Layer-by-layer etching of GaAs (110) with halogenation and pulsed-laser irradiation

B. Y. Han, C. Y. Cha, and J. H. Weaver
Department of Materials Science and Chemical Engineering, University of Minnesota, Minneapolis, Minnesota 55455

(Received 1 August 1997; accepted 14 November 1997)

We have investigated the effect of laser irradiation on the terrace morphology of Br-covered GaAs (110). Layer-by-layer etching of GaAs (110) is demonstrated through laser-induced etching and atomic desorption. Nanosecond pulsed-laser irradiation ($h\nu = 2.3$ eV, pulse power ~ 35 mJ cm^{-2}) of Br–GaAs (110) initially produces a high density of small, single-layer etch pits as Br is consumed. Continued laser irradiation causes Ga and As desorption from pit edges so that pits grow and thereby remove the remnant of the top GaAs layer. When there is Br on the surface, pit growth reflects the Br chemisorption structure (elongated along [001]) but subsequent atom desorption favors growth along $[1\bar{1}0]$. © *1998 American Vacuum Society.* [S0734-2101(98)01502-4]

I. INTRODUCTION

Semiconductor surface etching with halogens can be activated by photon or particle irradiation. Several studies of laser-enhanced etching have shown the importance of electronic excitations of the reactant/surface ensemble, in which photocarriers participate directly in the reaction.[1–5] In addition, relaxation and recombination of these photocarriers lead to a surface temperature rise and possibly thermally activated etching.[1,2] The relative importance of these two components, photocarrier-induced etching and laser heating, depends on the intensity and wavelength of the laser as well as the optoelectronic and thermal properties of the system under investigation. In the context of laser–solid interaction studies, several investigations have explored atomic desorption from defect sites on semiconductor surfaces during irradiation below the ablation threshold.[6,7] This phenomena is similar to desorption induced by electronic transition in gas/solid systems.[8]

A suitable combination of laser-enhanced halogen etching and laser-induced atomic desorption offers the possibility of achieving layer-by-layer removal of a semiconductor surface, a desirable process in optimizing the quality of the surface and in modifying the surface for nanoscale applications. Several previous studies have explored halogen etching of semiconductors that are enhanced by ultraviolet laser irradiation[3,9] or low-energy Ar ions.[10,11] In most of these studies, however, microscopic structural characterization of the sample was not performed. Using a mechanical stylus to measure the overall etching depth over several tens of etching cycles, Aoyagi *et al.*[10] reported a self-limiting etching of GaAs (100) by alternative etchant (Cl_2) feeding and low-energy ion bombardment. They attributed this behavior to two-dimensional-like etching. In this article, we report on the realization of layer-by-layer etching for GaAs (110) using chemical etching and laser-induced desorption of Ga and As from the etch-patterned surface. This procedure alternatively roughens the surface by monolayer pitting (with Br) and then smooths it by pit growth and coalescence. Scanning tunneling microscopy (STM) makes it possible to monitor the surface morphology at all stages.

II. EXPERIMENT

The experiments described here were performed in an ultrahigh vacuum chamber with a base pressure of 5×10^{-11} Torr. Clean GaAs (110) surfaces were obtained by cleaving p-type crystals (Zn-doped at 1×10^{18} cm^{-3}; MCP Wafer Technology, Ltd., UK) which had initial dimensions of about 3 mm$\times$3 mm$\times$10 mm. The density of initial defects on terraces, mostly in the form of small point defects or adatoms, was typically $\leqslant 1\times10^{12}$ cm^{-2}. A molecular beam of Br_2 from a solid-state electrochemical cell operating in ultrahigh vacuum[12] was used to dose the sample. The typical operating current in the source was 5 μA; in our experimental configuration, 100 s Br_2 exposure at room temperature produced a GaAs (110) surface with Br coverage of about 0.25 ML [1 ML$=8.84\times10^{14}$ cm^{-2}, the planar density of GaAs (110)]. The sample could be heated by a tungsten filament, using a thermocouple to monitor the temperature. A frequency-doubled Nd-YAG laser emitting 2.3 eV (532 nm) photons with a pulse duration of $\sim$6 ns and a repetition rate of 10 Hz was used to irradiate the sample at normal incidence. The laser beam had an approximate 5 mm $1/e$ spot diameter and an energy fluence of $\sim$35 mJ cm^{-2} per pulse incident on the sample, as measured by a pyrolytic power meter and a photodiode. No additional Br_2 was supplied after the initial dosing. After each reaction step, the sample was transferred to the STM stage and constant-current, occupied-state images (As-sublattice) were recorded at room temperature. Imaging during irradiation or heating was not possible, and it was not possible to return to exactly the same portion of the surface during sequential processing. The images presented here have $[1\bar{1}0]$ running from lower right to upper left. They are representative images that reflect surface Br concentration, etch pit density, and area in various etching stages. The vacuum during Br_2 exposure, photon irradiation, and STM measurement was better than $\sim 8\times10^{-11}$ Torr.

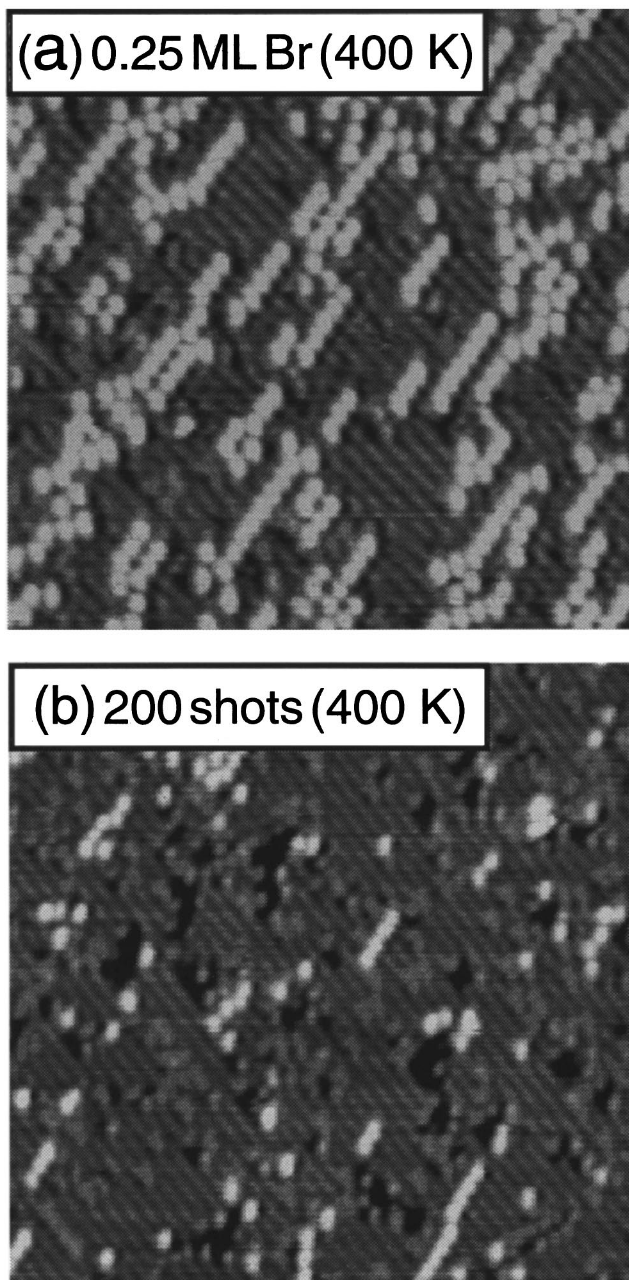

FIG. 1. (a) Occupied-state image of GaAs (110) after dosing with 0.25 ML of Br at 400 K. The bright $2\times 1/c(2\times 2)$ islands and chains elongated along [001] reflect Br bonded to As sites. Within these structures, all Ga sites and half of the As sites are Br terminated (200×200 Å^2). (b) Surface morphology after 200 laser pulses (pulse fluence ~ 35 mJ cm^{-2}) while the sample was heated to 400 K. Irradiation produces a large number of small etch pits. Residual Br decorates the pit edges. Some Br chains and small islands are also visible (250×250 Å^2).

III. RESULTS AND DISCUSSION

The micrograph of Fig. 1(a) represents the surface after condensing ~ 0.25 ML of Br at 400 K. The surface is decorated with bright features that form two-dimensional islands and chains elongated along [001], i.e., perpendicular to the substrate atomic row direction [$1\bar{1}0$]. As discussed previously,[13,14] Br_2 chemisorbs dissociatively on GaAs (110) and these features reflect Br bonded to As. Associated with them are Br–Ga features, but they are obscured by the brightness of Br–As. The Br coverage, θ_{Br}, was determined by direct counting. Irradiation with 200 laser shots while the sample was held at 400 K produced small, single-layer deep etch pits, as shown in Fig. 1(b). The typical pit size was less than ten surface unit cells, and the pit density was as high as 1.5×10^{13} cm^{-2}. About 13% of the top layer in Fig. 1(b) had been removed by 200 shots, as θ_{Br} was reduced to 0.1 ML, reflecting desorption of bromides in laser-enhanced etching. Most of the residual Br adatoms appeared as scattered features around the etch pits, together with a few short chains and Br islands. The decoration of pit boundaries by Br reflects the fact that such sites have lower coordination numbers and are favorable adsorption sites.[13,14] Comparison with thermal etching[13,14] indicates that pulsed-laser-induced etching produced a much higher density of smaller and less regular etch pits.

Insights into the reaction pathways associated with laser etching of Br–GaAs can be obtained by comparison with results for Cl–GaAs. For submonolayer Cl coverages, the etch products are GaCl, $GaCl_3$, and As_x ($x=2,4$) with either thermal activation[15,16] or nanosecond UV laser irradiation.[3,9] In thermal etching, similar reaction pathways were observed for Cl–GaAs and Br–GaAs.[14] Terrace pit creation is a costly process in view of bond breaking and it involves formation/desorption of $GaBr_3$, while GaBr desorption is primarily involved in pit enlargement at low local Br concentration. The irradiation etch yield deduced from Figs. 1(a) and (b) is 0.87. Since the etch yields for trihalide and monohalide channels would be 2/3 and 2, assuming spontaneous As_x desorption, the observed yield of 0.87 implies that $\sim 85\%$ ($\sim 15\%$) of the Br was consumed via the trihalide (monohalide) channel. Based on a one-dimensional heat diffusion model, we can estimate that the surface temperature rise was ~ 250 K for a laser pulse fluence of 35 mJ cm^{-2} (Ref. 5). The resultant peak surface temperature of ~ 650 K was sufficient to activate both monohalide and trihalide channels; the former desorbs at 600 K whereas the latter (high concentration channel) can occur at 500 K.[14] Studies of etching at various pulse powers and substrate temperatures suggest the presence of photochemical contributions, as discussed elsewhere.[17] We did not observe a desorption difference between n-type (Si-doped, 1×10^{18} cm^{-3}) and p-type samples. This was because for nanosecond pulses with intensities more than 1 mJ cm^{-2} per pulse, the density of photocarriers in the depletion region exceeds the dopant concentration by orders of magnitude.[5]

The effects of subsequent laser irradiation were summarized in Fig. 2, which demonstrates etch pit growth and incremental removal of the top atomic layer. The base temperature was 300 K (instead of 400 K in Fig. 1) to avoid pitting of the exposed second layer. Figure 2(a) was obtained after 4×10^3 shots of the surface in Fig. 1(b). The pit density was reduced to 2×10^{12} cm^{-2}, about 13% of that in Fig. 1(b), as small pits expanded and overlapped. At this stage, $\sim 25\%$ of the top layer had been removed.

Pit growth due to irradiation for a surface that is partially

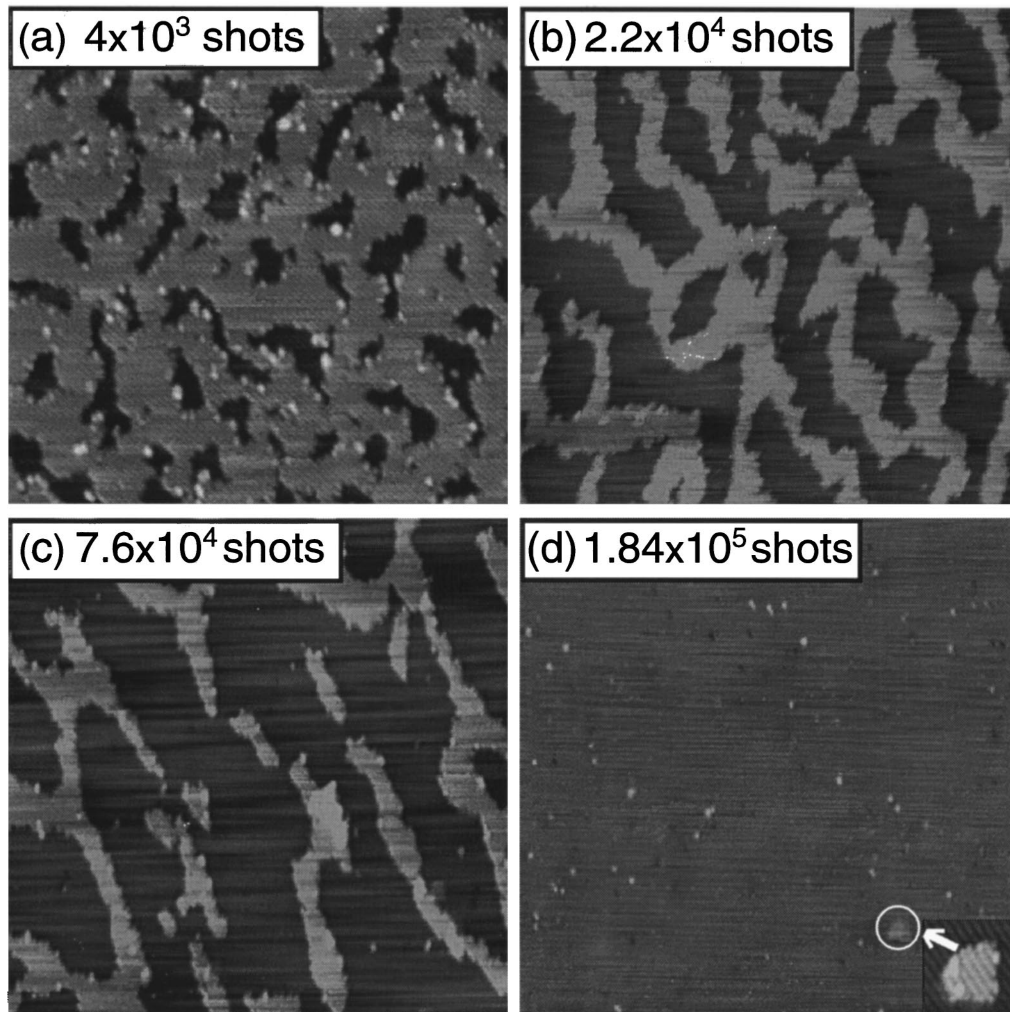

FIG. 2. STM micrographs showing that laser irradiation of the surface of Fig. 1(b) first produces irregular pits by enabling growth along [001], (a), until the Br is depleted. Thereafter, in (b) and (c), atom desorption prevails and causes enhanced growth along $[1\bar{1}0]$. In (d), $>98\%$ of the top layer has been removed. The inset in (d) highlights a small island of the top-layer remnant [550×550 Å^2 in (a), 800×800 Å^2 in (b), (c), and (d)].

Br covered occurs via Br etching and desorption of substrate atoms that come from the boundaries of existing pits. The etching reflects a combination of short-duration laser heating and substrate-mediated photocarrier-induced reaction. As far as thermal desorption of atoms from the pit boundaries is concerned, heating at 650 K for 10 min caused no such atom evaporation in the absence of Br.[14] Since the pulse fluence here gives rise to a peak surface temperature of only $\sim$550 K, we conclude that atom desorption was enabled by electronic excitation. This is supported by laser-induced atom desorption studies on GaAs (110) where the dependence of Ga^0 emission on laser wavelength (at powers comparable to ours) revealed a direct correlation between the Ga^0 desorption and the density of photo-generated two-dimensional electron–hole pairs.[7] Surface defects such as adatoms, steps, and vacancies represent favorable sites for localization of the electronic excitation energy. The modification of the charge state by excitation or by trapping of carriers causes local bond distortion that leads to atom desorption.[6,7] In control experiments, we irradiated a pristine GaAs (110) with 1.2×10^4 laser shots at the same pulse fluence (35 mJ cm^{-2}) and found no increase of terrace defect density.

The effects of both Br etching and atom desorption from pit boundaries are evident in Figs. 2(a) and 2(b). The former occurs with minimal surface diffusion of Br, so it tends to mimic the chemisorption structure [Fig. 1(a)] and enhances pit elongation along [001]. On the other hand, laser-induced Ga or As desorption favors pit growth along $[1\bar{1}0]$ because of the weaker bonding of nominally twofold coordinated atoms at pit ends. The result is that the overall pit shapes are highly irregular at first. With extended laser irradiation to produce Fig. 2(b), progressing from 2(a) where the Br concentration was <0.02 ML, the morphology reflects atom emission with pit elongation along $[1\bar{1}0]$. In Fig. 2(b), the exposed second layer accounts for 52% of the surface. The incremental removal associated with those 1.8×10^4 laser shots was 0.27 ML and the emission yield was 1.3×10^{10} atoms/cm^2 per pulse ($h\nu=2.3$ eV, pulse fluence 35 mJ cm^{-2}).

Figure 2(c) shows that increasing the number of shots to 7.2×10^4 reduced the top layer to 0.25 ML. The remnants at this stage are long, thin strips. The corresponding emission yield was 3.8×10^9 atoms cm^{-2} per pulse, which is 28% of that when going from Fig. 2(a) to Fig. 2(b). This lower yield reflects a decreasing number of available atom desorption sites (total of pit-boundary atoms) due to shrinkage of the top layer, and a smaller proportion of boundary atoms on steps across $[1\bar{1}0]$.

Finally, Fig. 2(d) was produced by exposing the surface to a total of 1.84×10^5 laser shots. This corresponds to the removal of $\geqslant$98% the top GaAs (110) layer. The only remnants of the top layer are small scattered islands consisting of several to several tens of atoms. In addition, some small pits of 1–4 surface unit cells are visible on the second layer of Fig. 2(d) (density $1.5\times 10^{12}\ cm^{-2}$, 0.008 ML removed). Analysis shows that the emission yields per available site from a terrace site and pit boundary site differ by $\sim 10^3$ under our experimental configuration. This ratio can be further improved by decreasing the laser pulse energy but this would increase the number of laser shots necessary to remove the top atomic layer (the emission yield follows a power law dependence on pulse energy[6,17]). While the number of laser shots used for monolayer removal via this two-step process is large, we note that the laser–surface interaction time is only ~ 1 ms.

In summary, we have demonstrated layer-by-layer removal on GaAs (110) by first seeding the surface with vacancies (laser-assisted halogen etching) and subsequently using the laser to induce pit growth. Initially, the surface morphology reflects the Br chemisorption structure but it changes as Br is depleted. Minimal disruption of the exposed second layer was observed because of the higher pulse fluence needed for terrace atom desorption. The halogenation/irradiation cycle presented here provides a protocol for layer-by-layer removal of semiconductor materials. Tuning the initial halogen coverage, the laser power, and the photon energy will give another dimension to surface patterning and removal.

ACKNOWLEDGMENTS

We thank G. S. Khoo and C. J. Palmstrøm for stimulating discussions. This work was supported by the Army Research Office under Grant No. DA/DAAH04-95-1-0112.

[1]See C. I. H. Ashby and J. Y. Tsao, *Laser Microfabrication*, edited by D. J. Ehrlich and J. Y. Tsao (Academic, San Diego, 1989), and references therein.
[2]T. J. Chuang, Surf. Sci. Rep. **3**, 1 (1983).
[3]G. Hasse, V. Liberman, and R. M. Osgood, Jr., J. Vac. Sci. Technol. B **10**, 206 (1992).
[4]F. A. Houle, Phys. Rev. Lett. **61**, 1871 (1988).
[5]C. Y. Cha, B. Y. Han, and J. H. Weaver, Surf. Sci. Lett. **381**, L636 (1997).
[6]N. Itoh, K. Hattori, Y. Nakai, J. Kanasaki, A. Okano, C. K. Ong, and G. S. Khoo, Appl. Phys. Lett. **60**, 3271 (1992); A. Okano, J. Kanasaki, Y. Nakai, and N. Itoh, J. Phys.: Condens. Matter **6**, 2697 (1994).
[7]J. Kanasaki, A. Okano, K. Ishikawa, Y. Nakai, and N. Itoh, Phys. Rev. Lett. **70**, 2495 (1993).
[8]For a recent review, see R. D. Ramsier and J. T. Yates, Jr., Surf. Sci. Rep. **12**, 243 (1991).
[9]M. Ishii, T. Meguro, T. Sugano, K. Gamo, and Y. Aoyagi, Appl. Surf. Sci. **79/80**, 104 (1994).
[10]Y. Aoyagi, K. Shinmura, K. Kawasaki, T. Tanaka, K. Gamo, S. Namba, and I. Nakamoto, Appl. Phys. Lett. **60**, 968 (1992).
[11]M. Balooch, M. Moalen, W.-E. Wang, and A. V. Hamza, J. Vac. Sci. Technol. A **14**, 229 (1996).
[12]N. D. Spencer, P. J. Goddard, P. W. Davies, M. Kitson, and R. M. Lambert, J. Vac. Sci. Technol. A **1**, 1554 (1983).
[13]J. C. Patrin and J. H. Weaver, Phys. Rev. B **48**, 17 913 (1993); J. C. Patrin, Y. Z. Li, M. Chander, and J. H. Weaver, Appl. Phys. Lett. **62**, 1277 (1993).
[14]C. Y. Cha, J. Brake, B. Y. Han, D. W. Owens, and J. H. Weaver, J. Vac. Sci. Technol. B **15**, 605 (1997); B. Y. Han, C. Y. Cha, and J. H. Weaver, Phys. Rev. B **56**, 4966 (1997).
[15]G. C. Tyrrell, D. Marshall, J. Beckman, and R. B. Jackman, J. Phys.: Condens. Matter **3**, S179 (1991).
[16]C. Su, H.-Q. Hou, G. H. Lee, Z.-G. Dai, W. Luo, M. F. Vernon, and B. E. Bent, J. Vac. Sci. Technol. B **11**, 1222 (1993).
[17]B. Y. Han and J. H. Weaver (unpublished).