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Surface Modification of SiO_2 Thin Film using High-Dose Ion Implantation Technique as a Manufacturing Worthy Process

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Abstract

We studied surface modification of SiO_2 films by high-dose ion implantation. The wet etching rate of HF solution can be enhanced or suppressed by changing the ion species. The wet etching rate increases with B^+ and P^+ implantation and decreases with C^+, N^+, O^+, and Si^+ implantation. We also demonstrated the selective etching process with self-aligned manner for a 3D structure. This technique can be quite useful for the device fabrication as a manufacturing worthy process.

1. Introduction

From early 1970s, ion implantation technologies have been the industry standard for semiconductor device fabrications [1]. With respect to doping processes, it is recognized that ion implantation techniques are still key process technologies as of today [2]. High-dose ion implantation attracts a lot of attention for surface modification of thin films. However there have been only a few reports for this application because of the need for high dose [3],[4],[5]. Increased beam current of ion implanter enables the high dose implantation for more than 1E16 /cm^2 with a reasonable process time. This improvement turns surface modification application into reality. Doping of high-dose ion species into a thin film can change various film properties such as both dry and wet etching rate, reflectivity, hardness, and strain. By using photo-lithography, selective doping can be easily realized. Moreover localized property changes can be achieved with a combination of directional characteristics of ion beam and 3D device structure. This unique feature can offer a flexibility for recent very complex fabrication process for advanced logic and memory devices. In this paper, we investigated surface modification process of SiO_2 thin film by ion implantation.

2. Experimental

We prepared the PE-CVD SiO_2 films with a thickness of 30nm on Si wafer as a starting material to evaluate the wet etching rate (WER). The implantation was carried out by using Nissin's new ultra-high-current ion implanter. We investigated B^+, C^+, N^+, O^+, Si^+ and P^+ as ion species. We used the Monte Carlo simulation to determine the implantation conditions. The implantation energy was adjusted to have the same projected range of 4nm that corresponds to 1.0keV for B^+ and 2.0keV for P^+, respectively. The implantation dose was varied from 1.0E16 to 3.0E16 ions/cm^2. Almost all ions were retained within 20nm depth of SiO_2 film. Some samples were densified with a relatively low thermal budget at 650 degC for 1min using Rapid Thermal Annealing (RTA). The wet etching was carried out using diluted HF solution. We also evaluated the binding states by X-ray photoelectron spectroscopy (XPS). To demonstrate the selective etching process of SiO_2 film, we prepared the three-dimensional (3D) structure wafer, which has L/S silicon trench pattern covered with a 30nm thick SiO_2 film.

3. Results and Discussion

Fig.1(a) shows dose dependency of HF WER with ion species as a parameter. WER increases as implantation dose of B^+ and P^+ increases. For P^+ case, WER monotonically increases with dose and becomes almost twice faster. WER of B^+ implanted sample rapidly increases at a dose of 3.0E16 ions/cm^2. On the contrary, WER of C^+, N^+, O^+ and Si^+ implanted samples decrease as implantation dose increases. Especially, C^+ and Si^+ implanted samples are hardly etched even at the dose of 1.0E16 ions/cm^2. Fig.1(b) shows WER after RTA. The general behavior of WER as a function of dose is almost same with that of as-implantation case, although WER value becomes smaller due to the densification effect. It should be noted that the surface modification by ion implantation can be realized without additional annealing step. This means this process can be easily introduced into the device fabrication processes.

We investigated detailed etching characteristics for P^+ implanted sample as shown in Fig.2. The simulated P profiles in the SiO_2 film are also plotted in this figure. The slope of each line is corresponding to WER. In the case of 3.0E16 ions/cm^2 sample, a large WER was observed to the depth of 12nm, which corresponds to the highly doped region, then it becomes close to that of un-implanted one at deeper region. The large WER at highly doped region from 4nm to 10nm was also observed for the 1.0E16 ions/cm^2 sample. This suggests that we can control WER based on the dopant profile which we can easily change and control by changing implantation energy and dose.

Fig.3 shows XPS spectra of P^+ and Si^+ implanted SiO_2 films after RTA. The peak based on O-Si-O decreases by P^+ implantation. This means that the bond of O-Si-O is broken and weakened by P^+ implantation and easily reacts with F in HF solution. In addition, Phosphosilicate Glass (PSG) may be locally formed by P^+ implantation. The etching rate of

PSG is faster than that of SiO_2 [6]. On the other hands, in the case of Si^+ implantation, the peak based on O-Si-O disappeared and the peak based on Si-O-Si became prominent probably because SiO_2 at near surface became Si rich film by Si^+ implantation. As a result, HF can hardly etch this Si rich film.

Fig.4 shows cross-sectional SEM and TEM images of (a) as-implantation, (b) after etching for the sample with P^+ implantation and (c) that with Si^+ implantation. RTA process was not applied for both implanted samples. 8nm thick SiO_2 film remains at the trench sidewall for P^+ implanted sample, even though the thickness of SiO_2 at sidewall is thin compared to that at top and bottom of trench due to the top coverage issue. On the other hands, only sidewall SiO_2 film can perfectly be removed with almost no etching at top and bottom film for Si^+ implanted sample. As shown here, one can realize selective etching with self-aligned manner using high dose ion implantation technique. Ion beam has directional, characteristics therefore the WER of only top and bottom region can locally be controlled. This technique would be very useful for the advanced device fabrication with complex processes.

4. Conclusions

We have found that the wet etching rate of HF solution can precisely be controlled by high-dose implantation. The etching rate of B^+ and P^+ implanted SiO_2 film increased. On the contrary, that of C^+, N^+, O^+ and Si^+ implanted films decreased. The local etching rate can be varied by changing implantation dose and energy. Consequently, selective etching with self-aligned manner can be realized by high-dose ion implantation technique due to the unique directional property of ion beam. This novel application of ion beam would be useful for the device fabrication as a production worthy process.

Acknowledgements

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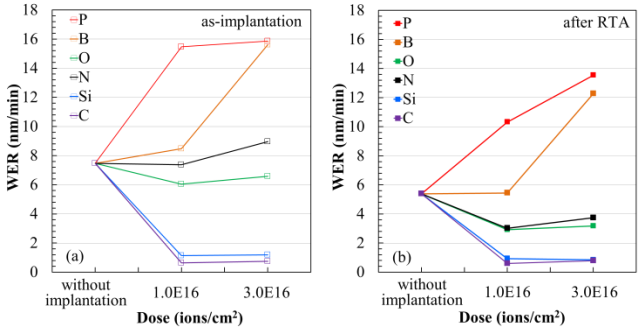

Fig.1 Dose dependency of WER (a) as-implantation, (b) after RTA

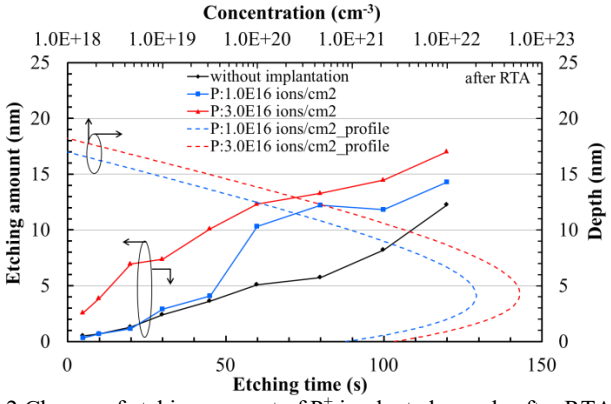

Fig.2 Change of etching amount of P^+ implanted sample after RTA

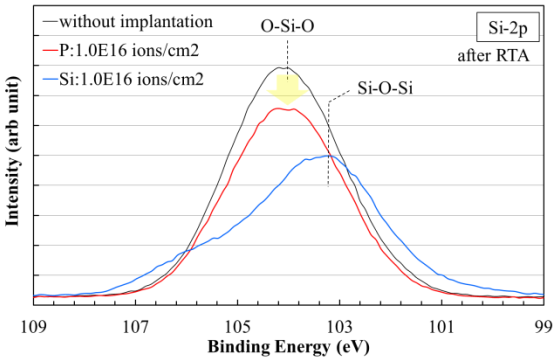

Fig.3 XPS spectra of P^+ and Si^+ implanted SiO_2 films after RTA

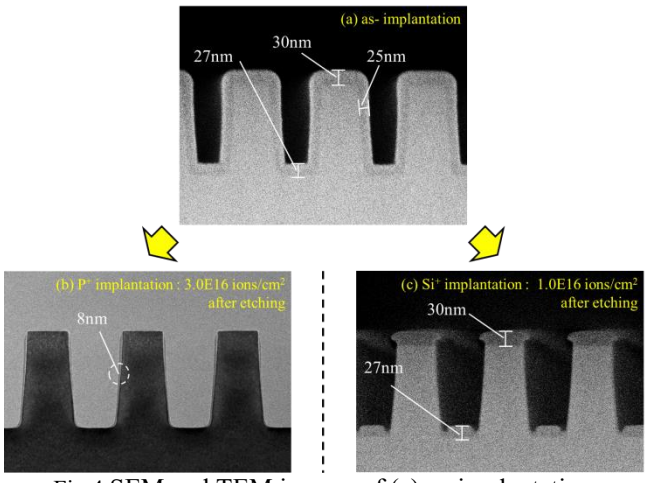

Fig.4 SEM and TEM images of (a) as-implantation, (b) after etching for the sample with P^+ implantation and (c) that with Si^+ implantation