature photoluminescence intensity for samples etched using cryoetching (*solid circles*) and RIE (*open circels*). The cryoetching conditions were: 140 K, 5 mTorr Cl_2 , 20 mJ/cm^2 , 60 Hz. The RIE conditions are described in the text. Intensities are normalized to that of a chemically cleaned unetched sample

4.2.2 Quantum-well material. While the above-described measurements on bulk material are particularly useful in providing information on accumulated etch damage, they do not provide a sensitive method for measuring bulk damage or near-surface damage on the sidewalls of small-scale features, such as are important in submicrometer-scale devices. The central problem in using photoluminescence in this case is emission from the underlying substrate. This obscures emission from the etched regions near the etched values - particularly since these nearsurface regions rare highly quenched for small surface features. Instead a more useful approach is to use epitaxygrown material with wavelength-distinctive quantum wells, the PL of which is shifted significantly from that of the substrate. In this case, the etching process leaves the QW material only in the features which are etch-defined [14].

In fact, there has been much recent interest in the study of the luminescence from quantum-well material etched with deep-submicrometer lateral resolution [21-27] in order to understand the importance of bulk or near-surface damage induced by dry-etching. For instance, Clausen et al. [23] found that the luminescence efficiency of features RIE-etched from GaAs/AlGaAs quantum wells decreased as the etch depth was increased beyond the depth needed to etch through the quantum-well layer. Also, they were unable to detect any luminescence from etched features with radii smaller than 100 nm for certain etch conditions, indicating the formation of a damage layer that increases in size with plasma exposure. K. Kash et al. [25] found that ion-beam-assisted etching of InP/InGaAsP quantum wells with large feature size $(\sim 2 \,\mu m)$ altered the quantum-well luminescence due to etch-induced damage. Several studies have shown enhancement of the luminescence features etched from quantum wells, but did not examine the effects of feature size on the luminescence efficiency, making it difficult to identify precisely the mechanism for the enhanced luminescence [26,27], Picosecond laser studies have also been successfully used to study sidewall recombination in quantum wires [24b].

Thus, for the experiments described here, a photoluminescence test pattern consisting of arrays of squares fabricated on a multiple-quantum-well substrate was etched into the semiconductor surface. The substrate consisted of three 50 Å GaAs quantum wells (QWs), separated by 250 Å $Al_{0.3}Ga_{0.7}As$ barriers, with a 50 Å GaAs layer cap layer. The three QWs were sufficiently close to the surface that all absorbed significant excitation light; thus the use of three QWs served to enhance the PL signal which was degraded by the small geometric fill factor and a metal-capping layer of the sample array. All epitaxial layers were undoped, grown on a SI GaAs(100) wafer by MOCVD. Etching through the multiple quantum wells typically required 15 min. The test pattern consisted of 250 µm square arrays of smaller squares with a contactmask dimensions ranging from 250 to 2000 nm (full width), with a pitch of three times this dimension. Previous reports have indicated that etch-induced damage may limit the luminescence efficiency of features of these lateral dimensions [23,25]. The surface mask was fabricated by using electron-beam lithography to pattern a thin film of 200 Å Au/50 Å Cr. Similar masks of 700 Åthick Ni films were also fabricated. Figure 7 presents an electron micrograph of an array of features with sides 250 nm in length, etched to a depth of 0.12 µm, showing that the mask pattern has been faithfully transferred into the sample.

One accepted procedure [24, 28] for measuring the bulk or near-surface process damage in etched samples is to compare their luminescence efficiency to the luminescence efficiency of samples fabricated by an etching technique which is commonly accepted to be damage-free, typically wet etching. Note that while wet-etched samples are free from bulk damage, their etched surface, after exposure to air contains a thin native oxide; also, wet etching does not exhibit a single directional anisotropy. In our case, submicrometer boxes were also fabricated by wet etching in a (1:8:50) solution of H_2SO_4 : H_2O_2 : H_2O_3 . Figure 8 shows scanning electron micrographs of the comparison samples formed by wet etching. These features were etched to a depth of 0.20 µm, after being immersed in the etch solution for 30 s. As shown in the top view of Fig. 8, crystallographic anisotropy of the wet etching results in significant undercutting. Specifically, the etched feature is rectangular, despite the square etch mask, indicating that the wet-etch rate is, as expected, different in the two crystallographic axes.

Photoluminescence spectroscopy measurements were conducted to determine the bulk damage in the etched structures [2, 23–27]. PL was measured by using a backscattering geometry (both the 488 nm Ar⁺ laser excitation and luminescence collection were normal to the sample surface). The beam spot size was 20 μ m, so an ensemble of the same type of features was measured in each measurement. The excitation laser power used in these experiments was 20 mW, which caused negligible sample heating of the sample, cooled in a cryostat to 9–12 K. A 0.85 m double spectrometer with 2.7 Å resolution was used to disperse the luminescence. Photon counting was used for



Fig. 7. Cryoetched submicrometer structures. This sample has a Ni etch mask (fabricated courtesy of the Army Research Laboratory, Ft. Monmouth, NJ). The etch mask has not been removed from the sample



Fig. 8a,b. Wet-etched submicrometer structures (a) in perspective, and (b) top view. A large undercut of the etch mask is apparent

luminescence detection. The luminescence measurements were conducted with the etch masks on the sample, so both the excitation laser and luminescence-signal intensity were attenuated by $\sim 50X$ by the mask. Spectroscopy was performed by scanning the detected luminescence wavelength at 0.4 Å/s, with a time constant of 3 s. Sampling of several regions within an array of the same feature

size showed the intensity varied by < 10%, slightly more than the 6% variation expected due to variations in the number of boxes in the laser spot. Luminescence was also examined from a large (250 μ m × 1000 μ m) mesa, to allow us to compare the intensity with that of unetched material. Following the luminescence measurements, the size of the etched features was measured by using scanning electron microscopy. The dimensions of a representative number of features of the same nominal size were measured and averaged, and the fill factor (the fraction of the sample surface occupied by the quantum wells) was determined. To determine if the sample etch depth was sufficient, luminescence of an unpatterned, etched area near the test pattern was measured. No quantum-well luminescence was detected during this measurement, indicating that the sample was etched deeply enough. Further, no change in PL was seen when the etch depth was varied from 0.12 to $0.18 \,\mu\text{m}$, which also confirmed that the etch depth was sufficient. The luminescence efficiency of the features relative to that of the unetched area was determined by dividing the luminescence signal, corrected for the fill factor, by the luminescence signal from the large, unetched mesa.

Figure 9 shows a typical quantum-well photoluminescence spectrum of an array of 500 μ m effective-radius features. In general, the luminescence peak energy of these etch-defined structures exhibited a blue-shift as the feature size decreased. For 500 nm effective-radius features, this shift was about 10 Å (~2 meV). As the feature size decreased, the luminescence spectra remained symmetric and the peak width remained constant (7.0–8.0 meV, FWHM), indicating that variations in the feature size and sidewall quality are negligible.

This peak energy shift is much larger than the energy shift ($\sim 0.01 \text{ meV}$) due to confinement in square-well potential with dimensions equal to that of the feature. A reasonable explanation for this blue shift is the additional lateral confinement of charge carriers by electrostatic band bending arising from the GaAs-air interface. The quantum-well layers are not intentionally doped, thus the small carrier concentration would result in a large surface depletion layer width. For example, for the doping density of 10¹⁶/cm³, expected in such material, with a built-in potential of 0.5 V, the depletion layer thickness would be \sim 250 nm [29]. For the small-feature-dimension array, the dimension of the etched feature will be on the order of, or smaller than, this width, and the entire etch-defined structure will be depleted of majority charge carriers. The photogenerated charge carrier will be confined by the electrostatic charge of the ionized donors. Calculations based on this model [30] show that this confinement potential leads to an energy shift of the magnitude that we observe. Similar confinement was reported by Lebens et al. [31] for selective epitaxy-grown quantum boxes.

Figure 10 shows the normalized etched-feature luminescence signal as a function of etched feature size. For consistency with the model of the luminescence efficiency described below, the feature size is defined as the radius of the circle having the same area as the etched feature. For comparison, this figure also includes PL from samples fabricated by wet etching. The cryoetched feature data are composed of the results from four different



Fig. 9. Photoluminescence spectrum of a 500-nm-effective radius etched structure



Fig. 10. The luminescence efficiency as a function of etched-feature size, for samples fabricated by wet etching and cryoetching, and samples passivated by using a NH₄S surface treatment after cryoetching. The *line* shows the model discussed in the text, with $S = 10^6$ cm/s and $1 = 1 \mu$ m.

samples indicating that these results are consistent from sample to sample. The radius of the smallest feature in these data is 95 nm. This radius represents a reduction in size from the smallest design dimension, and may result from an erosion of the contact mask during etching.

Both laser- and wet-etch samples have the same luminescence efficiency, indicating that our etching induces little or no near-surface damage to the feature. The lack of damage seen in our cryoetched sample is a direct consequence of the purely photochemical nature of this etching.

In order to determine the consistency of the data obtained from wet-etched material as a standard for undamaged bulk material, a mathematical model which gives the quantum-well luminescence efficiency as a function of feature size for a sample with no near-surface damage was used. Specifically, in such a case, the luminescence efficiency is limited only by non-radiative surface recombination at the non-ideal *surface* sample sidewall. In this model, proposed by Clausen [23], the excess minority charge carrier density, *n*, can be described by Fick's Law:

$$D\nabla^2 n - n/\tau + c = 0, \tag{1}$$

where *D* is the minority carrier diffusion coefficient, τ is the bulk carrier radiative lifetime, and *c* is the carrier generation rate. Assuming a circular feature (to simplify the analysis) of radius *R*, the minority carrier density at radius *r* is given by

$$n(r) = c\tau - \frac{Sc\tau I_0(kr)}{DkI_1(kR) + SI_0(kR)},$$
(2)

where k is the inverse of the carrier diffusion length $l = (D\tau)^{1/2}$, I_0 and I_1 are the modified Bessel functions the zeroeth and first order, respectively, and S is the non-radiative surface recombination velocity, given by the boundary condition

$$D\frac{\delta n}{\delta r} + Sn = 0.$$
(3)

The normalized luminescence efficiency is found by integrating (2) over the area of the etched feature, then dividing by the area.

Guided by previous results in the modeling of the materials system [21,23], S is assumed to be large (10^6 cm/s) . For reasonable values of the diffusion length $(\sim 1 \ \mu\text{m})$ for this materials system, the model predicts that the luminescence efficiency of samples of the lateral dimensions investigated here is insensitive to S for $S \ge 10^6 \text{ cm/s}$. The value of the carrier diffusion length, which is highly dependent on the quality of the quantum-well material, is determined by fitting to the experimental data. Assuming that $\tau = 10^{-9} \text{ s}$, $c = 10^9/\text{cm}^3 \text{ s}$, and $S = 10^6 \text{ cm/s}$, the wet-etched data in Fig. 10 can be well fit by a carrier diffusion length of 1 μm ; indicating that, as expected, the model is suitable for wet-etched samples, since they have no near-surface etch-induced damage and exposed surfaces containing traps.

For the cryoetched samples, if there was significant etch-induced bulk damage present, it would result in a reduction of the luminescence efficiency below that predicted by this model, which includes the influence of oxide-exposed sidewalls. Because the luminescence efficiencies of both the cryoetched and wet-etched samples are described well by this model, we believe that etch-induced bulk or near-surface damage is not significant in these samples. Note also that this model can also be used to estimate an upper limit of the thickness of any near-surface "dead" layer (by linearly shifting the model curve to the right). Comparison with the cryoetching data and the model show that this "dead" layer, if present, is <50 nm.

Since the luminescence efficiency of our etched features is limited by the exposed surface, the application of surface passivation techniques should result in raising the PL efficiency of bulk GaAs ambient samples. To examine this approach, a cryoetched sample was soaked in NH_4OH : $H_2O(1:1)$ for 10 min, rinsed in DI water, soaked in NH₄S (21.9% in water) for 10 min, and then dried with flowing N_2 [32]. The luminescence efficiency for different regions of constant feature size on this sample are shown in Fig. 10. We see a small but noticeable gain in the luminescence efficiency of the smallest features, which shows that the luminescence of these features is sensitive to surface quality. The NH₄OH:H₂O soak is important in this process, probably because the ammonium hydroxide etches away the native oxide and any process-related contaminants. The improvement in photoluminescence efficiency achieved by using NH₄S passivation can be explained by a reduction of the surface recombination velocity, S, by a factor of 10, to 10^5 cm/s. This rather modest improvement may be a result of insufficient wetting of the surface by the NH₄S solution.

5 Summary

We have shown that etch anisotropy and resolution in photon-induced cryoetching is sufficient to transfer submicrometer patterns into the surface of a variety of III-V bulk and epilayer materials. Further, measurements of the photoluminescence of etch-defined submicrometer structures suggest that this etching technique induces very little or no bulk or near-surface damage to the sample. The agreement of our luminescence data with the predicted simple drift-diffusion model suggests that drift-diffusion of charged carriers to the oxygen-exposed sidewall limits the luminescence efficiency of the smallest features observed in our samples. Although not discussed here, cryoetching has been used in the fabrication of QW linear and ring lasers, which exhibit high optical and electrical performance [9, 33]. Finally, while only data on GaAs/AlGaAs are presented in this paper, the etch technique is applicable to a wide variety of other III-V materials, which may be used in other laser and tunnelling-transistor applications.

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