3-nm GAP FABRICATION USING GAS PHASE SACRIFICIAL ETCHING FOR QUANTUM DEVICES

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ABSTRACT

We report nanometer-scale gap (nangap) fabrication using gas-phase sacrificial layer etching. Sacrificial etching of 3-nm-thick sputtered Si films by XeF₂ gas was demonstrated for the first time. The same thick Si sacrificial layer was not etched by TMAH solution, and neither HF/CH₃OH vapor nor BHF solution etched a 3-nm-thick SiO₂ sacrificial layer. A nangap formation by etching the 3-nm-thick Si sacrificial layer was ascertained by TEM observations. The undercut depth of a 3-nm gap reached 20 μm, which is large enough to use for quantum devices. The etching results were also found to reflect molecular behaviors.

1. INTRODUCTION

In surface micromachining techniques, selective etching of a sacrificial layer has been a major method in making three-dimensional structures. Sacrificial etching has usually been conducted in a liquid phase using KOH [1] and TMAH solutions for Si [2] and using HF-based solutions for SiO₂ [3]. Gas-phase etchants, such as XeF₂ gas for Si [4] and HF/CH₃OH vapor for SiO₂ [5], have gradually become more commonly used because they can make smaller patterns with a higher yield [6].

Nano devices applying quantum effects are attracting much more attention with their abundant potential, and they have been intensively investigated as a result. Specifically, the tunneling effect is very promising because it can vastly improve the efficiency of the thermionic and Peltier cooling device. For example, Hishinuma et al. proposed a cooling device with a high Peltier coefficient applying vacuum tunneling [7]. For these quantum devices, a gap smaller than 10 nm is necessary to realize the tunneling effect, but at present, such small gaps are quite difficult to fabricate and have been seldom fabricated or studied. Although sacrificial layer etching seems to be useful, no studies have reported forming gaps smaller than 10 nm.

In this work, we investigated nanometer-scale Si and SiO₂ sacrificial layer etching by wet and dry methods. The molecular scale effects on the etching behavior were also studied.

2. EXPERIMENTAL

Sample preparations

Both Si and SiO₂ sacrificial layers up to 50 nm thick were used for this experiment. Sample structures with the Si and SiO₂ sacrificial layers are depicted in Figures 1(a) and (b), respectively. The etching hole diameter ranged from 1 to 10 μm.

The sacrificial layer of Si was deposited by sputtering on thermally oxidized Si wafers. The deposition rate of the layer was 0.1 nm per second, and the thickness was 1, 3, 5, 10, and 50 nm. It was covered by a plasma CVD SiN film with a thickness of 0.5 μm.

A SiO₂ sacrificial layer was formed by thermal oxidation on a Si wafer, and the thickness was 3 and 50 nm. The upper layer on the SiO₂ sacrificial layer was a CVD amorphous Si with a thickness of 0.2 μm.

Sacrificial etching

Before the sacrificial etching of Si, the native oxide on the Si surface was removed by a dilute HF solution. The Si layer was etched by both the wet and dry methods. The wet etching was conducted using 22 wt.% TMAH solutions at 90°C for 1 hour. The dry etching was performed by XeF₂ gas using the pulse etching method at 25°C, and the pressure in the etching chamber was set to 1 torr.

The SiO₂ layer was etched by both the wet and dry methods. The wet etching was carried out using buffered HF solutions (BHF) containing surfactants at room temperature for 1 hour. The dry etching was conducted using HF/CH₃OH vapor at room temperature for 1 hour. The HF and CH₃OH flow rates were 200 and 120 sccm, respectively, and the total pressure in the etching chamber was 30 torr.

In these experimental conditions, the upper layers on the sacrificial layers are transparent. Therefore, if the etching proceeds, the border of the etched region can be seen through the upper layer in the optical microscope images.

![Figure 1: Schematics of samples with (a) Si sacrificial layer and (b) SiO₂ sacrificial layer.](image-url)
Cross sectional images were taken by TEM to observe the formed gap and to measure the fabricated gap width.

3. RESULTS

Nanogap formation

The wet and the dry etching were conducted for the Si and SiO₂ sacrificial layers. Figure 2 shows the optical microscope image of a sample with the 3-nm thick Si sacrificial layer after 15 cycles of pulse etching by the XeF₂ gas. It can be seen through the upper layer that the sacrificial etching proceeded, and the underetch depth reaches up to 20 μm.

Figure 2: Top view of sample with 3-nm-thick Si sacrificial layer after 15 cycles of pulse etching by XeF₂ gas. The etching hole diameter is 10 μm.

The wet and dry etching results of all the samples are summarized in Table 1. Both 50-nm-thick Si and SiO₂ sacrificial layers were etched by the wet and dry methods, but the results were different when the sacrificial layer thickness decreased to 10 nm. Si sacrificial layers not thicker than 10 nm were etched only by the XeF₂ gas and not by TMAH solutions. However, a 1-nm-thick Si sacrificial layer was not etched even by the dry method. In addition, the SiO₂ sacrificial layer thinner than 10 nm was not etched by either the wet or the dry method.

From these results, dry etching of the Si sacrificial layer appears to be suitable for nanogap fabrication.

We conducted the TEM observations to ascertain the nanogap formation and to measure the fabricated gap width. Figures 3(a) and (b) show the cross sectional TEM images of samples with the Si sacrificial layers after 5 cycles of pulse etching by XeF₂ gas. The sacrificial layer thickness in these figures is 10 and 3 nm, respectively.

Figure 3: Cross sectional TEM images of samples with Si sacrificial layers after 5 cycles of pulse etching by XeF₂ gas. (a) and (b) are of the samples with the 10 and 3-nm-thick Si sacrificial layers, respectively.

The Si sacrificial layer lay between SiN (upper) and SiO₂ (lower) layers before the dry etching, but the space between the SiN and SiO₂ layers became the white line after the etching, as is indicated by the arrow in the figure. This means that no materials in that region are present. It also proves the gap formation.

As seen in the figures, the width is not constant in one nanogap. For example, the nanogap width in Figures 3(a-1), 3(a-2), 3(b-1), and 3(b-2) is 10, 17, 7, and 9 nm, respectively. It was also found that the measured widths were larger than the expected values of the sacrificial layer thickness.

Underetch depth

Figure 4(a) shows the dependence of the underetch depth on the cycles of the pulse etching. Figures 4(a-1), 4(a-2), 4(a-3), and 4(a-4) are of the samples with the 3-nm-thick Si sacrificial layers after 3, 5, 10, and 15 cycles of the pulse etching by XeF₂, respectively. For the sample with the 10 cycles of the pulse etching (Figure 4(a-3)), the water residue of the HF-pretreatment was replaced with ethanol and acetone. The other samples were dried using N₂ blow after the HF-pretreatment without the substitution. The underetch depth increases as the etching hole diameter increases, and it almost saturates above 4-μm-diameter holes. A decrease in the underetch depth in the smaller holes is caused by the water residue of the HF-pretreatment. This was determined by the results of 10 cycles of the pulse etching after eliminating the water (Figure 4(a-3)), in which the underetch depth through smaller holes is increased compared with that of 15 cycles of the pulse etching without water removal (Figure 4(a-4)).

Table 1: Summarized etching results.

<table>
<thead>
<tr>
<th>sacrificial layer material</th>
<th>thickness</th>
<th>etched: O, not: ×</th>
<th>wet etching</th>
<th>dry etching</th>
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<td>×</td>
<td>O</td>
<td></td>
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<td>3 nm</td>
<td>×</td>
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<td>Si</td>
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<td>O</td>
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</tr>
<tr>
<td>SiO₂</td>
<td>1 nm</td>
<td>×</td>
<td>×</td>
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<tr>
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<td>3 nm</td>
<td>×</td>
<td>×</td>
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</tr>
<tr>
<td>SiO₂</td>
<td>50 nm</td>
<td>O</td>
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difficulty in passing through a narrow path than gas does. This is why the 3-nm-thick sacrificial layer was not etched by the wet method, whether the sacrificial layer was Si or SiO₂. We also found from the results that the liquid etchants can go through the 50-nm-wide paths and etch the sacrificial layer. The threshold width where the liquid etchant can go through lies between 3 and 50 nm, and it depends on the etchant materials.

The reaction of the Si etching by XeF₂ is expressed as follows.

\[ \text{Si} + 2\text{XeF}_2 \rightarrow \text{SiF}_4 + 2\text{Xe}, \]  

(1)

In this reaction, the XeF₂ molecules need to reach the Si surface passing through the nanogap, and the produced SiF₄ molecules and Xe atoms go to the open vacuum space through the nanogaps.

The molecular sizes of XeF₂, SiF₄, and Xe are 0.7 [8, 9, 10], 0.6 [8, 9, 10], and 0.4 nm [11], respectively. Therefore, the 1-nm gaps are too small to exchange the etchants and the products. This is why the 1-nm-thick Si sacrificial layer was not etched by the dry method. The sacrificial etching proceeded because a gap as wide as 3 nm or wider had enough space to exchange XeF₂, SiF₄, and Xe.

The SiO₂ etching reaction is more complicated than the Si etching reaction and includes two steps as follows.

\[ 2\text{HF} + \text{CH}_3\text{OH} \rightarrow \text{HF}_2^- + \text{CH}_3\text{OH}^+ \]  

(2)

\[ \text{SiO}_2 + 2\text{HF}^- + 2\text{CH}_3\text{OH}^+ \rightarrow \text{SiF}_4 + 2\text{H}_2\text{O} + 2\text{CH}_3\text{OH} \]  

(3)

In these reactions, HF₂⁻ ions are quite important to etch a SiO₂ sacrificial layer. It is also necessary that HF₂⁻ ions react with the SiO₂ surface before they react with the CH₃OH⁺ ions, losing their charges. This means that the reaction (2) must occur near the SiO₂ surface. The molecular sizes of HF and CH₃OH are 0.2 [8, 9, 10] and 0.3 nm [8, 9, 10], respectively, and the 3-nm gaps seem to have enough space to introduce these molecules. However, the gap width is too small to introduce these molecules to the SiO₂ surface almost at the same time. This makes etching the 3-nm-thick SiO₂ sacrificial layer impossible. The 50-nm-width gaps were big enough to introduce these reactants freely, and the sacrificial etching proceeded.

From the TEM observations, the formed gap width was not constant in one nanogap. This may reflect the local fluctuations of the sacrificial layer thickness. However, the gap space tends to be larger near the etching holes. Hence, it is more reasonable that the upper layer bent upward owing to its tensile internal stress.

We also observed that the nanogaps were wider than the expected values and that the gap surface was not clear but relatively fuzzy. The following is thought to be the reasons.

(1) During the TEM observations, the nanogap widths expanded. This was interpreted as the electron beam irradiation causing the evaporation of the atoms on the gap surfaces. This means that the TEM image shows wider nanogaps than it was previously.

(2) The lower layer may have protrusions on the surface and may make the upper layers bumpy, or the sputtered Si film itself may be rough. As a result, the nanogap surface became uneven. In the TEM image, the protrusions on the surface were transmitted, and they appeared as fuzzy shadows and became a part of the nanogap. This led to the nanogap width

4. DISCUSSION

Etching reaction in the nanogap

For the nanogaps to be fabricated, the etchant must reach the sacrificial layer surface passing through the nanogaps, and the reaction products must get out through the nanogaps. The path becomes narrower as the layer thins.

Liquid etchants have stronger viscosity and have more
being overstated.
(3) Because the internal stress of the upper layer (SiN) is tensile, the released upper layer bends upward, making the gap space larger.
(4) Owing to the apparatus fluctuations, the deposition rate of the Si sacrificial layer was not stable, especially in the beginning.

Underetch depth dependence

The underetch depth equals the distance that the molecules must proceed, and the nanogap becomes increasingly difficult to pass through inversely to the underetch depth. As the cycles of the pulse etching increase, the underetch depth increases, and it becomes more difficult to go through the nanogap. This makes the gas exchange slower, and as a result, the etching rate decreases. The underetch depth saturates at a distance that is too long for the molecules to pass through, and the etching reaction stops. This is consistent with the experimental results in Figure 4(a), and the saturated underetch depth is from 18 to 19 µm above 10 cycles of the pulse etching in these experimental conditions. However, the gas can go through the nanogap easier proportional to the gap width. Also, the necessary amount of XeF₂ molecules to etch the Si by some depth is in proportional relation to the sacrificial layer thickness. This means that the etching rate is the same independent of the sacrificial layer thickness, which is inconsistent with the experimental results in Figure 4(b). Therefore, we must consider the influence of the upper and the lower layers to interpret the etching dependence in Figure 4(b).

During passing through the nanogap, the XeF₂ molecules collide with the gap surface many times. As a result, the XeF₂ adsorption onto the gap surface occurs, and the nanogap becomes narrower by the adsorbate size. This suppression is more effective for thinner layer etching. For example, if one XeF₂ molecule is adsorbed onto the surface, the nanogap width decreases to 78, 86, 93, and 99% in the 3, 5, 10, and 50-nm nanogaps, respectively. These adsorbates work most effectively when the sacrificial layer thickness is 3 nm, and the underetch depth becomes the shortest (Figure 4(b-1)). For the 50-nm-thick layer etching, the effects are the weakest, and the underetch depth becomes the longest (Figure 4(b-4)). For the 5-nm-thick Si layer etching, these factors work as effectively as for the 10-nm-thick layer, and the underetch depth takes similar values (Figure 4(b-2) and 4(b-3)). Therefore, it is important to inhibit the adsorption of the XeF₂ onto the gap surfaces to increase the underetch depth. For example, the less polarized surface is preferable as the gap surface because XeF₂ molecules have polarizations.

5. CONCLUSION

Dry etching of a Si sacrificial layer was found to be effective in fabricating nanogaps. Cross sectional TEM observations found nanogap formation. The underetch depth reached 20 µm, which is long enough for use in quantum devices. The underetch depth depended on the cycles of the pulse etching and the sacrificial layer thickness, reflecting the molecular behaviors.

REFERENCES