Focused ion beam iodine-enhanced etching of high aspect ratio holes in InP photonic crystals

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(Received 10 June 2007; accepted 8 October 2007; published 7 December 2007)

The authors investigate the focused ion beam (FIB) fabrication of photonic crystal (PhC) holes in InP combining physical sputtering using 30 keV gallium ions and iodine-enhanced etching at 150 °C with a protective platinum or tungsten layer. The authors show that it is equivalent to conventional dry-etching methods such as inductively coupled plasma reactive ion etching in terms of achievable aspect ratio (>10), surface roughness (12.6 nm rms), and stoichiometry. The protective layers can be selectively removed after fabrication. This new FIB fabrication method lifts the previous constraints of funnel-shaped holes and limited aspect ratios of physical sputtering and reduces the Ga implantation and amorphous layer. Thus, rapid prototyping (5 s fabrication time per hole) of planar PhCs or planar PhC elements, such as PhC Y splitters, becomes feasible. © 2007 American Vacuum Society. [DOI: 10.1116/1.2804607]

I. INTRODUCTION

Photonic crystals (PhCs) are metamaterials with a periodic spatial variation of the index of refraction. They allow for tailoring the dispersion relation of light and may exhibit forbidden frequency bands for photons, called photonic band gaps, within which no light propagation is allowed.¹ Planar PhCs generally consist of air-filled holes in a dielectric background substrate, thus influencing the light propagation in the horizontal plane perpendicular to the PhC. In the third dimension, the light is typically confined by a slab waveguide structure.

Indium phosphide (InP) is a direct-band gap semiconductor suitable for fabrication of active photonic devices such as semiconductor lasers at the 1.55 μm telecommunication wavelength. We work on PhCs in this material system, using air holes in the horizontal plane and an InP/InGaAsP layer stack with respective thicknesses 300 nm/522 nm grown by metalorganic chemical vapor epitaxy on an InP substrate in the vertical direction to guide the light. The lattice-matched InGaAsP quaternary material has a low refractive index contrast of $\Delta n=0.18$ to InP. Due to the low index contrast, the vertical optical mode is not tightly confined in the waveguide layer, but extends several microns (μm) deep into the InP substrate. For applications at $\lambda=1.55 \mu\text{m}$, typical hole diameters and lattice constants are about 250 and 400 nm, respectively. Thus, aspect ratios exceeding 10 have to be achieved with sidewall angles close to 90° to keep out-of-plane scattering low.

Dry etching techniques, such as inductively coupled plasma reactive ion etching (ICP-RIE), have been used successfully to etch high aspect ratio structures.² In this article, we show that focused ion beam (FIB) milling, assisted by molecular iodine, is capable to achieve structures in InP/InGaAsP/InP with similar aspect ratio and fabrication quality than ICP-RIE. Considering that FIB etching is a maskless process, rapid prototyping and testing of PhC structures becomes feasible.

II. EXPERIMENTAL PROCEDURES

A dual-beam FIB instrument (30 keV Ga^+ ions) was used for all etching experiments. Molecular iodine, stored in a heated crucible, was inserted into the vacuum chamber with a base pressure of 2×10^{-6} mbar through nozzles positioned $\sim 100 \mu\text{m}$ above the InP surface. The crucible was heated to 35 °C for the needle used for the etch-rate measurements and to 30 °C for the coaxial needle, which directs more gas molecules into the holes, used for high-aspect ratio structures. The latter needle has a circular opening of 300 μm diameter, through which the ion beam is directed. For both needles, the gas flux on the surface strongly depends on the nozzle-substrate distance. A heating stage was used to heat the InP substrate *in situ* up to 350 °C. The temperature was measured on the chromium-coated copper surface of the heating stage using a NiCr-Ni thermocouple. The characterization of the hole depths and thicknesses of the deposited layers is performed with scanning electron microscopy (SEM) on FIB cross sections, whereas the hole diameters were determined by scanning ion microscopy (SIM). Sputter

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FIG. 1. Sputtering and etching rates determined by SEM measurements of FIB-sputtered cross sections as a function of stage temperature and beam overlap (InGaAsP is not shown). Surface roughness was inspected by SEM micrographs. Maximum etch rate occurs at 200 °C, but with poor surface quality. Best fabrication conditions are at 150 °C and -200% overlap. The standard deviation has been determined by measuring 18 identical squares and is 12%.

and etch rates were determined by irradiating 20 μm wide squares with an ion current of 313 pA and dwell time of 100 ns during 108 s in InP with and without I_2 and measuring the depth of the holes by SEM. The beam was scanned in a raster pattern to allow gas replenishment on the surface between irradiations. Beam overlaps $\text{Ol} = (D - P)/D$, where Ol is the overlap, P the distance between irradiated pixels, and D the beam diameter, were calculated for beam diameters D of 25 nm at 300 pA and 10 nm at 10 pA. Atomic force microscopy (contact mode in air, SiN_x tip) was used to determine the surface roughness at the bottom of sputtered or etched squares. X-ray photoelectron spectroscopy (XPS) ($\text{Al K}\alpha$ line, base pressure $< 10^{-9}$ mbar) was utilized to analyze the surface stoichiometry and the Ga content. The depth profile was acquired by alternating measurement of the photoelectron energies and sputtering of the area of interest with 3 keV Ar^+ at 45° angle of incidence. The atomic concentrations were calculated with Shirley background subtraction and normalization to 100%. The Y splitters were characterized with an end-fire setup,³ using two tunable laser sources with a wavelength range from 1470 to 1630 nm.

III. RESULTS AND DISCUSSION

A. Milling rate

The sputter rates of InP and InGaAsP were determined at 1.27 and 0.36 $\mu\text{m}^3/\text{nC}$, respectively. Both do not vary with temperature (Fig. 1). The sputter rate of InP is accordingly about nine times larger than the one of Si. Therefore InP allows faster fabrication times, but is more sensitive to ion irradiation. In the case of sputtering, the depth does not vary considerably with the beam overlap, as for low aspect ratio structures ($20 \times 20 \times 0.15 \mu\text{m}$), redeposition is not impor-

tant (the depth of a sputtered crater at a single pixel at 0° angle of incidence is < 1 nm for InP, allowing sputtered particles to escape efficiently). Therefore, the depth is directly proportional to the ion fluence, which was kept constant by adapting the number of passes for each beam overlap. When adding I_2 to the sputter process at room temperature, we observe about a tenfold increase of the etching rate (Fig. 1), due to the spontaneous chemical reaction of I_2 with nonoxidized InP and Ga and ion-induced intermixing, namely an ion-enhanced diffusion of I_2 from the surface to the bulk and from reaction products from the underlying bulk to the surface, and the creation of numerous dangling bonds.⁴ The ion-induced intermixing has a range of 62 ± 6 nm.⁵ However, InI_3 does not sublime but remains on the surface, which limits the etching rate.⁶ InI_3 starts to desorb above 80 °C (Ref. 7) and we observe a maximum etching rate of $83.2 \mu\text{m}^3/\text{nC}$ at 200 °C stage temperature, a 66-fold increase over the sputter rate. This increase can be explained by the thermal desorption of InI_3 from the surface. At temperatures above 200 °C, the etching rate decreases (Fig. 1). This is due to the lower sticking probability of I_2 on the hot surface or the thermal desorption of I_2 before a chemical reaction can occur. Above 330 °C, InI_3 decomposes into involatile InI and InI_2 and volatile I_2 .⁸ InI_x ($x=1,2$) forms a passivating layer which leads to a decreased etching rate at 350 °C because of the lower chemical contribution. At even higher temperatures, P_2 evaporates noncongruently.⁹ From Fig. 1 it can be clearly seen that the beam overlap influences the etching rate, especially between -200% and 0%. By increasing the overlap, the dwell time, or the current, the ion fluence increases and more Ga will impinge per pixel, resulting in faster transition to the sputtering regime due to local I_2 depletion and thus lower etching rate. In order to minimize fabrication times while maintaining a good surface quality, we chose a beam overlap of -200%, 100 ns dwell time, and a stage temperature of 150 °C to etch the holes. At this temperature, the etching rate of InP is 51 times larger than the sputter rate.

B. Surface roughness

Surface roughness was determined by etching 50 μm broad squares at different stage temperatures with a fluence of 2.3×10^{15} ions/ cm^2 . We found that surface roughness increases with temperature up to 300 °C (Fig. 1). This may be due to the spontaneous formation and desorption of InI_3 , PI_3 , P_2 , and GaI_3 , aided by ion intermixing. By raising the stage temperature, a more efficient thermal desorption of the reaction products occurs, which results in craters and a larger surface roughness. Since the chemical etching rate is much larger than the physical sputtering rate, the surface roughness is no longer dictated by the beam overlap and does not vary considerably with the latter. Above 300 °C, the passivating InI_x ($x=1,2$) layer prevents strong chemical etching and the surface becomes smoother accordingly. At 150 °C, we determined the surface roughness to be 12.6 nm rms at the bottom of the 250 nm deep square over an area of 25 μm^2 [Fig. 2(a)]. We achieve similar rms surface roughness as was re-

FIG. 2. (a) Atomic force microscopy measurement of the InP surface etched at 150 °C. rms roughness is 12.6 nm over 25 μm^2 . (b) SEM micrograph of a facet etched at 150 °C in InP/InGaAsP/InP. No differential etching between InP and InGaAsP is observed. Pt was deposited to protect the InP surface. (c) SEM micrograph of holes etched at 150 °C in two stages: first 3 s per hole at 10 pA with a beam overlap of 36.6% and dwell time of 52.1 μs to sputter through the 113 nm thick W mask. Subsequently, I_2 is added and the beam overlap changed to 0% with a dwell time of 100 ns during 2 s. The maximum aspect ratio achieved is larger than 10.

ported for RIE.¹⁰ rms surface roughness for iodine-assisted etching at room temperature was determined to be 2.7 nm, due to the presence of InI_3 islands. Physical sputtering of InP has a rms surface roughness of 1.3 nm, due to the presence of In islands.⁶ Here we summarize the measured rms surface roughnesses:

1. unirradiated InP wafer: 0.3 nm,
2. sputtering at RT: 1.3 nm,
3. iodine-assisted etching at RT: 2.7 nm, and
4. iodine-assisted etching at 150 °C: 12.6 nm.

For PhC holes, however, the sidewall roughness is more important than the roughness at the bottom of the hole. To estimate the roughness, we simulated the longitudinal range and straggling (standard deviation) of 30 keV Ga^+ ions impinging on InP with SRIM (Ref. 11) for incidence angles of 0° and 85°, corresponding to incidence at the bottom of the hole, and on a sidewall, respectively. The calculations showed that the longitudinal range and straggling of Ga^+ ions at the bottom of the hole is 21 ± 11 nm. Under grazing inci-

FIG. 3. XPS depth profile of the bottom area of a square etched at 150 °C with a beam overlap of ~200%. The surface is P rich and contains O and C resulting from the transfer in air from the FIB to the XPS system. Iodine contamination is low and Ga contamination is below the detection threshold. Steady-state conditions are reached after a depth of about 70 nm. The In-rich steady-state is a result of preferential sputtering of P_2 .

dence it decreases to 10 ± 7 nm. Accordingly, we expect the surface roughness to be smaller on the sidewalls than on the etched surface perpendicular to the ion beam.

C. Ga implantation and stoichiometry

Ga irradiation leads to Ga implantation and results in damage to the crystal lattice by the creation of interstitials and vacancies and ultimately amorphization of the monocrystalline InP substrate for fluences above $1.7 \times 10^{13} \text{ cm}^{-2}$ (Ref. 12) which will scatter light. Ga implantation also changes the index of refraction. Both factors have an influence on the performance of the PhC device and should therefore be minimized. Also the stoichiometry of InP should not be altered during fabrication, since it will induce a change of the index of refraction. The XPS measurement in Fig. 3 shows that a surface layer of 20 nm thickness is P enriched. This is explained by a favored reaction of I_2 with In. For depths larger than 70 nm, the In and P concentrations are constant and In rich, a result of the preferential removal of P_2 from InP due to the physical sputtering by Ar^+ to acquire the depth profile.¹³ Iodine is detected up to a depth of ~50 nm. This can be attributed to trapped InI_x ($x=1-3$) or remaining InI_x ($x=1-2$) reaction products on the surface, which sublime only at higher temperatures. Ga atomic concentration is below detection threshold at all depths, whereas the Ga content in InP after sputtering exceeds 20 at. % at a depth of 20 nm.⁶ This is due to the greatly enhanced etching rate and the spontaneous thermal desorption of GaI_3 . Assuming that the range and straggling of Ga ions in InP is not altered by the addition of I_2 , the enhanced etching rate removes most of the Ga-contaminated surface layer and consequently, the amorphous layer is thinner.

D. Maximum aspect ratio

Prior to etching holes, the InP cladding layer has to be protected from stray ion (ions outside the main Gaussian distribution, forming the “beam skirts”) irradiation. To do this and prevent the formation of a funnel in InP, a tungsten (W) or platinum (Pt) protective layer was deposited. W was sputter coated in a physical vapor deposition system with a base pressure of 5×10^{-8} mbar. Pt was deposited using electron beam chemical vapor deposition of the metalorganic precursor $C_9H_{12}Pt$. Pt deposition has to be performed using the electron beam to avoid damaging the cladding layer. Considering that Pt can only be deposited at room temperature due to the decreased sticking probability and decomposition of the precursor above 40 °C and W has a lower sputter rate, we preferred W deposition. Each hole was sputtered in two steps: first, we sputtered the mask during 3 s at 10 pA with a dwell time of 52.1 μ s and 36.6% overlap. This ensures a uniform ion distribution. Then iodine was added and the hole was exposed to I_2 and Ga^+ for 2 s. The dwell time was 100 ns at 10 pA and 0% overlap. W was subsequently selectively wet etched using H_2O_2 (30 vol %) under ultrasonic at room temperature for 15 min. Pt was removed *in situ* by gas-enhanced etching at 150 °C stage temperature using XeF_2 , which permits one to use very low Ga^+ fluences.

The maximum achievable aspect ratio is limited by lateral underetching of InP beneath the mask caused by Ga^+ scattering from the heavy W or Pt atoms at the mask edge. To suppress the underetching, one can use thinner masks to suppress multiple scattering of ions while simultaneously reducing the sputtering time and the aspect ratio in the mask or reduce the etching time. No differential etching rate was observed between InP and InGaAsP and smooth facets could be produced [Fig. 2(b)]. We found that using a 113 nm thick W mask and 2 s etch time yields the best results and show the holes in Fig. 2(c). Good sidewall verticality and an aspect ratio of about 11 for a hole diameter of 270 nm is achieved.

IV. APPLICATION: PHOTONIC CRYSTAL Y SPLITTER

We demonstrate the capability of the new fabrication process on a PhC Y-power splitter³ in which we fabricate the central hole by FIB, whereas the surrounding PhC is patterned by electron beam lithography (EBL) and transferred into the semiconductor by ICP-RIE etching [Fig. 4(a)]. Details of the fabrication process can be found elsewhere.³ Precise control over the positioning of the central hole is required, as this influences the intensity distribution in the two arms of the splitter.³ We further compare fully ICP-RIE fabricated power splitters with power splitters where the central hole is fabricated by iodine-enhanced FIB etching. The filling factor of the splitters is kept constant at $r/a=0.23$ for the PhC holes surrounding the splitter, r being the hole radius and a the lattice constant of the PhC. For the central hole, $r/a=0.19$ was chosen. An 80 nm thick W protection layer was used. The devices were cleaved after fabrication. By using lithographic tuning¹⁴ with $a=375$ –500 nm in 25 nm steps, the reduced wavelength of $u=\lambda/a=0.23$ –0.34 is

FIG. 4. (a) SEM micrograph of a power splitter fabricated by EBL/ICP-RIE without central hole. (b) SIM micrograph of the central hole fabricated by FIB in the center of the Y splitter. (c) End-fire characterization of the power splitter branches (smoothed to eliminate Fabry–Pérot fringes) for EBL/ICP-RIE (red) and FIB (blue) and comparison with W1 (single defect line, green) PhC waveguides for different lattice constants a .

covered. We show a power splitter with a FIB-fabricated central hole in Fig. 4(b). Figure 4(c) shows the measurement results for W1 waveguides (PhCs with a single defect line) and for the two power splitter branches with FIB-fabricated and EBL/ICP-RIE fabricated central holes. Except for the tuning step with $a=375$ nm, both fabrication methods yield equivalent transmission levels. We therefore conclude that FIB fabrication quality (aspect ratio, surface roughness, and shape of the hole) is equivalent to EBL/ICP-RIE fabrication.

V. SUMMARY

Focused ion beam iodine-enhanced etching of InP at 150 °C is superior to physical sputtering or iodine-enhanced etching at room temperature. The etching rate at 150 °C increases 51 times over physical sputtering, enabling the reduction of the fabrication time per hole to 5 s. The amorphous, Ga-contaminated layer formed while sputtering is greatly reduced and the buildup of In and In_3 islands, as occurring during sputtering and etching at room temperature, is suppressed. The surface roughness is comparable to other physical-chemical etching processes, such as ICP-RIE. However, due to the stray ions and the enhanced etching rate, the areas surrounding the fabrication area have to be protected. This can be done *in situ* using electron beam deposition of Pt and removal using XeF_2 -enhanced FIB etching. Considering the low sputter rate of W, it is preferable to proceed with a previously sputtered W layer, which can be selectively wet etched by H_2O_2 after the fabrication process. Cylindrical holes with aspect ratios exceeding 10 have been obtained using this method and PhC Y splitters with equivalent characteristics to EBL/ICP-RIE have been fabricated and charac-

terized. Thus, FIB rapid prototyping of InP-based planar PhCs becomes possible.

ACKNOWLEDGMENTS

The authors would like to thank U. Müller of EMPA for performing the XPS measurements, P. Langlet of EPFL Center of MicroNano Technology for the W depositions, O. Homan and E. Gini of FIRST Center of Micro- and Nanoscience of ETH Zurich for technical support and wafer-growth, respectively, as well as the financial contribution of the ETHZ INIT project “composite doped metamaterials” and EIPBN conference 2007 for the student grant.

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