JVSTB Journal of Vacuum Science & Technology B

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Citation: Journal of Vacuum Science & Technology B **8**, 1357 (1990); doi: 10.1116/1.585077
View online: http://dx.doi.org/10.1116/1.585077
View Table of Contents: http://scitation.aip.org/content/avs/journal/jvstb/8/6?ver=pdfcov
Published by the AVS: Science & Technology of Materials, Interfaces, and Processing

Nanostructure fabrication in InP and related compounds

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(Received 29 May 1990; accepted 25 July 1990)

Nanometer-scale gratings have been fabricated in InP and InGaAs/InP heterostructures using electron-beam lithography and reactive-ion etching in methane-hydrogen plasmas. It is shown that the slight overcut obtained in the etch profiles during a single-step etch in CH_4/H_2 is due to polymer formation on inert mask surfaces and edges. Intermittent removal of the deposited polymer film is shown to be effective in obtaining anisotropic profiles. Highly anisotropic 35-nm-wide InP lines at 70-nm pitch demonstrate the potential of this fabrication process. The formation of 100-nm-wide free-standing InP wires is also presented.

I. INTRODUCTION

Remarkable progress has been made over the last few years in the fabrication of artificial structures with dimensions comparable to the electron wavelength in which the wave-like properties of electrons become prominent. This has essentially resulted in the emerging field of nanostructure physics and fabrication.[1] The quenching of Hall effect[2] and the Aharonov–Bohm effect[3] are some novel phenomena that have been observed in semiconductor nanostructures. High-speed devices such as the quantum modulated transistor[4] and the electron wave diffraction transistor[5] that are based on these novel effects have been proposed. By far, the activities on nanostructures have concentrated mainly on GaAs (Refs. 1–3) and Si (Ref. 6) materials with minimal activities reported on InP and related compounds.[7,8] This situation is because, of all these materials, the processing of indium-based materials is the least developed. In particular, the pattern transfer aspects of nanostructure fabrication in InP need further development. Inamura *et al.*[9] have made initial progress in this direction by using electron-beam lithography (EBL) and selective wet chemical etching to realize fairly anisotropic fine line gratings with 70-nm period. A severe limitation in using wet etching is that lines must be oriented along certain crystallographic directions to obtain anisotropy. For a more flexible process, dry etching must be utilized for pattern transfer.

Currently, reactive-ion etching (RIE) is the most widely used dry etching technique. Reactive-ion etching of InP in chlorinated plasmas is limited by the problems associated with the low volatility of $InCl_x$.[10] Recent reports[11–13] have shown that these problems can be overcome by etching InP and related compounds in plasmas containing mixtures of methane (CH_4) and hydrogen. This gas mixture etches InP by removing In as a volatile organometallic compound and P as phosphine.[11,14] Gratings with periods down to 200 nm in InP, InGaAsP, and InGaAs have been fabricated using CH_4/H_2 plasmas with good anisotropy and good surface morphology.[13,15] Although 30-nm-wide isolated lines have been fabricated in GaAs,[16] the potential of CH_4/H_2 plasmas for transferring nanometer-scale lines and grating structures into InP and related compounds has not been investigated.

In this paper, we present our results on nanostructure fabrication in InP and related compounds using high-resolution electron-beam lithography and reactive-ion etching in CH_4/H_2 plasmas. Highly anisotropic grating structures with periods down to 70 nm are demonstrated. The processing sequence required to achieve this type of structure will be described. In addition, our initial progress in fabricating free-standing nanometer-scale wires of InP suitable for transport studies will be presented.

II. EXPERIMENTAL PROCEDURES

The samples used in this work were nominally undoped InP and InGaAs/InP heterostructures epitaxially grown on semi-insulating InP using organometallic vapor-phase epitaxy (OMVPE). Nanometer-scale pattern definition on these samples was accomplished using high-resolution electron-beam lithography and a bilayer resist process. The lithography was performed on a Cambridge S360 scanning electron microscope (SEM) with typical beam characteristics of 40 kV accelerating voltage, 10 pA beam current, and < 10 nm beam diameter. The beam blanking and X-Y scan signals were computer controlled using a personal computer and a custom-built vector-scan pattern generator. The 14-bit digital to analog converters used provided a pixel size of 3.4 nm $\times$ 2.5 nm across the typical exposure field of 55 μm $\times$ 43 μm area. The polymethyl methacrylate (PMMA) bilayer resist consisted of 46-nm, 950-K PMMA on 51-nm, 200-K PMMA. The positive attributes of this type of resist system for liftoff processing have been discussed extensively elsewhere.[17] Following exposure, development was carried out in a 1:7 methyl isobutyl ketone (MIBK):isopropyl alcohol (IPA) solution for 20 s at 22 °C. After development, 10 nm

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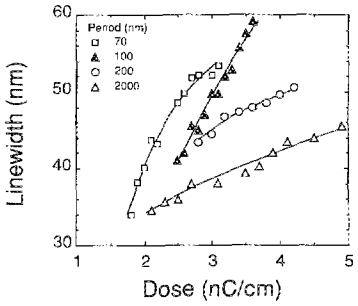

FIG. 1. Linewidth vs dose for different NiCr gratings pitch on InP.

NiCr was thermally evaporated and lifted off to serve as mask for subsequent etching steps.

Pattern transfer was accomplished by RIE in a commercial planar diode system manufactured by Plasma Technology and operated at 13.56 MHz. This system has previously been used to investigate the etching characteristics of InP, InGaAsP, InGaAs, and InAlAs.[13,15] A typical set of operating conditions adopted for the present work consisted of 100 W power, 15 mT pressure, and 40 sccm gas flow rate with a plasma self-bias voltage of 500 V. These etching conditions have been shown to produce good anisotropy, good surface morphology, and negligible RIE-induced damage in InP.[13,15,18] The etch rate of InP using the foregoing plasma conditions was 60 nm/min for large-area geometries. The polymer deposited during etching[11–16] was removed using an oxygen plasma. The patterned samples were examined in the S360 SEM both after NiCr liftoff and after etching.

III. RESULTS AND DISCUSSION

A. Grating structures

The results obtained for electron-beam lithography are displayed in Fig. 1. Explicitly, the figure shows the linewidths of NiCr wires on InP as a function of line dose and grating period. It is seen that linewidths down to 35 nm and

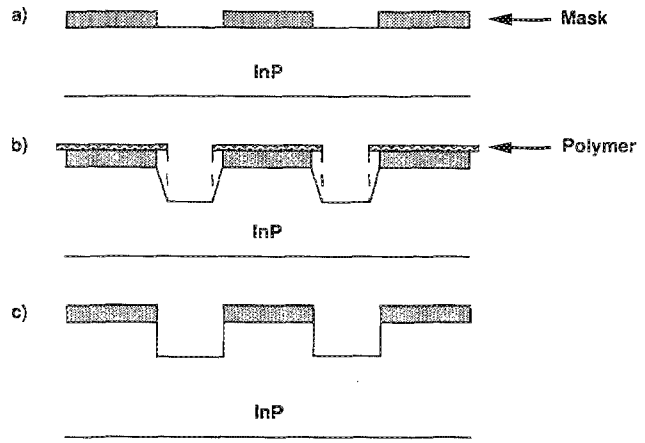

FIG. 3. Schematic illustration of conditions leading to overcut and anisotropic profiles in CH_4/H_2 etching of InP. (a) Substrate with mask. (b) Substrate etched in CH_4/H_2 plasma with polymer film deposition on the top and edges of mask which continuously shields the etched sidewall from reactants. This results in overcut profile. (c) Substrate etched using multiple steps of CH_4/H_2 etch / O_2 plasma clean to eliminate polymer film at intervals to obtain anisotropic profile.

grating period of 70 nm have been achieved. The results shown here are for gratings that could be lifted off reproducibly. Actually, we have obtained metal gratings with 60-nm period, however, the liftoff processing at these dimensions was not consistent. Further, the writing strategy of a single-pixel multiple-pass exposure is not conducive to obtaining the minimum possible linewidths but does result in uniform lines with high edge acuity. The dimensions obtained here are satisfactory for studying the etch profiles of nanometer-scale lines in InP. The etching has been performed with the plasma conditions described in Sec. II.

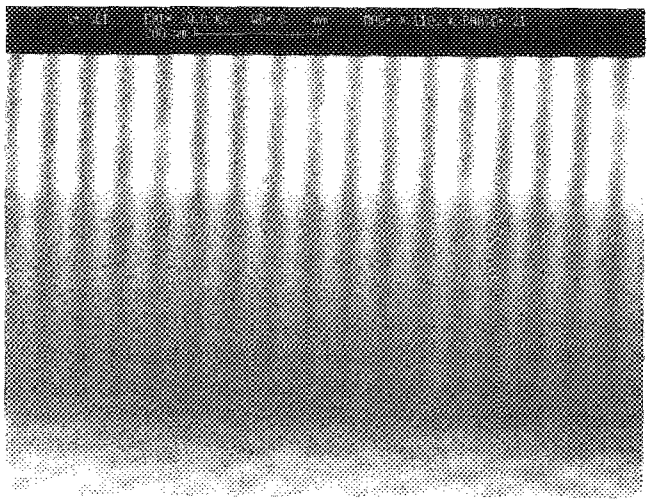

FIG. 2. Scanning electron micrograph of InP grating structure with 70-nm period and 300 nm deep etched in CH_4/H_2 plasma in one step. Note the slight overcut in the etch profile.

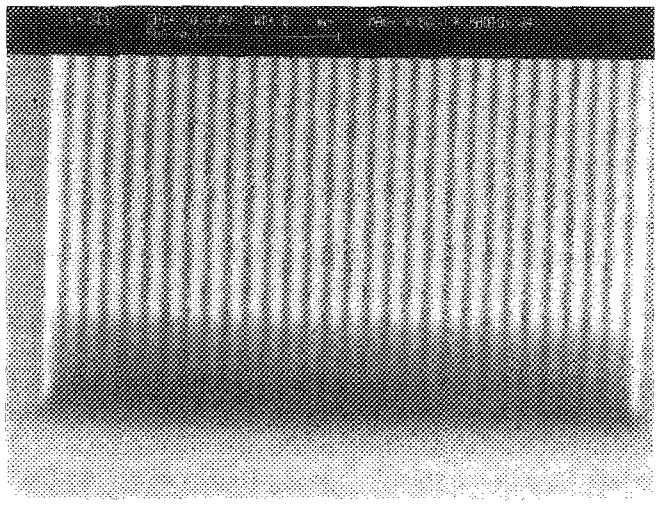

FIG. 4. Highly anisotropic InP gratings with 70-nm period and 300 nm deep etched in multiple CH_4/H_2 etch / O_2 plasma clean cycles.

Figure 2 is a scanning electron micrograph of a 70-nm-period and 300-nm-deep grating structure in InP that has been continuously etched for 9 min. The bright top in the micrograph is the NiCr mask. Close examination of the etch profile shows a slight overcut (outward slant from the mask edge) from the top to bottom similar to what is obtained for ion-beam etching. However, the overcut profile is not produced by ion activity but by shadowing effects due to polymer formation of the NiCr mask. It is well known that the formation of thin films of polymer on surfaces is a byproduct of RIE in methane-based plasmas.[11–16] The hydrogen, organic radicals, and ions produced in CH_4/H_2 plasmas interact on III-V surfaces to etch those materials, and interact on inert surfaces (e.g., NiCr, SiO_2) to form a polymer film.[12] Surface analysis techniques have shown that relatively thick polymers form on inert mask surfaces, whereas polymer deposition on active surfaces such as InP is insignificant even under conditions designed to enhance polymer formation.[19] Therefore, as illustrated in Fig. 3(b), polymer film deposition occurs on top and at the edge of the NiCr mask. The lateral increase of the polymer film with increasing etch time acts to continuously shadow the etch region thereby resulting in an overcut profile. Anisotropic profiles can be obtained as shown in Fig. 3(c) if the polymer film is eliminated. This can be achieved by multiple sequential steps of CH_4/H_2 etch and O_2 plasma clean in the same etching run. The oxygen plasma eliminates the polymer film following a short etch run. This process has been carried out resulting in highly anisotropic profiles. This is evident on the 70-nm-period, 300-nm-deep gratings in InP shown in Fig. 4. The profile was achieved by etching in three steps of 3-min CH_4/H_2 etch and 3-min O_2 plasma clean. It is observed that this structure was effectively etched for 9 min just like the continuously etched sample of Fig. 2. The etch depths of both gratings in Figs. 2 and 4 are identical at 300 nm which indicates that the etch rates for the continuous and multiple-

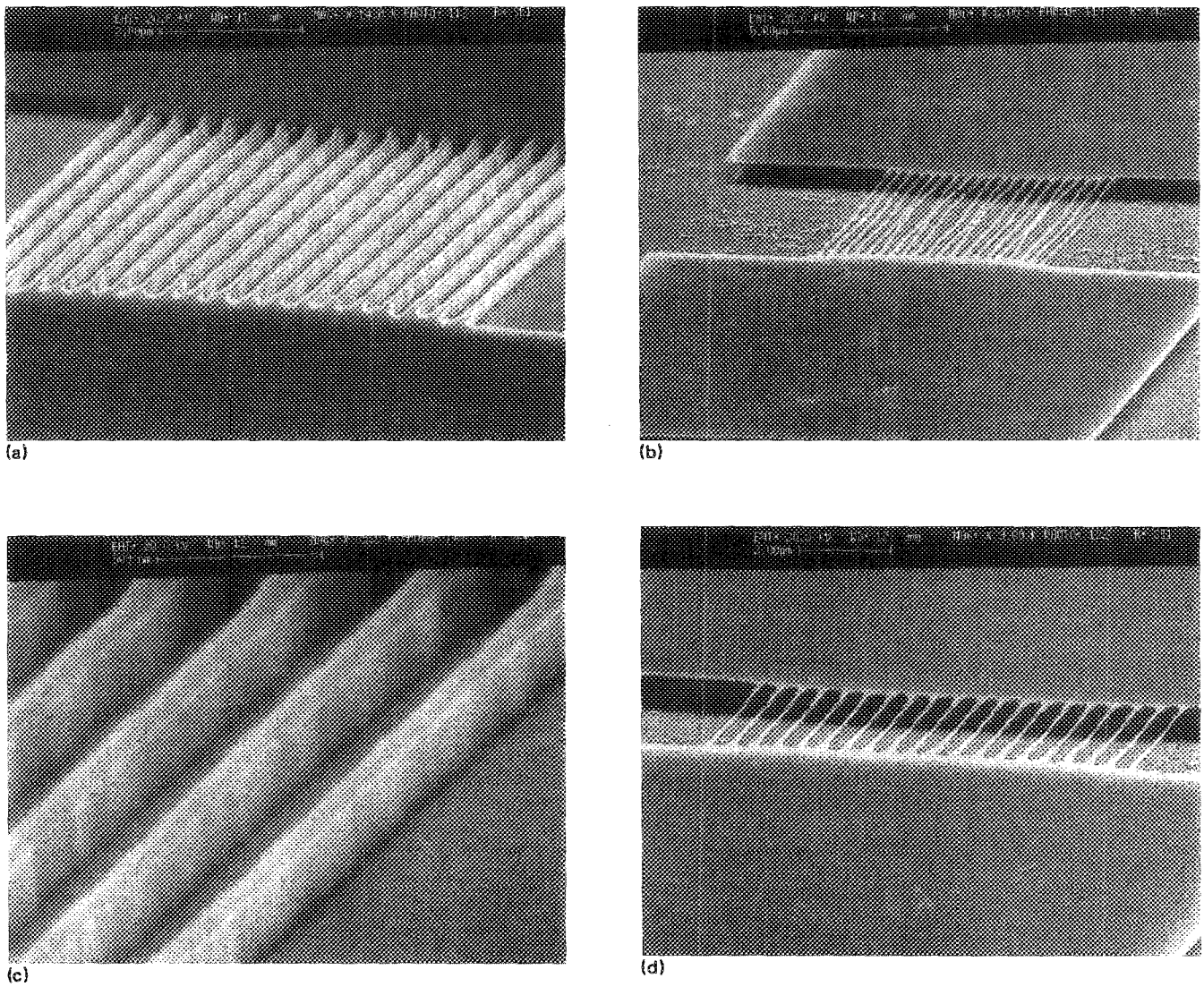

FIG. 5. (a) Grating structure (500-nm period and 100-nm linewidth) etched into an InP/InGaAs heterostructure. (b) Closeup of (a) showing the smooth sidewall and surface. The thin bright layer on top is SiO_2 mask which is removed at this stage. (b) 10-μm-long InP wires obtained after etching of structure in (b) in H_2SO_4-based selective etch solution to remove the underlying InGaAs layer. Note distortions due to the weight of the wires. (d) Same as (c) but InP wires are 5 μm long.

etch-step processes are the same at 33 nm/min. The reduced movement of etching species and products through the narrow etched regions is responsible for the reduced etch rate. It is noted that the multiple-etch technique increases the process time, however, it has the potential of producing highly anisotropic, high aspect ratio structures. This technique also indicates that anisotropy in CH_4/H_2 plasmas is not obtained by polymer passivation of the etch sidewalls since the oxygen cleaning step removes whatever "insignificant" polymer film is on the InP sidewalls. Therefore, anisotropy is imparted by ion bombardment.[12]

B. Self-supporting InP wires

Self-supporting structures of nanometer-scale dimensions in various materials (AuPd, Si_3N_4, GaAs) have been fabricated and used for electron and phonon transport studies.[20] Such structures have not been reported for InP. In this section, we report our initial attempt at fabricating free-standing InP wires using EBL, RIE and selective wet chemical etching. The undoped heterostructure used consisted of 250-nm InP grown by OMVPE on top of semi-insulating InP, followed by a 1-μm InGaAs layer and a 50-nm InP layer. The 500-nm-period grating structure with 100-nm linewidths defined and etched into the heterostructure using CH_4/H_2 RIE is shown in Figs. 5(a) and 5(b). Here SiO_2 was used as an etch mask for its ease of removal in HF solution. NiCr could not be used since it etches in HCl which also attacks InP. The etch depth of 150 nm means that the structure has been etched through the top InP into the InGaAs layer below. The sample was etched using the multiple etch/clean method described above. It is seen that the etched sidewall in Fig. 5(b) is smooth and that no change in anisotropy is evident in the transition from InP to InGaAs.

Many material-selective wet chemical etch solutions have been developed for indium-based compound semiconductors.[21] The mixture of $H_2SO_4:H_2O_2:H_2O$ at a ratio of 1:1:10 etches InGaAs at 31 nm/s at 40 °C but does not etch InP. The dry-etched structure in Fig. 5(b) was subsequently etched in the $H_2SO_4:H_2O_2:H_2O$ solution for 10 s and rinsed in H_2O. With the removal of $\sim$300 nm of material from the underlying InGaAs, free-standing InP wires were obtained. Two sets of 50-nm thick InP wires spanning 10 and 5 μm in length are shown in Figs. 5(c) and 5(d), respectively. The 10-μm-long wires have a length to width ratio of 100 which is perhaps too large causing the wires to sag and distort under their own weight. Further refinement of this process is being carried out in order to fabricate both InP and InGaAs wires to be used for electrical measurements.

IV. SUMMARY

Nanometer-scale lines and gratings in InP and InP/InGaAs heterostructures have been fabricated using high-resolution electron-beam lithography and reactive-ion etching in CH_4/H_2 plasma. It was shown that the slight overcut in InP etch profiles is due to polymer formation on the inert mask surface. By using multiple sequential steps of etching in CH_4/H_2 followed by cleaning in O_2 plasma, highly anisotropic structures were obtained. It can be concluded from this process that anisotropy in CH_4/H_2 RIE is due to the effects of ion bombardment. Highly anisotropic gratings with minimum linewidths of 35 nm at 70-nm period were demonstrated. Finally, free-standing, 50-nm-thick, 100-nm-wide, and 5-μm-long InP wires were fabricated and presented.

ACKNOWLEDGMENTS

The authors would like to acknowledge the technical assistance of A. Pawlowski and W. Guggina. This work was supported by National Science Foundation (NSF) Grant No. ECD 89-43166, Joint Services Electronics Program Grant No. N00014-90-J-1270, and NSF No. Grant DMR 89-20538.

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