Fabrication of nanocones by RIE on GaP

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Abstract. GaP(111)B substrate was etched through colloidal self-assembled randomly distributed 30nm Au nanoparticles by RIE. We looked into how GaP nanocones (NCs) formed with respect to the chamber pressure and etching duration, and the use of electron cyclotron resonance (ECR) RIE mode. The NCs were steep-walled in RIE, and those produced by ECR RIE were bell shaped. The NC length increased with etching duration for the same chamber pressure. The NCs were shorter and slightly steeper with decreased pressure for the same etching duration. The NCs that had the Au particles eradicated during the etching process became blunt and were gradually diminished.

1. Introduction
Nanostructured surfaces possess superior broadband and almost omnidirectional antireflection properties, far outperforming those of traditional planar antireflection thin film coatings [1]. It is because they expose the incoming light to a gradual change of the effective refractive index from the refractive index of the air to that of the light absorbing material [2]. Such nanostructures have features whose size and pitch are comparable to or smaller than the wavelengths of the incoming light. Biological nanostructured surfaces give an advantage to many animal and plant species [3, 4]. A number of researches have taken an inspiration from such structures for the design of artificial nanostructured surfaces from inorganic materials [5-7]. Such bio-inspired surfaces provide semiconductor solar cells with better antireflection surfaces, increased photon collection and absorption, and potentially higher efficiencies [8-12]. Bio-inspired nanostructured surfaces are also intensively studied and used for better light extraction from light-emitting diodes, boosting the responsivity of photodetectors, and for very sensitive biosensors and molecular sensors based on surface enhanced Raman spectroscopy (SERS) [13].

Reactive ion etching (RIE) of semiconductor wafers via self-assembled etching masks is a promising way to a low-cost production of two-dimensional nanostructured semiconductor surfaces, which can contain arrays of nanowires, nanopillars and nanocones. Self-assembly of such etching masks is believed to be essential to make the production of such surfaces wafer scalable, high throughput and low cost. The following approaches are usually taken: (1) nanoscale masks are self-formed in-situ from reaction products during RIE [14-16], (2) nanoscale masks are self-formed ex-situ from colloids before RIE [17-18], and (3) dewetted [19], patterned [20] or rough [21] metallic layers are used followed by RIE.

This paper reports on the fabrication of nanocones (NCs) by RIE and electron cyclotron resonance (ECR) RIE via self-assembled randomly distributed 30nm Au particles from a water-based colloidal solution on GaP substrate.
2. Experiment
The RIE and ECR-RIE experiment was performed on p-type Zn-doped GaP(111)B substrate ($p=1\times10^{18}\,\text{cm}^{-3}$). The substrate was etched through self-assembled randomly distributed $30\pm1\,\text{nm} \, \text{Au}$ nanoparticles that were deposited on the substrate at a density of $\sim 10^8\,\text{cm}^{-2}$ from a water-based colloidal solution. To achieve such a relatively low density of Au nanoparticles on GaP, the colloid was first diluted in acetone, and then several drops of the solution were delivered onto chips of the substrate so that they would be covered all over from edge to edge. The deposited solution was then dried slowly at room temperature under an air atmosphere saturated with acetone vapour. The chips were subsequently cleaned in boiling acetone, boiling isopropylalcohol, rinsed in deionized water, and blown dry with $\text{N}_2$. They were then transferred into a ROTH & RAU MICROSY 350 machine to be first treated in $\text{O}_2$ plasma and subsequently etched in $\text{CCl}_4 + \text{He}$ plasma under RIE mode (Table 1). The plasmas were generated by a radio-frequency (RF) field at 13.56 MHz supplied via a stainless steel electrode ($\phi$ 200 mm) stabilized at $\sim 25^\circ\text{C}$ using He flown into the chamber at 4 sccm. The $\text{O}_2$ plasma cleaning took 10 min at a chamber pressure of 6 Pa, $\text{O}_2$ flow of 20 sccm, power of 37 W, and substrate electrode bias of $-243\,\text{V}$. The chamber was then evacuated to a background pressure $< 5\times10^{-4}\,\text{Pa}$ before the introduction of a $\text{CCl}_4 + \text{He}$ gaseous mixture.

Table 1 shows the preliminary etching conditions that were aimed at a quick assessment of the role of the chamber pressure and etching duration, and the use of electron cyclotron resonance (ECR) on the formation of GaP NCs on the GaP(111) substrate. $\text{CCl}_4$ and He were flown into the chamber at 9.6 and 4 sccm, respectively. The RF power was 100 W and substrate electrode bias of $-175\,\text{V}$.

| Run | Mode  | Duration (min) | Pressure (Pa) |
|-----|-------|----------------|---------------|
| 1   | RIE   | 2              | 0.8           |
| 2   | RIE   | 4              | 0.8           |
| 3   | RIE   | 2              | 0.4           |
| 4   | ECR RIE | 4              | 0.8           |

3. Results
Figure 1 exemplifies images of GaP NCs taken by a scanning electron microscope (SEM) at a tilt of $\sim 88^\circ$ away from the [111]B substrate normal direction. In general, apart from run 3, some NCs had remnants of Au nanoparticle cap on top while some other NCs had their Au nanoparticle caps eradicated. The black arrows in figure 1 mark GaP NCs that were still capped with Au nanoparticles, and such NCs were measured for their length and base width to estimate the etching rate of GaP under the conditions of runs 1 to 4 (table 2).
Figure 1. GaP nanocones formed by RIE on (111)B GaP substrate in runs 1 (a), 2 (b), 3 (c), and 4 (d). The arrows mark remnants of Au nanoparticles on top of the revealed NCs.

For each etching run, the GaP NCs that were still Au-capped were steep-walled ((a)-(c)), but those produced by ECR RIE were bell-shaped (d). Figure 2 (left) shows that the NC length increased with etching duration at the same pressure, and the NCs were shorter and slightly steeper with decreased pressure for the same etching duration. When the particles were etched off, the NCs became blunt about the tops and were gradually etched away, i.e. their length and width at the base diminished.

Figure 2. Left: GaP nanocone length vs. width for runs 1 to 4. Only NCs with Au caps are included in the data points. Right: GaP NC length vs. width for run 1. NCs with Au caps (full circles) and NCs without Au caps (empty circles) are included in the data points.

The size of Au nanoparticles diminished under the four conditions, which suggests that Au nanoparticles were etched away. This resulted in NC broad length and width distributions, as is exemplified in figure 2 (right). Hence, the etching conditions and durations need to be further studied and optimized to achieve narrow GaP NC length and width distributions.
4. Conclusion

GaP nanocones were dry etched by RIE into GaP (111)B substrate via colloidal self-assembled randomly distributed Au nanoparticles. The GaP NC shape and size were manipulated via the chamber pressure and etching duration. RIE at a chamber pressure of 0.8 Pa during 2 and 4 min produced steep NCs with broad length and width distributions because the Au masking nanoparticles were mostly etched away. However, RIE at a chamber pressure of 0.4 Pa during 2 min yielded steep NCs with narrow length and width distributions. The ECR RIE experiment yielded GaP NCs with an interesting bell shape.

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Table 2. GaP NC height, width and etching rate.

| Run | Mode     | NC height (nm) | NC width (nm) | NC etching rate (nm/s) |
|-----|----------|----------------|---------------|------------------------|
| 1   | RIE      | 241 ± 10       | 104 ± 10      | ~2                     |
| 2   | RIE      | 338 ± 16       | 152 ± 14      | ~1,41                  |
| 3   | RIE      | 139 ± 3        | 44 ± 3        | ~1,16                  |
| 4   | ECR RIE  | 371 ± 4        | 260 ± 6       | ~3,09                  |
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