

Anomalous Enhancement of Etching Rate of Silicon Nitride
with HF Etchant by Ion Implantation

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An anomalous enhancement of an etching rate of silicon nitride with conventional HF etchant has been achieved by using ion implantation technique.

Etching of silicon nitride (Si_3N_4) is one of the most troublesome techniques in IC fabrication processes. Usually, an additional oxide layer must be prepared on a nitride layer, and it is used as a mask for a selective etching of the nitride layer. Then, the selective etching of nitride is made with hot H_3PO_4 . This is mainly due to the low etching rate of nitride with HF etchant.

Pre-implantation of high energy ions to a nitride layer before etching can enhance the etching rate to one order of magnitude larger than a normal one. Therefore, the selective etching of nitride can be made with the same method as that of oxide by utilizing ion implantation.

Several ions with different masses and different chemical properties such as B^+ , N^+ , P^+ , Ar^+ , Zn^+ and Sb^+ , were examined. Silicon nitride was deposited on silicon wafers by CVD method at 800°C with the thickness of $500\sim 3000 \text{ \AA}$. Implantation was made at $50\sim 200 \text{ keV}$ to doses of $10^{13}\sim 10^{15} \text{ cm}^{-2}$. The depth etched by diluted HF etchant ($\text{HF}:\text{NH}_4\text{F}=1:3$ or $\text{HF}:\text{H}_2\text{O}=1:3$) and the refractive index of the nitride layers were measured by ellipsometry.

Figure 1 shows the etched depth of nitride with diluted HF etchant ($\text{HF}:\text{NH}_4\text{F}=1:3$) implanted with Sb^+ ions as a parameter of implanted dose. The etched depth in the case of an unimplanted sample is also shown. Figure 2 shows the dose dependence of the etching rate of nitride. The etching rate is enhanced extremely by Sb^+ ion implantation. Typical etching rate is $300 \text{ \AA}/\text{min}$. in the sample implanted with 50 keV-Sb^+ ions to the dose of $5\times 10^{15} \text{ cm}^{-2}$, although the normal etching rate (unimplanted) is $15 \text{ \AA}/\text{min}$. The etched depth after the etching for one minute, is not in order of the implanted dose. This may be due to the contamination of the nitride surface during the implantation. The refractive index of the nitride layer after implantation is also shown in Fig. 2. The dependence of the refractive index on the implanted dose is similar to that of the etching rate. This correlation was also found in the case of other ions. As shown in Fig. 3, the refractive index came back to the normal value (1.98) at the depth of about 400 \AA . This means that the nitride in the region deeper

than the depth is not damaged seriously. The deviation of the refractive index from the normal value is caused by the change of the atomic density in the nitride induced by the radiation damage.¹⁾²⁾ On the other hand, the etching rate also became smaller and approached gradually to the normal one at the same depth (400 Å). These results indicate that the enhancement of the etching rate is caused by the radiation damage produced in the nitride layer.

The etching rate is controllable over the wide range with the implanted dose and energy. This etching technique will be valuable in semiconductor device fabrication.

The mechanism of this enhancement investigated by ESR measurements and the results in the case of other ions will also be presented.

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Reference

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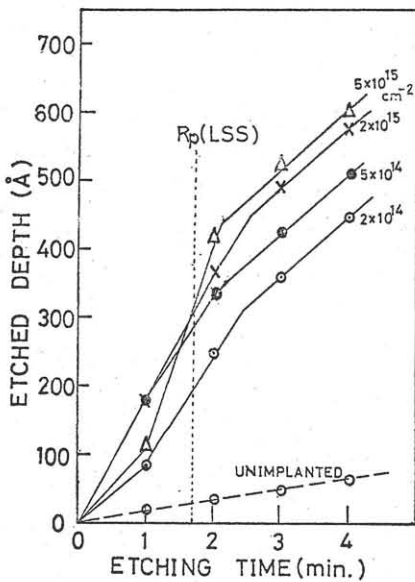


Fig. 1 Etched depth of nitride with diluted HF etchant (HF:NH₄F = 1:3) implanted with Sb⁺ ions.

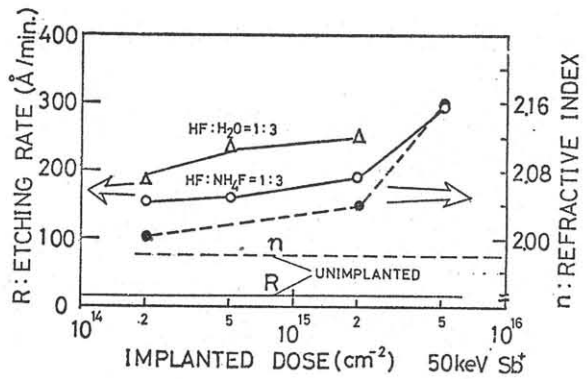


Fig. 2 Dose dependence of the etching rate and the refractive index.

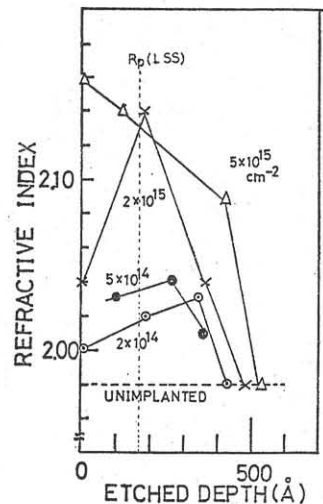


Fig. 3 Depth dependence of the refractive index implanted with 50 keV-Sb⁺ ions.