ELSEVIER

Journal of Crystal Growth 153 (1995) 81–89

JOURNAL OF CRYSTAL GROWTH

CH_3I vapor etching of masked and patterned GaAs

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Received 22 September 1994; manuscript received in final form 17 January 1995

Abstract

CH_3I vapor etching of masked and patterned GaAs substrates has been experimentally investigated. For GaAs samples masked with silicon nitride stripes that are wider than 30 μm, the etch depth increased compared to unmasked samples, the magnitude of which increased with increasing mask width. Etching of bulk substrates of (111)Ga and (111)As GaAs revealed a dependence of etch rate on crystal orientation, with (111)Ga > (100)GaAs > (111)As. Increasing etch temperature reduced the orientation dependence of etch rates. Orientation dependence of etch rates was also observed on non-planar GaAs substrates patterned to expose different orientations on wet-etched groove structures. In this case, etch rate differences between the different orientations were amplified when compared to the bulk substrate results. Finally, it was found that the extent of mask undercutting depended on the direction of mask stripes in a fashion consistent with the orientation reactivity results. Mask stripes on (100)GaAs oriented in the $[01\bar{1}]$ direction were severely undercut whereas stripes oriented in the [011] direction were undercut less.

1. Introduction

In-situ vapor etching of GaAs can be an effective pre-cleaning treatment for organometallic vapor phase epitaxy (OMVPE). Previously, we demonstrated CH_3I vapor etching of (100)GaAs substrates in an OMVPE reactor. Specular surface morphologies were obtained at etching temperatures several hundred degrees lower than were required to obtain specular surfaces with any other vapor etchant [1]. GaAs OMVPE regrowth on CH_3I vapor etched GaAs epilayers resulted in superior electrical characteristics at the growth interface compared to conventional wet-chemical substrate cleaning [2]. In addition, the etch rate of (100)AlGaAs epilayers was equal to that of GaAs [1]. This result is in contrast to HCl vapor etching for which the etch rate decreases with increasing AlAs mole fraction [3,4]. Thus, CH_3I vapor etching is a promising in-situ process for OMVPE.

In this paper, we investigate the application of CH_3I vapor etching for patterning GaAs substrates. Development of such an in-situ etch process would be especially advantageous for fabrication of buried heterostructure diode lasers, as previously proposed [3], since ambient exposure of AlGaAs, which leads to oxidation, could be avoided. However, vapor etching of masked sub-

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SSDI 0022-0248(95)00062-3

strates can be affected by diffusion of etchant species between the mask and substrate surfaces. Both surface diffusion and vapor phase ("volume") diffusion processes could lead to nonuniform etching near masked regions. In addition, an important parameter is crystal orientation, since sidewalls will evolve at the mask/substrate interface as etching proceeds. These sidewalls may possess different crystallographic orientations than the bulk substrate, which may have different reactivities toward the etch. An understanding of these effects is important for evaluating CH_3I vapor etching of masked or patterned GaAs.

Several aspects of CH_3I vapor etching of masked and patterned GaAs substrates are studied. Nonuniform etch profiles are observed on GaAs substrates masked with stripes of silicon nitride. The etch rate is enhanced near the mask/substrate surface boundary, consistent with a model of vapor phase volume diffusion from the region above an inert mask to the reactive GaAs surface. The etch rate of bulk GaAs substrates is found to depend on surface crystallographic orientation. These surface reactivity differences are also observed on nonplanar substrates which are patterned to expose micrometer-sized facets of different orientations on the bulk substrate. In this case, the etch rate differences between the different orientations are amplified when compared to the bulk substrate results.

2. Experimental procedure

The substrates used in these experiments were GaAs wafers which were either masked with silicon nitride or patterned with wet-etched groove patterns. To examine the effect of masks on etch uniformity, (100)GaAs substrates misoriented 2° to the (110) were covered with silicon nitride stripes of various widths. Silicon nitride, 100 nm thick, was deposited on GaAs substrates by plasma-enhanced chemical vapor deposition (PECVD) from SiH_4 and NH_3. The stripe pattern was then transferred to the nitride by conventional photolithography procedures. Two patterns were used for these investigations. The first had sets of 9 parallel stripes of increasing width centered over a 200 μm period. The stripes were oriented parallel to the [011] direction, which is shown to minimize mask undercutting effects. The widths of the stripes were 5, 10, 20, 30, 40, 50, 60, 80, and 100 μm. The second pattern had stripes of the same widths but each stripe width was repeated three times before the next width and the stripes were centered over a 250 μm period. After vapor etching, the etch profiles were measured by a mechanical surface profilometer after removing the remaining silicon nitride in a hydrofluoric acid solution.

Bulk etch rates of (111)Ga and (111)As substrates are measured on half-masked wafers. The mask was 100 nm PECVD silicon nitride which was then removed from half of the wafer using standard photolithographic procedures. Following vapor etching, the etched depth was measured with a surface profilometer after removing the remaining silicon nitride in a hydrofluoric acid solution. Reported etch rates are determined by dividing the etched depth by the etch time.

For studying the effect of the crystal orientation on vapor etching on non-planar surfaces, GaAs substrates, (100) misoriented 2° to the (110), were etched to expose either (111)Ga or (111)As surfaces by using an established wet-chemical etching procedure [5]. GaAs substrates were patterned with stripes of photoresist, 400 μm wide separated by 5 μm openings, oriented in the [011] or $[01\bar{1}]$ direction. Grooves were formed by etching the samples in a solution of 5 parts by volume H_2SO_4 (97 wt%), 1 part H_2O, and 1 part H_2O_2 (30%). "V" grooves were etched with stripes oriented in the $[01\bar{1}]$ direction and "dovetail" grooves for stripes in the [011] direction, as shown in Fig. 1. Although the initial opening in the photoresist was only 5 μm in width, the sample was etched under the edge of the mask and resulted in 20 μm openings after 3 min of etching. Additionally, (111)As GaAs substrates were patterned with photoresist stripes oriented in the [110] direction. Samples etched in the solution described above resulted in "lambda" grooves [5], shown in Fig. 1c. This structure exposes two additional sur-

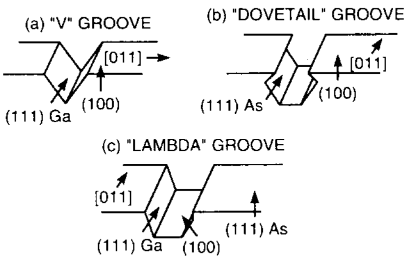

Fig. 1. Groove structures prepared by photolithography and wet-chemical etching: (a) V groove produced on (100)GaAs, (b) dovetail groove produced on (100)GaAs, and (c) lambda groove produced on (111)As GaAs.

faces, the (111)Ga and (100)GaAs. Before and after vapor etching, horizontal cross-sectional photographs of cleaved edges of the substrates were taken by Nomarski interference microscopy. Measurements taken from these photographs allow for quantitative evaluation of any changes in groove shape or size.

All of the CH_3I vapor etching experiments were performed in a horizontal reactor which has been described previously [1]. The vapor etch mixture was 1.7 mol% CH_3I carried in 2100 sccm of hydrogen. The reactor is operated at atmospheric pressure. Substrate temperature was varied between 480°C and 600°C. Etch times were chosen to ensure that the etched depth of the bulk substrate was > 3000 Å. Just prior to loading into the etching reactor, samples were cleaned by degreasing with successive rinses of trichloroethylene, acetone, methanol, and deionized water, placed in concentrated (97 wt%) H_2SO_4 for 2 min, rinsed again in deionized water and placed in concentrated (38 wt%) HCl for 2 min, and rinsed again in deionized water and loaded into the reactor.

3. Experimental results and discussion

3.1. Mask effects

Samples of (100)GaAs patterned with stripe masks of silicon nitride were vapor etched in a mixture of 1.7% CH_3I in hydrogen at 500°C and 525°C. Etch profiles are shown schematically in Fig. 2. For narrow stripes, the etch profile was uniform between the stripes and the etch depth, D_0, was equal to that of unmasked GaAs. For wide stripes, the profile was nonuniform, with a maximum etch depth, D_{max}, at the mask/substrate boundary and a concave etch profile. Also, the etch depth at the center between the wide masks was greater than the etch depth of an unmasked GaAs sample etched at the same conditions, indicating that the mask causes an enhancement in rate over the whole unmasked region. For all stripes, some mask undercutting was observed.

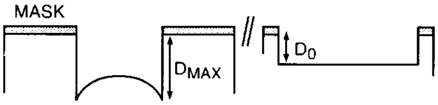

Fig. 2. Typical etch profiles observed on CH_3I vapor etched GaAs masked with Si_3N_4.

Etch rate enhancement is evaluated by taking the ratio of the maximum etch depth D_{max} at the mask/substrate boundary and the etch depth near the smallest stripe, D_0. In Fig. 3, the ratio D_{max}/D_0 is plotted as a function of x_m, the fraction of surface covered by the mask, for two sets of experimental conditions: 500°C with a mask stripe period of 200 μm, and 525°C with a mask stripe period of 250 μm. In both cases, no measurable etch rate enhancement is observed for $x_m < 0.075$. For cases where $x_m > 0.075$, D_{max}/D_0 increases with increasing x_m.

The etch rate enhancement due to masks observed in this study is similar to growth rate

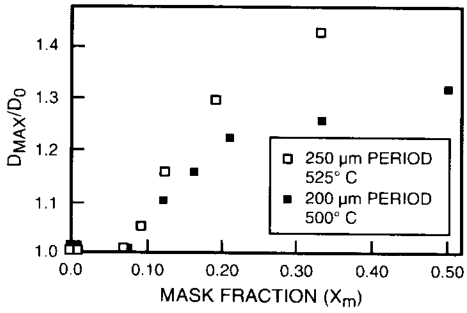

Fig. 3. Etch rate enhancement D_{max}/D_0 due to inert mask as a function of mask fraction (x_m).

enhancement near mask/substrate boundaries reported in several studies of vapor phase epitaxy [6–9]. In these cases, rate enhancements have been attributed either to gas-phase volume diffusion, surface diffusion, or to a combination of both diffusion mechanisms. Because CH_3I vapor etching of GaAs is rate limited by gas-phase kinetics [1], it is expected that volume diffusion of etchant species in the gas phase will be a major contribution to etch rate enhancements observed. However, volume diffusion will not explain the lack of enhancement observed for $x_m < 0.075$. In this case, secondary effects such as mask undercutting as a source of local etchant depletion and surface diffusion may act to offset volume diffusion effects.

3.2. Vapor etching of (111)Ga and (111)As bulk substrates by CH_3I

CH_3I vapor etching of (111)Ga and (111)As GaAs wafers was performed at several different temperatures in a mixture of 1.7% CH_3I in 2100 sccm H_2. The results are presented in Fig. 4, an Arrhenius plot comparing etch rates of (111)Ga and (111)As substrates to previously reported data from (100)GaAs substrates [1]. It is clear that (111)Ga is the fastest etching orientation, especially at lower temperatures. At 504°C the ratio of the etch rates (111)Ga : (100)GaAs : (111)As is 3.0 : 1.8 : 1.0 and at 555°C the ratio is 1.7 : 1.5 : 1.0. The activation energies, found by a least-squares fit to the data are 50 kcal/mol for the (111)As, 45 kcal/mol for (100)GaAs, and 43 kcal/mol for the (111)Ga surfaces.

The surface morphology of etched (111)As and (111)Ga substrates is shown in Figs. 5a–5d, and of etched (100)GaAs substrates in Figs. 5e and 5f. The (111)As face is characterized by the formation of features with a threefold symmetry as can be seen in Fig. 5a for a sample etched at 500°C to a bulk depth of 600 Å in 5 min. In Fig. 5b, for an etch time of 45 min at 500°C, the surface has become more sharply faceted and these facets appear to approach (011) orientations. Similar faceting behavior has been observed when OMVPE growth of GaAs was performed on the (111)As surface from trimethylgallium and arsine [10]. A typical surface for a CH_3I vapor etched (111)Ga sample is shown in Figs. 5c and 5d for samples etched at 500°C to a total depth of 10 000 Å and at 575°C to a depth of 13 000 Å. Although etch pits on these surfaces exhibit a threefold symmetry, the edges are very rounded and the etch pit is nearly circular. Away from the etch pits, the surface is rough with no apparent symmetry or faceting. Etched surface morphology for (100)GaAs substrates etched at 500°C for 30 and 120 min is shown in Fig. 5e and 5f. As with (111)As, the surface becomes rougher with increased etch time. The etch pits on the (100)GaAs substrates are elongated in the [011] direction.

Since differences in etch rates and morphologies are observed on different orientations under otherwise identical conditions, gas-phase kinetics production of etchant species cannot be the sole rate-limiting step. Additional surface effects such as different etch product compositions on different orientations or a condition of mixed control with both surface and gas-phase kinetics may be present.

It is instructive to note that the slowest etching surface, the (111)As, produced the most sharply faceted and most degraded surfaces. Since the etch pit density of these substrates is < 500 cm^{-2}, the facetted morphology cannot be derived from substrate defects. The (111)As surface is unstable

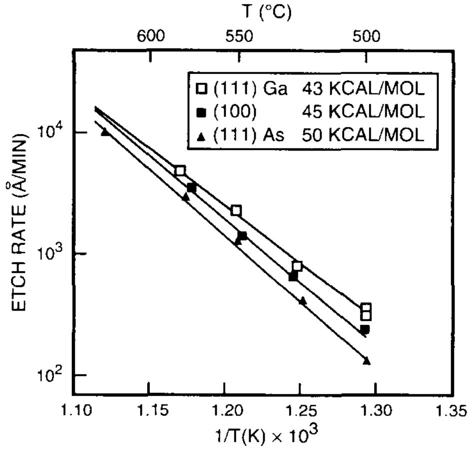

Fig. 4. Arrhenius plot comparing etch rates of the three GaAs bulk substrate orientations studied: (111)Ga, (100)GaAs, and (111)As.

under CH_3I vapor etching, apparently because of its low reactivity. Although no comprehensive theory for explaining facet evolution exists, it is generally accepted that a deposition or etch process for which mass transport is the rate-limiting step will produce smooth surfaces since the surface topology is solely determined by the flux of species to the surface. The same can be said for gas-phase kinetics rate-limited processes. Under mixed control, however, excess chemical potential will exist at the surface which provides a driving force for increasing surface area. Therefore, the

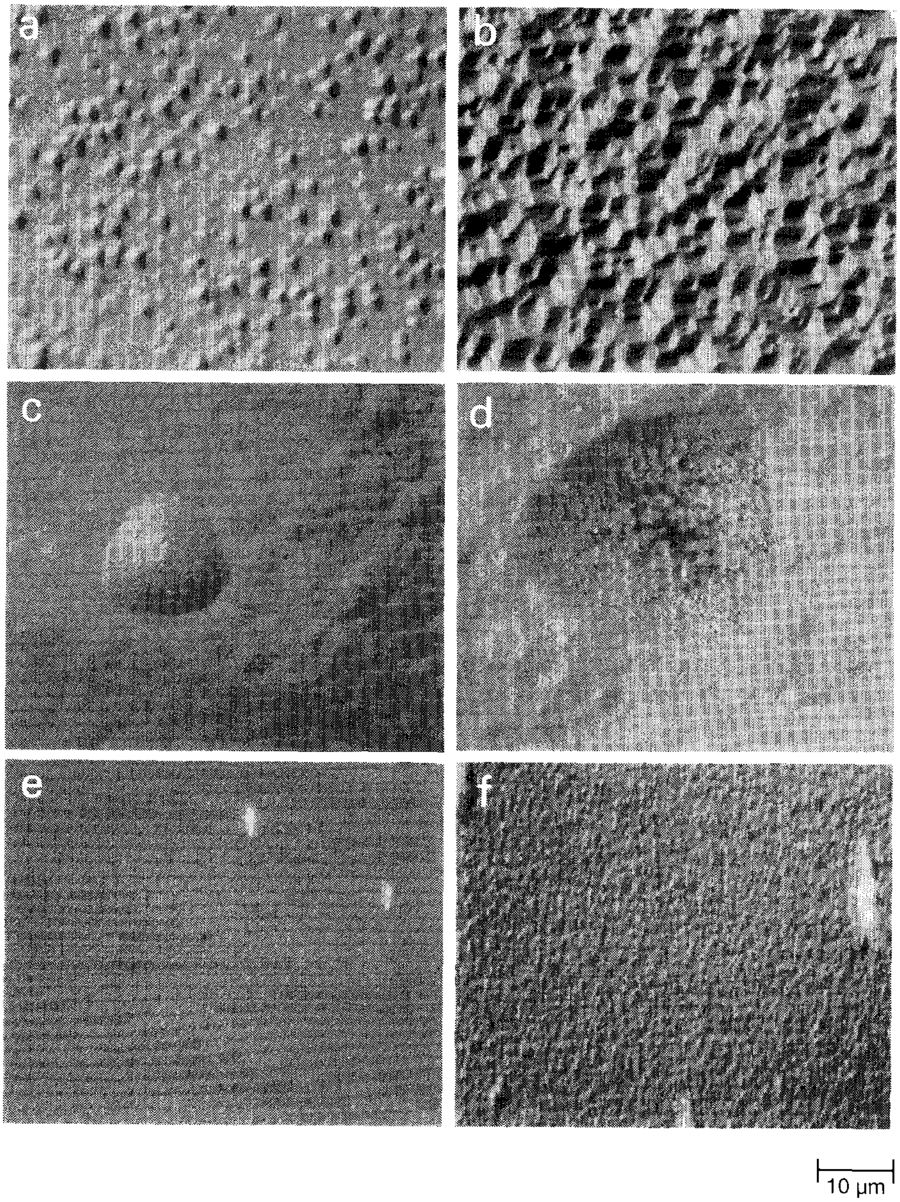

Fig. 5. Surface morphologies of etched GaAs surfaces: (a) (111)As etched at 500°C for 5 min (600 Å), (b) (111)As etched at 500°C for 45 min (6000 Å), (c) (111)Ga etched at 500°C for 30 min (10 000 Å), (d) (111)Ga etched at 580°C for 3 min (13 000 Å), (e) (100)GaAs + 2°(110) etched at 500°C for 30 min (6000 Å), and (f) (100)GaAs + 2°(110) etched at 500°C for 120 min (24 000 Å).

Table 1
Comparison of etched depths of microfacets exposed on bulk substrates of GaAs versus the bulk etched depth

Bulk orientation	Groove type	Facet orientation	Etch T (°C)	Bulk etched depth (μm)	Facet/ bulk
(100)GaAs	V	(111)Ga	480	1.0	2.8
(100)GaAs	V	(111)Ga	520	0.9	2.5
((100)GaAs	V	(111)Ga	530	1.3	2.8
(100)GaAs	V	(111)Ga	576	2.7	2.9
(100)GaAs	Dovetail	(111)As	576	2.8	NA
Masked (100)GaAs	V	(111)Ga	530	2.7	5.7
(111)As	Lambda	(111)Ga	500	0.25	18
(111)As	Lambda	(100)	500	0.25	7.4
Masked (111)As	Lambda	(111)Ga	500	0.25	18
Masked (111)As	Lambda	(100)	500	0.25	7.4

observed surface degradation of the slow etching (111)As surface suggests that mixed control is present.

3.3. CH_3I vapor etching of faceted structures of GaAs: interactions between surface heterogeneities and lateral diffusion processes

CH_3I vapor etching of faceted structures (Fig. 1) provides additional data on how surface reactivity differences interact with lateral diffusion processes. The results of these experiments are summarized in Table 1 as ratios of etched depths of the grooved sidewall facets versus the bulk surface etched depth for the various orientations of GaAs substrates. The etch rate of the (111)As surface exposed on (100)GaAs substrates (the dovetail groove) was too low to be measured. The evolution of the dovetail structure is shown in Figs. 6a and 6b. The overhang was rapidly etched off, exposing a new facet. This facet is inclined approximately 36° (144°) to the (100) plane, corresponding closely to the (211)As orientation. It is expected that this facet is another relatively slow etching orientation.

A typical evolution of a V groove structure with (111)Ga sidewalls is shown in Figs. 7a and 7b. The initial V opens up laterally, forming a structure with sidewalls of approximately the same starting angle and a bottom which is apparently (100) in character but is somewhat curved. The curvature of the bottom is most likely due to kinetic effects; as a new (100) surface is exposed by the receding sidewalls, it begins to undergo etching in the downward direction. The sidewall facet angle also changed as the etching proceeded and, therefore, the (111)Ga facet was not preserved. In reporting etch rates of these sidewalls, an average value was taken between the initial and final sidewalls. The sidewall angles only changed by a few degrees and therefore these sidewalls are still chemically similar to the (111)Ga facet. Vapor etch rates of these (111)Ga surfaces were consistently 2.5–2.8 times higher than the (100)GaAs bulk substrate etch rate. Since

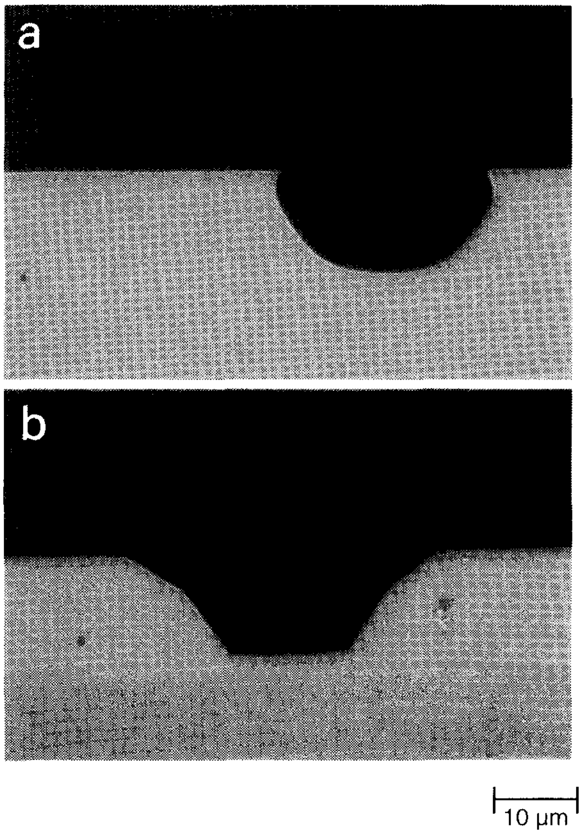

Fig. 6. Evolution of dovetail structure: (a) initial groove shape and (b) groove shape after CH_3I vapor etching at 575°C for 8 min, $y_{CH_3I} = 0.017$.

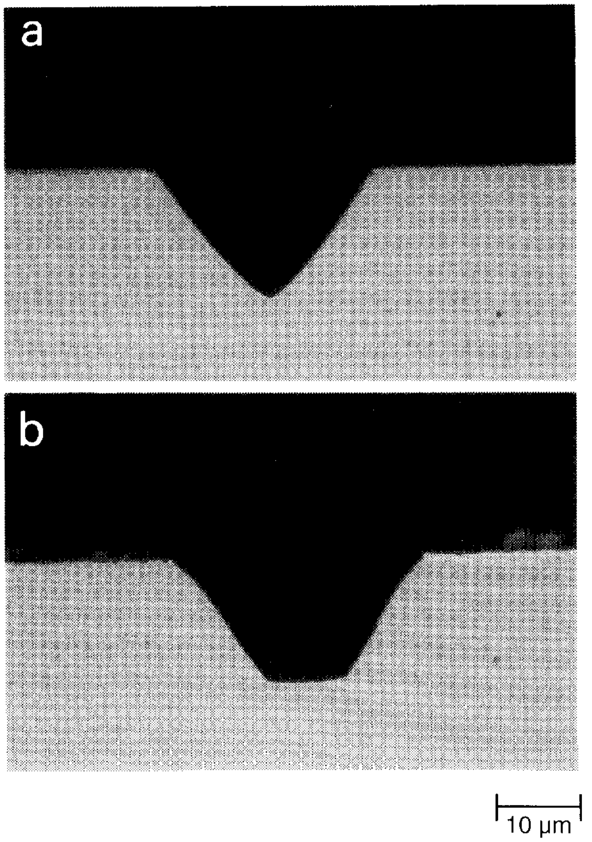

Fig. 7. Evolution of V groove structure: (a) initial groove shape and (b) groove after CH_3I vapor etching at 480°C for 120 min, $y_{CH_3I} = 0.017$.

this ratio did not depend on temperature, it is supposed that diffusion processes are causing this rate enhancement. This diffusion is the lateral diffusion of active etchant species from the less reactive (100)GaAs bulk substrate to the more reactive (111)Ga microfacets. The etch rate ratio between (100)GaAs and (111)Ga is amplified when compared to the results from bulk substrates discussed in the previous section. At 504°C, the bulk (111)Ga/(100)GaAs etch rate ratio was 1.7 : 1 and at 555°C the ratio was 1.1 : 1, both smaller than the 2.5 : 1 to 2.8 : 1 ratio observed in these experiments.

The vapor etching of the lambda groove structures exposed on the (111)As substrates allows for comparison between the slow etching (111)As facet and the faster etching (100)GaAs and (111)Ga facets which could not be observed on the dovetail structure. Under etching, the lambda groove retained its shape and both the (111)Ga and (100) sidewalls receded laterally. The etching conditions were the same as for the unmasked sample, and the etch rate of (111)Ga : (100) etch rate ratio was thus determined to be 2.5 : 1.0. From these two experiments, it was determined that the ratio of etched depths (111)Ga : (100) : (111)As was 18 : 7.4 : 1. Compared to the ratio on bulk samples of 3.0 : 1.8 : 1.0, enhanced selectivity is again observed. Additionally, the cross-sectional images from the masked and unmasked lambda groove samples are nearly identical, indicating that the (111)As bulk surface is effectively inert.

Finally, based on these results, a strategy for aligning parallel line masks on (100)GaAs substrates is proposed which should minimize mask undercutting. It would be desirable to promote the formation of a sidewall facet with the (111)As orientation on the (100)GaAs surface. The (111)As is a slow etching facet and this slowness will be exaggerated in this situation where the bulk of the surface is more reactive. Orientation of stripes parallel to the [110] direction on the (100)GaAs surface should promote the appearance of (111)As facets much in the same fashion as the wet-chemical etch preparations of the samples used in this study (i.e., the dovetail groove). Conversely, stripes oriented parallel to the $[01\bar{1}]$ should exhibit a large degree of undercutting because of the high reactivity of the (111)Ga sidewalls that will be exposed. Cross-sectional scanning electron microscope (SEM) images of two such samples are shown in Fig. 8. Fig. 8a is an image of the undercutting which occurred with silicon nitride stripes oriented parallel to the [011] direction after etching with CH_3I vapor (500°C, 1.5 mol% CH_3I, 20 min). The sidewalls exposed are sloped 45°, smaller than the expected angle between (100) and (111)As of 56.7°, and the ratio between the etched depth and the undercut distance (measured at the top of the slope) is 1 : 1. This undercutting ratio is larger than was expected based on the previously determined reactivity ratio between (100)GaAs and (111)As of 7.4 : 1. One possible explanation for the discrep-

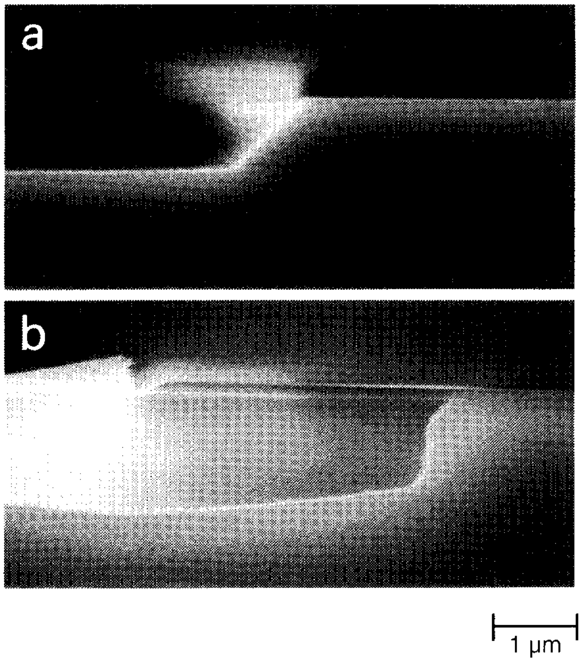

Fig. 8. Scanning electron micrograph cross sections of undercutting by CH_3I vapor etching on patterned (100)GaAs substrates: (a) mask stripes oriented parallel to the [011] and (b) mask stripes oriented parallel to the [01$\bar{1}$].

ancy is the possibility of poor mask adhesion near the mask/substrate boundary augmented by the difference in the coefficient of thermal expansion between GaAs and silicon nitride. Fig. 8b shows the undercutting which occurred with silicon nitride stripes oriented parallel to the [01$\bar{1}$] direction after etching with CH_3I vapor (525°C, 1.5 mol% CH_3I, 10 min). In this case, formation of the (111)Ga facet is not necessarily expected because of its high reactivity. As can be seen from Fig. 8, the undercut ratio of 2.5 : 1 is the same as the ratio of (111)Ga to (100)GaAs etch rates (Table 1) of 2.5 : 1 at 520°C. The exposed sidewall is close to a (011) orientation. The results shown in Fig. 8 are consistent with those in Table 1.

4. Conclusions

Experimental results have been presented relevant to the problem of applying CH_3I vapor etching to patterning of masked substrates of GaAs. It was shown that diffusion from inert mask surfaces to reactive ones can locally enhance etching by as much as 30 to 40% for stripe masks. GaAs substrates of various orientations were found to etch at different rates; the (111)Ga surface was the fastest, followed by the (100)GaAs and the (111)As. In situations where surfaces of different orientations are in close proximity, i.e., groove structures, lateral diffusion processes lead to enhanced surface reactivity differences and produce etch rate ratios as large as 18 : 1. For etching of masked substrates of (100)GaAs, it was determined that orienting mask stripes parallel to the [110] direction promoted the formation of slow etching sidewalls inclined at a 45° angle to the surface. This mask alignment minimizes mask undercutting and is, therefore, of technological importance. When mask stripes are oriented parallel to the [01$\bar{1}$] direction, mask undercutting is far more pronounced, consistent with the findings for etch rate enhancements on groove structures.

Acknowledgements

The authors would like to thank M.K. Connors, W.L. McGilvary, C.H. Anderson, Jr., and J.H. Reinold for their technical assistance. This work was sponsored by the National Science Foundation and by the Department of the Air Force.

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