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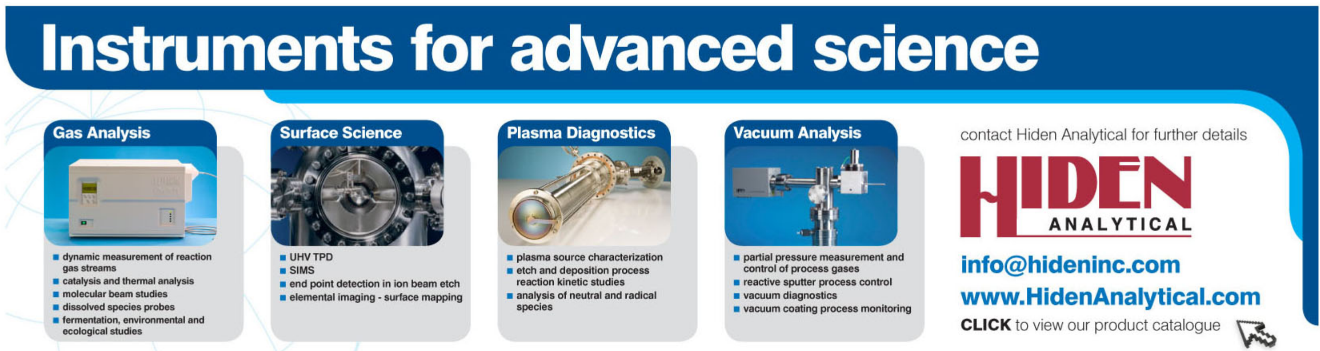

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Crystallographic dependence of the lateral undercut wet etch rate of $Al_{0.5}In_{0.5}P$ in diluted HCl for III–V sacrificial release

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The authors investigated the use of InAlP as a sacrificial layer lattice-matched to GaAs when diluted hydrochloric acid is used for sacrificial etching. They show that InAlP can be used to fabricate submicrometer air gaps in micro-opto-electro-mechanical systems and that a selectivity toward GaAs larger than 500 is achieved. This selectivity enables fabrication control of the nanometer-size structures required in photonic crystal and high-index contrast subwavelength grating structures. The crystallographic dependence of the lateral etch rate in InAlP is shown to be symmetric around the $\langle 110 \rangle$ directions where an etch rate of 0.5 μm/min is obtained at 22 °C in $HCl : 2H_2O$. Since the etch rate in the $\langle 100 \rangle$ directions exceeds by ten times that of the $\langle 110 \rangle$ directions, InAlP may be used in sacrificial release of high-aspect ratio structures. Free-hanging structures with length to air-gap aspect ratios above 600 are demonstrated by use of critical point drying following the sacrificial etch. © *2013 American Vacuum Society*.
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I. INTRODUCTION

Sacrificial wet etching of compound semiconductors is a necessary step during fabrication of nanophotonics devices such as photonic crystals, tunable vertical-cavity surface-emitting lasers, and photodetectors.[1–4] By removal of sacrificial material, an air-gap may be fabricated and, thus, high-index contrast and movable mechanical structures are enabled. Preferably, the sacrificial wet etch should be isotropic, selective to other materials present, and have an etch rate on the order of 1 μm/min. For crystalline materials, however, the etch process is usually anisotropic, though the two other requirements may be met. The etch selectivity must be high since during fabrication of nanophotonic devices, the wet etch must remove one material without significantly affecting nanometer-sized patterns realized in other materials.

The device topology often requires that multiple binary, ternary, and/or quaternary materials are present at the same time, and thus it becomes a challenging task to find an appropriate etch chemistry. Compared to silicon microelectromechanical systems where hydrofluoric acid is well-established for sacrificial etching of silicon oxide and a significantly smaller variety of materials are present, sacrificial etching of III–V compound semiconductor materials is much more complicated. For a comprehensive review on III–V sacrificial etching, we refer to the article of Hjort.[5] For devices based on GaAs substrates, the main sacrificial materials reported in literature are $Al_xGa_{1-x}As$, $Al_{0.5}In_{0.5}P$ and $In_{0.5}Ga_{0.5}P$, since they may all be grown lattice-matched to GaAs substrates.[6–8]

Anhydrous (water-free) citric acid ($C_6H_8O_7$) mixed with hydrogen peroxide (H_2O_2) and ammonium hydroxide (NH_4OH) has been reported for etching GaAs selective to $Al_{0.15}Ga_{0.85}As$ with selectivities up to 100.[9] Hydrofluoric acid is favored for etching $Al_xGa_{1-x}As$ with $x \geq 0.5$ where high etch rates and selectivities are obtained simultaneously.[7,10] $Al_xGa_{1-x}As$ can be difficult to use as a sacrificial material since it may also appear both in the fabrication of high-reflectivity distributed Bragg reflectors and piezoelectric layers and, hence, high selectivity toward $Al_xGa_{1-x}As$ is often desired. In order to selectively undercut GaAs, sacrificial layers of AlInP or InGaP have been reported, with hydrochloric acid (HCl) used for sacrificial wet etching.[6,11] The lateral etch rate of InGaP has been reported for different crystallographic orientations but not for AlInP. Studies on AlInP have focused only on the etch rate of the (100) plane.[8]

Here, we report the first results on the lateral wet etch rate of AlInP using an $HCl : xH_2O$ etch solution. We show that AlInP can be etched at a rate of 0.5 μm/min with a selectivity toward GaAs exceeding 500. Furthermore, we show that released mechanical structures can be achieved by use of critical point drying to overcome stiction. This is of critical importance for successful release of large structures where the mechanical stiffness may be insufficient to overcome the capillary forces occurring during drying, due to the surface tension of the liquid.

II. EXPERIMENTAL METHODS

For epitaxial growth, 2 in. (100) GaAs wafers with the major flat cut along $[0\bar{1}\bar{1}]$ were used. Epitaxial growth was conducted in an Emcore D-125 Turbodisc®-equipped metal-organic vapor phase epitaxy rotating disk reactor. The

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sacrificial $Al_{0.53}In_{0.47}P$ layer was grown at 610 °C to a thickness of 540 nm and capped with a 280 nm thick GaAs layer. The lattice mismatch, $\Delta a/a_{GaAs}$, was characterized by x-ray diffraction to be less than 10^{-3}. The wafers were patterned using photoresist (AZ5214E) and conventional UV lithography. A pattern of 40-μm-squares rotated at angles from 0° to 45° in steps of 2.65° was then transferred to GaAs by Cl_2/Ar inductively coupled plasma etching at 20 °C. During over-etching, the exposed AlInP was dry-etched at a lower etch rate. The samples were then etched with one part hydrochloric acid diluted in x parts of deionized water (37% HCl : $x$$H_2O$) at room temperature. After etching, the samples were rinsed in deionized water and dried. Samples for lateral etch rate measurements were dried in N_2, while samples with released beams were rinsed in 2-isopropanol and dried using critical point drying. Since the etch process is surface reaction limited, the rate is strongly temperature-dependent[6] and, therefore, the temperature was monitored using a thermometer to ensure reproducible results. The undercut was imaged using an optical microscope fitted with a Nomarski prism for differential interference contrast (DIC), while the etch profile was imaged using scanning electron microscopy (SEM).

III. RESULTS AND DISCUSSION

We find that wet etching of AlInP in HCl : $2H_2O$ is limited by {111}A planes that etch at 0.5 μm/min at 22 °C. Figure 1 shows the etch profiles of AlInP in (a) the $[0\bar{1}1]$ and (b) the $[0\bar{1}\bar{1}]$ directions after etching in HCl : $2H_2O$. Similar results have been shown for the $[0\bar{1}\bar{1}]$ direction by Lee *et al.*[11] The etch profile in Fig. 1(a) is typical of anisotropic reaction-limited etching with a slope of 54.7° corresponding to the angle between the $(1\bar{1}\bar{1})$ plane and the (100) surface. The angle in Fig. 1(b) is around 125°, which shows that the column-III-terminated {111}A plane is the slowest etching plane.[5]

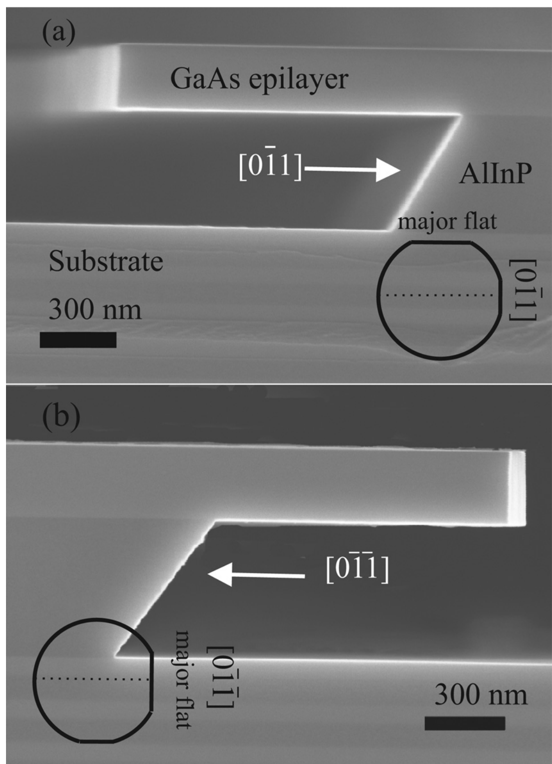

FIG. 1. Scanning electron microscope image of the etch-profile along (a) minor flat $[0\bar{1}1]$ and (b) major flat $[0\bar{1}\bar{1}]$. The sample has been cleaved using a diamond-scribe.

The DIC images in Fig. 2 show the undercut (light grey) of unmasked squares (dark grey) aligned to (a) the $[0\bar{1}\bar{1}]$, (b) 23.8° from the $[0\bar{1}\bar{1}]$, and (c) the $[0\bar{1}0]$ direction, respectively. The etched pattern is limited by the low etch rate of the {111}A planes, which intersects the (100) plane along ⟨110⟩ directions and thus the outline of the etched pattern will proceed until it is bounded by ⟨110⟩ directions.

Figure 3 shows the crystallographic orientation dependence of the etch rate in AlInP as a function of the angle relative to the $[0\bar{1}\bar{1}]$ direction for two HCl-based etch solutions. The etch rate in the ⟨100⟩ directions is several times higher than that in the ⟨110⟩ directions, and this anisotropy is seen to be dependent on the HCl concentration, whereas the etch rate in the $[0\bar{1}\bar{1}]$-direction is (within experimental error) the same in the two etch solutions while the etch rate in the $[0\bar{1}0]$-direction increases with increasing HCl concentration. Figure 3 shows that the etch rate is symmetric around the $[0\bar{1}0]$ direction but slightly skewed toward the $[0\bar{1}1]$ direction, which is clearly seen in Fig. 2(b). Similar results have been observed during wet etching of InGaP in HCl and attributed to atomic surface reconstruction during etching.[8] The lithographic pattern was aligned to the wafer major flat, specified to within 3 ° of the $[0\bar{1}\bar{1}]$-direction, and the resulting possible misalignment to the crystal direction may explain the off-set of the symmetry point of the curve from the $[0\bar{1}0]$-direction.

Previous studies have shown that wet etching of AlInP in HCl : H_2O has perfect selectivity (above 10^6) to GaAs.[5,6] In contrast to this, we find a GaAs etch rate on the order of 1 nm/min in the ⟨110⟩ directions; that is, the selectivity of GaAs to AlInP is >1:500. The etch rate was deduced from line width measurements on lines of nominal 130 nm width and 460 nm pitch. Line widths were measured using SEM before and after 10 min of wet etching in HCl : $2H_2O$. Etching of GaAs is usually mediated by an oxidizing agent and, thus, the nonzero etch rate is an unexpected result. It is commonly assumed that HCl does not etch GaAs and, in general, the oxidizing agent H_2O_2 is added for GaAs wet etching. Four different possible explanations for the incomplete selectivity are identified: anodic etching due to the presence of metal pads, photochemical etching, crystal quality, and oxidation by H_2O. However, we do not see any sign of surface pitting, which is commonly seen in anodic etching.[12] Photochemical wet etching of GaAs has also been reported but at higher light intensities.[13] Since the etch rate was measured on GaAs grown on top of AlInP, an increased etch rate of the GaAs epilayer could be due to a higher number of crystal defects or impurities, such as the presence of Al, In, or P. Also, H_2O can act as an oxidizing agent in acidic solutions where Ga_2O_3 is formed, and although the oxidation

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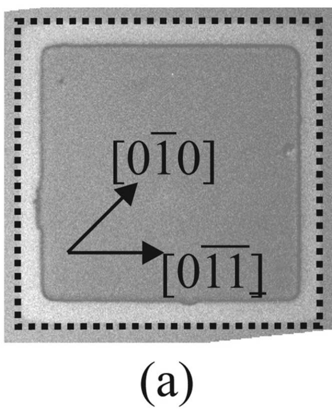

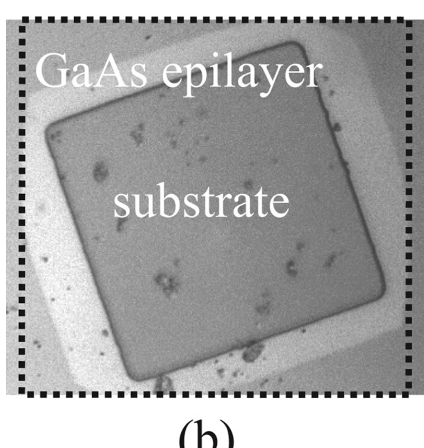

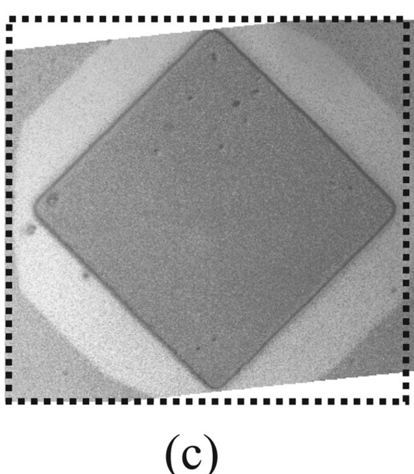

FIG. 2. Optical microscope image showing structures etched out of 40 $\times 40\,\mu m^2$ square mask windows aligned to (a) the [0$\bar{1}\bar{1}$] direction, (b) 23.8° from the [0$\bar{1}\bar{1}$] direction, and (c) the [0$\bar{1}$0] direction. The undercut region is the bright area. The samples were etched for 15 min in HCl : $5H_2O$. The limiting ⟨110⟩ directions are outlined with a dashed line.

rate is very low (≈0.5 nm/h for pure H_2O), it can significantly increase when the pH-value of the mixture is lowered.[14] Further studies are needed to clarify the unexpected etching of GaAs.

Undercutting of support structures is an issue in mechanical systems. The anisotropy of the wet etch can be exploited to reduce undercutting of the supports relative to structures that are to be fully released and thus fully

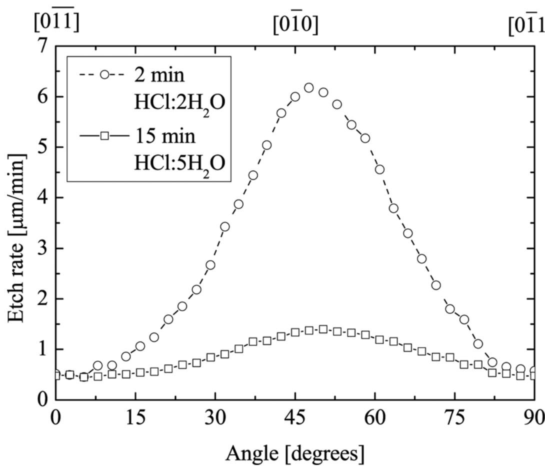

FIG. 3. Plot of the etch rate of $Al_{0.5}In_{0.5}P$ in different directions relative to the ⟨110⟩ direction. The etch rate is highest in the ⟨100⟩ direction.

undercut. This is achieved by aligning the support structures to the ⟨110⟩ directions, while the free-hanging structures are aligned to the ⟨100⟩ directions. Another critical issue is stiction, which is related to the surface tension and wetting properties of the liquids used and the stiffness of the structures to be released. Stiction is a well-known problem and may be avoided by critical point drying.[15] In this technique, the rinse liquid is substituted with liquid CO_2, which is brought to its critical point. By maintaining the temperature above the critical point, the pressure is then lowered in the gas-phase. Figure 4 shows released cantilevers with an air-gap spacing of 0.5 μm. The longest cantilevers are 350 μm long and the cantilevers to the left are 40 μm wide, while the cantilevers to the right are 10 μm wide. All cantilevers have been successfully released, i.e., none of them are stuck to the substrate surface. The inset in Fig. 4 shows a magnification of a shorter cantilever, where the shadow due to the air-gap is clearly visible. The slight curvature of the cantilevers that is observed in Fig. 4 may be explained by a thin residue layer left over from incomplete etching. Note in Fig. 1 that no etch product residual is observable.

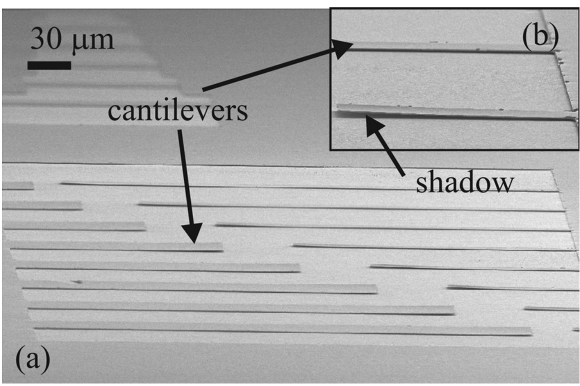

FIG. 4. Scanning electron microscope image of suspended beams released by critical point drying. The image (a) shows an overview of 10 and 40 μm wide beams. The inset (b) shows a zoom-in on a single cantilever.

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IV. SUMMARY AND CONCLUSION

The lateral etch rate of AlInP in diluted hydrochloric acid and its use as a sacrificial layer have been investigated. We find that the etching of AlInP in diluted hydrochloric acid shows a selectivity toward GaAs of 1:500. This compares favorably with the highest selectivity reported for InGaP of 1:100 using the same etchant. Furthermore, the etch rate of AlInP in HCl is much higher than that of InGaP. The more rapid sacrificial release makes high-aspect ratio structures more feasible. Therefore, AlInP is a good candidate for sacrificial layers in micro-opto-electro-mechanical systems.

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