Extremely high aspect ratio GaAs and GaAs/AlGaAs nanowaveguides fabricated using chlorine ICP etching with N₂-promoted passivation

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Abstract
Semiconductor nanowaveguides are the key structure for light-guiding nanophotonics applications. Efficient guiding and confinement of single-mode light in these waveguides require high aspect ratio geometries. In these conditions, sidewall verticality becomes crucial. We fabricated such structures using a top-down process combining electron beam lithography and inductively coupled plasma (ICP) etching of hard masks and GaAs/AlGaAs semiconductors with Al concentrations varying from 0 to 100%. The GaAs/AlGaAs plasma etching was a single-step process using a Cl₂/BCl₃/Ar gas mixture with various fractions of N₂. Scanning electron microscope (SEM) observations showed that the presence of nitrogen generated the deposition of a passivation layer, which had a significant effect on sidewall slope. Near-ideal vertical sidewalls were obtained over a very narrow range of N₂, allowing the production of extremely high aspect ratios (>32) for 80 nm wide nanowaveguides.

1. Introduction
Nanowaveguides are the key single-mode structure for light-guiding applications in nanophotonics. More specifically, GaAs/AlGaAs nanowaveguides have attracted significant interest, owing to their intrinsic material properties such as a strong nonlinear coefficient. This coefficient is important in nonlinear optics phenomena like second harmonic generation [1].

In nanophotonic structures, low loss light propagation, especially in bends, requires waveguides which can strongly confine light. Three kinds of propagation geometries in GaAs/AlGaAs heterostructures can be found. The simplest one is a nanowaveguide with a high aspect ratio geometry, where the height must be sufficient to increase vertical confinement and thus minimize leak losses to the substrate. Other structures, not studied here, are hybrid nanowires embedded in a low index cladding [2] and photonic crystals [3]. To avoid the collapse of the high aspect ratio nanowaveguide, almost perfectly vertical sidewalls are mandatory. The critical fabrication step to obtain near-perfect anisotropic profiles is plasma etching. This process needs to be finely tuned to obtain the right accuracy and non-selectivity with respect to the various heterostructure layers.

GaAs-based semiconductor plasma etching is most frequently carried out using chlorine-based chemistries. Chlorine forms volatile reaction products and can readily achieve rapid, smooth and anisotropic etching at room temperature [4]. Commonly used gases are chlorine (Cl₂) [5] and boron trichloride (BCl₃) [6, 7]. Silicon tetrachloride (SiCl₄) is also used, but it produces slower etch rates [8] and sometimes contaminates the chamber [9]. Other chemistries are available but they each present some drawbacks. Methane/hydrogen (CH₄/H₂) [10] produces a slow
etchant process can be adjusted by varying relative flow rates. We chemistry since the balance between physical and chemical etching species, such as argon (Ar), are often mixed with reactive gases. To improve the degree of control on the anisotropy, in combination of isotropic chemical and anisotropic physical etching. It is thus required to protect sidewalls with an inhibiting layer that prevents lateral etching, i.e. a passivation layer. Such a passivation layer will prevent undercutting, a critical issue for nanowaveguides, and will thus allow a wider range of etching parameters, leading to higher aspect ratios.

When using a photoresist mask, it has been shown that BCl3 passivates sidewalls through the formation of a diboron tetrachloride (B2Cl4) thin polymer layer [23]. Again, N2 addition to BCl3 or Cl2 chemistries helps sidewall passivation and the fabrication of vertical profiles on InP [24, 25] and on GaAs [26]. Different explanations can be found for this effect: the deposition of a boron-nitride-like film [27], the formation of a compound-nitride-like passivation layer on the surface of Ge [28] and InP [29] or, in contrast, no nitridation of the InP surface [17]. However, as far as GaAs/AlGaAs is concerned, the nature of the N2-promoted passivation layer has not been specifically identified so far. The most recent result related to this work has been reported by Braive et al [26], who observed the formation of a passivation layer on GaAs using Cl2/N2 plasma etching, assumed to be silicon oxide by analogy to previous work on InP etching.

The use of N2 with a Cl2/BCl3/Ar chemistry with a hard mask is therefore the main focus of our work for the realization of extremely high aspect ratio nanowaveguides.

2. Experiments

2.1. Sample preparation and processing steps

Our GaAs/AlGaAs nanowaveguides were fabricated using a four-step process, as shown in figure 1. The cleaned samples were prepared with a 180 nm silicon dioxide (SiO2) layer deposited by means of plasma-enhanced chemical vapour deposition (PECVD) and 15 nm of chromium (Cr) deposited using e-beam evaporation.

The first key fabrication step (figure 1(a)) is the high-resolution electron beam lithography carried out using a Leica UHV B6 e-beam writer on a maN2403 negative electroresist layer limited to a thickness of 65 nm in order to ensure high resolution. Then the resist pattern was transferred to the Cr layer using inductively coupled plasma (ICP) etching with a chlorine chemistry (figure 1(b)). The Cr pattern was then etched down into the SiO2 hard mask layer (figure 1(c)) using another ICP etching reactor dedicated to fluorine chemistries.

![Figure 1. Fabrication process flow of nanowaveguides. (a) GaAs substrate, with or without epitaxial heterostructure, capped with a 180 nm PECVD SiO2 layer and 15 nm evaporated Cr layer. Features are defined in the maN2403 electroresist. (b) Cr hard mask plasma-etched. (c) SiO2 hard mask plasma-etched. (d) GaAs-based nanowaveguides plasma-etched. Etch depth is deeper in large opening area, which is typical of RIE lag effect. (This figure is in colour only in the electronic version)](image-url)
The first two ICP etching processes had been previously optimized to ensure high pattern resolution transfer. The last key step (figure 1(d)) of the fabrication consists in transferring patterns into GaAs/AlGaAs using ICP etching based on Cl2/BCl3/Ar/N2 chemistry.

2.2. Description of the ICP reactor used for GaAs/AlGaAs heterostructure etching

Experiments were carried out in an STS (Surface Technology Systems) ICP reactor, which meets industrial standards for wafers up to 8" (200 mm) diameter. The plasma source power ($P_{\text{ICP}}$) is powered up to 1000 W at 13.56 MHz and generates a plasma through an inductively coupled coil around a ceramic tube. The wafer holder is separately driven at 13.56 MHz with a power ($P_{\text{BIAS}}$) between 0 and 300 W in order to independently control the bias from the plasma density. This is the main advantage of the ICP reactor among the different available plasma etching methods. It can thus achieve high etch rates, due to a high chemical species density controlled by $P_{\text{ICP}}$, with almost no structural damage, low ion energy and good directionality controlled by $P_{\text{BIAS}}$.

To avoid chamber contamination, this ICP reactor is dedicated exclusively to chlorine chemistries like Cl2, SiCl4 or BCl3 and wafers were introduced into the reactor through a vacuum pumped loadlock. Wafers were mechanically clamped on the holder and helium was flowed across its back-side to improve the thermal contact with the temperature controller (10–180°C). The gas mixture was injected using mass flow controllers.

2.3. GaAs/AlGaAs heterostructure etching process

As a chamber pre-treatment, we carried out a 30 min conditioning to ensure reproducibility throughout our experiments. Typical samples measuring 5 × 5 mm² were positioned on 8” silicon wafer carriers using heat conducting paste.

The non-selective plasma etching recipe was first developed using micrometric waveguides defined by standard photolithography. Waveguides were etched to evaluate sidewall profile and post-etch surface roughness. The plasma recipe was then optimized for etching nanometre scale structures.

Our preliminary recipe is a mixture of Cl2/BCl3/Ar gases with 10/10/10 sccm (standard cubic centimetres per minute) respective fluxes. Other important parameters are: reactor pressure at 5 mTorr, $P_{\text{ICP}}$ at 500 W, $P_{\text{BIAS}}$ at 50 W and temperature of 20°C. Typically, the GaAs/AlGaAs etch rate is around 500 nm min⁻¹ and the selectivity factor with the SiO2 mask is higher than 20. This process has been validated for AlGaAs layers with Al content at least as high as 90%. In this paper, various amounts of nitrogen were added to this Cl2/BCl3/Ar plasma chemistry in order to passivate the sidewalls simultaneously with the single-step etching process. With optimized parameters, etch rate increased to 1500 nm min⁻¹ and selectivity was close to 100.

2.4. Characterization

Etching characterization was carried out using GaAs and GaAs/AlGaAs samples with the same nanostructures. These samples were cleaved through the nanowaveguide structures and analysed by energy dispersive x-ray spectroscopy (EDX). Sidewall composition was analysed by energy dispersive x-ray spectroscopy (EDX).

3. Results and discussion

As nitrogen was added to the Cl2/BCl3/Ar plasma chemistry, the GaAs/AlGaAs etch rate increased to almost three times its value. This trend remains until the nitrogen fraction reaches 10% of the total flow, beyond which the etch rate starts to decrease.

The abrupt increase may be attributed to the enhancement of BCl3 dissociation with N2 in atomic and molecular chlorine [30] that leads to increased concentration of such reactive neutrals and chlorine-based ions. Thus more volatile products are formed at the semiconductor surface from the chemical and physical etching. Beyond the 10% concentration threshold of nitrogen, the decrease in the etch rate may be related to nitrogen producing a non-volatile deposit, such as a passivation layer. It has also been demonstrated that the addition of N2 to the chlorine plasma could lead to a decrease in the total positive ion density [17] beyond a certain amount of nitrogen. The reaction then becomes limited by Cl-based ions and neutrals.

3.1. SiOx passivation layer promoted by N2

SEM imaging of the etched waveguides, see figure 2, show a passivation layer deposited on sidewalls when nitrogen was added to the Cl2/BCl3/Ar plasma chemistry. Based on numerous SEM observations, we suggest that the passivation layer deposition occurs continuously during etching. This layer prevents lateral etching of the sidewall, with a striking effect on the etch anisotropy. When etching the remaining SiO2 hard mask with a buffered oxide wet (BOE), we can observe that the passivation layer is etched away as well.

Figure 2. Cross section of the top of a nanowaveguide. A 30 nm passivation layer is observed on the sidewalls (brighter part). The hard mask is not visible as it peeled off during sample cleavage.
Figure 3. Evolution of GaAs nanowaveguide profiles after the BOE wet etch to remove the passivation layer and remaining hard mask with nitrogen fractions of (a) 0%, (b) 10.4%: −0.5° slope and aspect ratio of 37, (c) 11.8%: 0° slope and aspect ratio >32, (d) 13.0%: +0.5° slope and aspect ratio >25, (e) 14.3%, roughness on the bottom of the etched features.

*Ex situ* spatially resolved EDX (energy dispersive x-ray spectroscopy) analysis showed that the passivation layer is composed of silicon (Si) and oxygen (O), with no detectable fraction of nitrogen. Due to the thickness of the layer and the proximity to the GaAs surfaces, we were not able to precisely determine the presence of Ga and As in this layer. However, as the SiO$_x$ etch rate is slower than SiO$_2$ PECVD, one can assume that limited amounts of Ga, As, Al and/or N are part of the composition.

The silicon-and oxygen-containing amorphous layer has previously been observed on InP when nitrogen was added to a BCl$_3$ chemistry by Lee et al [17] and to a Cl$_2$ chemistry by Bouchoule et al [31]. However, on GaAs-based semiconductors, a similar layer has been observed mainly with other chemistries, SiCl$_4$–O$_2$ by Varoutsis et al [32], SiCl$_4$–N$_2$–O$_2$ by Golka et al [9], HBr–O$_2$ by Bouchoule et al [33] and finally Cl$_2$/N$_2$ chemistry by Braive et al [26].

In studies by Bouchoule et al [31, 33], the Si sample carrier was essential to the passivation mechanism, based on the deposition of a silicon oxide layer on the etched sidewall but they used SiN$_x$ dielectric hard masks. In our case, the silicon oxide deposition may come from the dielectric hard mask (SiO$_2$) or from the sample carrier (Si wafer) during the etching. The source of oxygen can be residual oxygen gases or reaction by-products from the hard mask.

As no nitrogen element is observed along the sidewalls, the hypothesis of direct N$_2$ sidewall passivation is weak. It is more likely that the presence of N$_2$-related species helps to promote the formation of a passivation layer. The details of the mechanism remain unclear at this point.

Therefore we report the formation of a SiO$_x$ passivation layer promoted by nitrogen addition to Cl$_2$–BCl$_3$–Ar chemistry on GaAs/AlGaAs, which is yielding extremely high aspect ratio nanostructures.

### 3.2. Anisotropy and sidewall slope dependence on N$_2$ flux

We varied the amount of nitrogen added to the Cl$_2$/BCl$_3$/Ar plasma to investigate the effect on the etching process. The evolution of the profile is shown in figure 3. Picture (a) shows a profile without nitrogen, where no deposition of the passivation layer is observed. Pictures (b)–(d) show a gradual change in sidewall angle, from negative to positive. Corresponding N$_2$ fluxes are 10.4%, 11.8% and 13.0% of the total flux. Then picture (e) corresponds to a nitrogen fraction of 14.3%. Beyond this value, structures are still positively profiled but a significant roughness appears at the bottom of the etched area.

First of all, mask edges are preserved during the etching. This means that the sidewall angle is not a result of mask erosion but of surface passivation. As soon as nitrogen is added to the Cl$_2$/BCl$_3$/Ar plasma chemistry, a passivation layer is deposited and sidewalls are almost perfectly straight. That shows that the SiO$_x$ layer is thick and dense enough to prevent chemical etching reactions between neutral chlorine species and sidewalls.

To control the structure profile, a passivation layer is beneficial when anisotropic physical bombardment effectively removes it from horizontal surfaces, while leaving it intact on the sidewalls. Once more, the balance of physical and chemical etch processes is essential. If there is too much passivation deposition, the etch rate decreases and sidewalls become positively profiled. Alternatively, if the etch is too physical, the passivation layer is removed from the bottom and
from the sidewalls resulting in undercutting of the mask and negatively profiled sidewalls.

For nanowaveguides fabricated in this work, a very narrow range of nitrogen (10–13%) is suitable to obtain near-ideal anisotropic structures. Moreover, as soon as the nitrogen flux crossed a threshold of 14% for our experiments, very strong surface roughness appeared at the bottom of the etched area. This grass-like roughness is so high that it appears as a grey haze or even black in denser areas of the sample surface due to vertical nanostructures that trap light. Beyond the N2 threshold value, the enhanced passivation effect causes micromasking. Despite direct exposure to the ion bombardment, the SiOx passivation layer is likely to be too thick and inhibits etching locally. Of course, this micromasking phenomenon significantly reduces the etch rate. Furthermore, the SiOx passivation deposition certainly appears on the top of the hard mask too. This deposition may partially compensate the SiO2 etching and could explain the increase in selectivity from 20 without nitrogen to 100 with optimized parameters.

3.3. Nanowaveguide etching

We fabricated near-ideal anisotropic GaAs and GaAs/AlGaAs nanowaveguides with an extremely high aspect ratio. Our best result is shown in figure 4. GaAs nanowaveguide dimensions are 80 nm wide and 2.6 μm high. The aspect ratio value is higher than 32. Figure 5 shows an anisotropic GaAs/AlGaAs nanowaveguide with Al containing layer up to 70%.

Near-ideal vertical sidewalls were obtained on GaAs and GaAs/AlGaAs with the plasma Cl2/BCl3/Ar recipe described in section 2 to which we added 4 sccm of N2, i.e. 11.8% of the total flux. Etch rate was close to 1500 nm min\(^{-1}\), the selectivity depending on aluminium composition is nil and the SiO2:GaAs selectivity was greater than 100.

High aspect ratio structures have been reported in recent years with top-down fabrication methods, but each had some limit, such as dynamic modification of the etch conditions [32, 34], etch parameters that depend on the structural dimensions [35], non-ideal sidewall verticality [19, 34] or non-demonstrated ability to etch aluminium alloys [35, 36]. In this report, we propose a method that uses a single-step process to produce near-ideal vertical structures with extremely high aspect ratios on GaAs and AlGaAs alloys.

3.4. Dense nanowaveguide array etching

In areas where dense nanowaveguide arrays were etched without nitrogen, we observed the typical bowing profile, see figure 6(a). Sidewall etching is more pronounced in narrow openings due to the non-directional impact of ions because of the angular distribution [37]. Ions are reflected or scattered from the hard mask and from the interior sidewall of the etched aperture. In narrow features only, these ions can reach the opposite sidewall and thus increase the sidewall etching. That explains why sidewall bowing is mainly observed in narrow openings.

The addition of nitrogen to the Cl2/BCl3/Ar plasma chemistry promoted sidewall passivation of isolated nanowaveguides, as seen in figures 4 and 5, but also of nanowaveguide arrays, see figure 6(b).

We etched with the same conditions a dense nanowaveguide array composed of GaAs/AlGaAs. The profile is shown in figure 7. The profile is nearly ideally vertical whatever the percentage of Al is in different layers.

The passivation layer promoted by N2 prevents lateral etching, thus producing anisotropic profiles. These nearly ideal vertical sidewalls prove that the addition of nitrogen to Cl2/BCl3/Ar plasma chemistry can be useful for dense structures, such as nanowaveguide arrays or for photonic crystals in GaAs/AlGaAs.
3.5. No aluminium dependence for anisotropy

It can be seen in figures 5 and 7 that the nanowaveguide profiles are not influenced by the Al composition, from no Al in GaAs, through $\text{Al}_{0.2}\text{Ga}_{0.8}\text{As}$ or $\text{Al}_{0.7}\text{Ga}_{0.3}\text{As}$ up to a pure AlAs layer. This property is particularly interesting for high aspect ratio nanowaveguides in GaAs/AlGaAs heterostructures.

Moreover, a major difficulty in the fabrication of a nanometre scale structure related to the Al-containing layer is spontaneous oxidation, especially for AlAs layers, which leads to the formation of friable aluminium oxide structures. This oxide can destroy nanostructures by provoking their collapse. On the nanowaveguide array shown in figure 7, the remaining hard mask and passivation layers have been removed using a BOE wet etch right before SEM characterization. It means that the passivation layer prevented oxidation of the AlAs layer, which is still partially conserved after the BOE dip. This phenomenon could be exploited to protect the nanowaveguide sidewalls from air exposure after plasma etching if the passivation layer is not removed, which could play an important role in nonlinear optical experiments provided that absorption in these layers would not be significant.

3.6. Process advantages

The well-established deep Si etching ‘Bosch’ process consisting of a passivation deposition phase and an etch phase reproduced in part on GaAs [9] leads to scalloped sidewall features that would be detrimental for nanophotonics applications. The GaAs/AlGaAs etching process, exposed in this paper, is a single-step process based on a Cl$_2$/BCl$_3$/Ar/N$_2$ chemistry with no requirement for a time-multiplexed process.
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