# Fabrication of Defect-Free Sub-10 nm Si Nanocolumn for Quantum Effect Devices Using Cl Neutral Beam Process

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# 1. Introduction

Semiconductor devices are shrinking in size in keeping with Moore's Law. However, it is pointed out that the conventional silicon ULSI will have the cost and technological limitations in near future. To breakthrough the problems, quantum effect devices are one of the main candidates.

To fabricate such nanometric devices, the damage-free etching process is necessary. The conventinal plasma etching technology has been so much progressed that several tens nm size structures can be produced. It is still difficult, however, that the plasma etching process fabricates structures with damage free surface. The damages are caused by high-energy ion bombardment, charge build-up and UV photon radiations. Since the quantum effect devices need the nanometric structures, even thin damage layer is fatal. A technique which settles this problem is strongly needed.

We have developed a neutral beam (NB) etching technique to satisfy this demand [1]. Combining biologically produced nanodots mask and NB etching, we have successfully fabricated Si nano-columnar structure with 7 nm diameter [2].

In this study, we analyzed defects in 7-nm Si nanocolumnar structure using transmission electron microscopy (TEM) and electron spin resonance (ESR). It is clarified that our developed neutral beam could fabricate defect-free sub-10nm Si nanocolumn for quantum effect devices.

# 2. Neutral Beam Source

Figure 1 shows our newly developed NB source. In this system, to generate low energy (~10eV) collimated neutral beam with sufficient flux (~1mA) and high neutralization efficiency (100%), negative ions (CI) are used. Inductively coupled  $Cl_2$  plasma (ICP) is generated in the quartz chamber by a 13.56 MHz radio frequency (rf) power. The rf power is modulated at a pulse timing of several tens of microseconds to generate a large amount of negative ions in the plasma. The negative ions were extracted through apertures at the bottom electrode by the negative bias

voltage between the top and bottom electrodes, and were efficiently neutralized by a charge-exchange with the aperture wall; positive ions  $(Cl_2^+)$ , however, are not neutralized as well (~50%). UV and VUV photon irradiations are also suppressed using the pulse-time modulated plasma and the apertures at the bottom electrode. In this condition, no plasma radiation damage should be realized.

## 3. Experimental

An outline of the experimental procedure is shown in Fig. 2. The experimental details are described elsewhere [2]. The crystalline silicon substrate was coated with less than 1 monolayer of recombinant ferritin. Ferritin is one of proteins and has a spherical protein shell with a cavity of 7 nm in diameter. It can biomineralize iron as hydrated iron oxide in the cavity and store it in vivo. Ferritin protein shell was removed and only 7-nm iron core was remained on the substrate by heat treatment. By using the iron core as an etching mask, 7-nm Si nanocolumn was fabricated in the Cl NB. The ferritin iron core mask was removed using HCl solution after the etching.

#### 4. Results and Discussion

Figure 3 shows a SEM image for an etched sample. 7-nm Nanocolumn structures were clearly observed. Their top diameter and height were about 7 nm and 50 nm, respectively. Figure 4(a) and (b) show a cross-sectional TEM image of the Si nanocolumn. It is clearly shown that the crystalline Si is conserved completely even in the nanocolumn and no distortion of Si lattice were observed even close to the surface. To fully analyze the surface defects in the nanocolumn, ESR spectra were also investigated. Figure 5(a) and 5(b) show ESR spectra of cleaned crystalline silicon substrate and Si nanocolumn structure fabricated on the Si substrate, respectively. A little bit increase in intensity of P<sub>b</sub> center (Si dangling bond) was detected by fabricating Si nanocolumn structure on the substrate. The dangling bond density is estimated to be in the order of 10<sup>10</sup> cm<sup>-2</sup> at most. It is just corresponding to the density of surface dangling bonds. This result clarifies that our newly developed NB could accomplish defect-free ultimate top-down etching process for the first time.

## 5. Conclusion

By combination between biomaterial etching mask (ferritin iron core) and neutral beam etching, fabrication of sub-10nm Si nanocolumn and the crystal defects in the nano-structure were investigated. We found that the crystalline Si was completely conserved even in the sub-10 nm nanocolumn structure. The Si dangling bonds were existed just at surface and the density was estimated to be in the order of  $10^{10}$  cm<sup>-2</sup> at most. This top-down etching process is very promising candidate for future quantum effect devices.

#### References

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Figure 1. Neutral beam source. The apparatus consists of two chambers, an ICP chamber and an etching chamber. Inductively coupled plasma was extracted via many apertures at the bottom electrode. The plasma particles were neutralized by the bottom electrode and then reacted with the sample.



Figure 2. Process flow of this research. The substrate was cleaned (a) and then processed using an UV/ozone stripper (b). The ferritin layer was prepared by spin coating (c), and the protein shell was removed by UV/ozone treatment (d). The sample was then etched (e). Finally the iron-core mask was removed by HCl (f).



Figure 3. SEM image of fabricated Si nanocolumns (observation angle: 15 deg, acceleration voltage: 30 kV).



Figure 4. TEM images of a nanocolumn (a) and its magnified image (b). A rectangle in (a) indicates the part which is magnified to generate (b).



Figure 5. ESR spectra of a silicon substrate before etching (a) and a wafer with nanocolumns fabricated by NB (b).