

A novel fabrication technique for MOS structure by oxidation methods using chemical solution

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Abstract— So far, the diameter of a Si wafer has been increased to reduce the manufacturing cost of semiconductor chips. However, it is considered that this makes it difficult to form uniform thickness thin films on the entire surface of the wafer by a conventional film forming method. Therefore, we have proposed an oxidation method using chemical solution that can form a film just by immersing it in a chemical solution. In this study, HfO_2 , a high-k material with a high dielectric constant, was formed on a Si substrate by chemical solution oxidation, and its electrical properties were compared with those of a thermal oxidation method. As a result, the MOS structure was successfully fabricated by oxidation method using chemical solution. However, this method has a problem of improving interface characteristics.

Keywords—Si, HfO_2 , chemical solution oxidation method, MOSFET.

I. Introduction

A. The issue for thin film fabrication on large scale semiconductor wafers

From the beginning of the semiconductor industry, the diameter of Si wafer has been large to reduce the manufacturing cost per one transistor and/or one chip. In recent years, the thickness of thin films tends to as thin as several nanometers, and the diameter of Si wafer would be 300[mm]~450[mm]. Especially, to fabricate MOS-FETs (Metal Oxide Semiconductor Field Effect Transistors), which are one of the representative electronic devices, it is necessary to form insulating films with a few nanometer thick uniformly over the entire surface of the wafer. So far, thermal process has been frequently used to form the insulating films with a few nanometer thick. Under the situation of wafer size to be larger, however, it is difficult to form such insulating films uniformly on the wafer, because growth rate of it strongly depends on temperature and there would be the temperature difference on the large scale semiconductor wafers. In this research, we have proposed an oxidation method using chemical solution to form an oxide insulating film. A schematic diagram of the oxidation method is shown in figure 1. In this method, oxidation can be performed by immersion in a heated chemical solution with a temperature range around 100 degree of C. It is expected to form insulating films with a uniform thickness over the entire surface of the wafer because isothermal chemical solution can be easily obtained and growth rate is expected to be the same on the wafer. We have attempted to form the insulating films such as SiO_2 and HfO_2 on Si

wafers by the oxidation method using chemical solution to fabricate the MOS structure and evaluated its electrical characteristics.

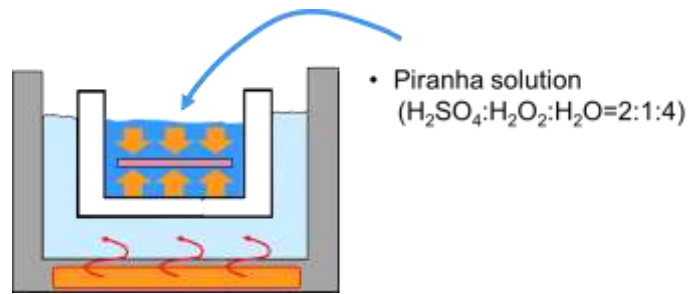
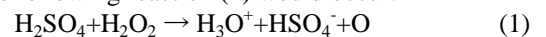


Fig.1 Schematic diagram of oxidation method using chemical solution

II. Experimental method

A. SiO_2 formation on Si wafers by oxidation method using chemical solution

Before oxidation, a conventional organic chemical cleaning and HF dipping had been carried out to obtain clean surface of the p-type Si wafers. A so called piranha solution (sulfuric acid : hydrogen peroxide solution : water = 2 : 1 : 4) was used to oxidize Si wafers. In the piranha solution, the following reaction (1) would occur.



Large amount of oxygen atoms can be generated when sulfuric acid and hydrogen peroxide solution are mixed together, and Si wafers in the piranha solution would be oxidized.

The temperature of the piranha solution during the oxidation of Si wafers was controlled to be 130 degree of C as is shown figure 2. Oxidation times were 5 [min], 10 [min] and 15 [min], to form SiO_2 with different thickness on Si wafer. After that, the samples were subjected to Al vapor deposition to form electrodes, and C-V measurement and I-V measurement were performed.

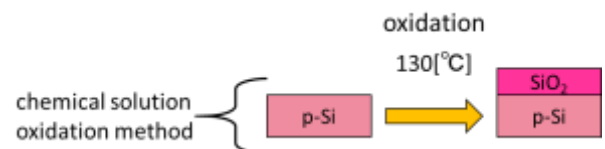


Fig.2 Formation of SiO_2 on Si wafer by oxidation method using chemical solution

B. HfO_2 formation on Si wafers by various oxidation method

The same cleaning process of section A had been carried out to obtain clean surface of the p-type Si wafers. On the Si wafers, metal Hf with the thickness of 10 [nm] and 30 [nm] had been deposited, respectively, by a sputtering method to fabricate metal Hf/Si structure. Each sample was subjected to oxidation using piranha solution (sulfuric acid: hydrogen peroxide solution: water = 2: 1: 4) at a temperature around 100 degree of C. The oxidation times were set to 5 [min], 10 [min], and 15 [min], to form HfO_2 with different thickness on Si wafer, as is shown in figure 3 (1), (2). For the sake of comparison, conventional thermal oxidation process was used to form HfO_2 /Si structure. The thermal oxidation condition was 400 degree of C, for 40[min] in 100[%] O_2 atmosphere, as is shown in figure 3 (3). Then, Al was vapor-deposited on all samples to form electrodes. C-V and I-V measurements of the fabricated MOS structure mentioned above were performed to evaluate electrical characteristics.

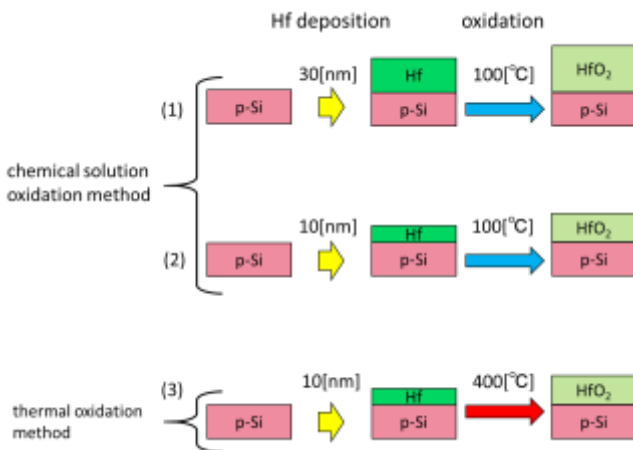


Fig.3 Formation of HfO_2 on Si wafer by various oxidation methods

III. Results and discussion

A. SiO_2 formation on Si wafers by oxidation method using chemical solution

Figure 4 shows C-V characteristics for each oxidation time. Since typical C-V curves have been obtained, it was confirmed that the SiO_2 film could be formed by the oxidation method using chemical solution. The thickness of the SiO_2 film can be calculated using the maximum capacitance value of C-V curve shown in figure 4. For the oxidation time of 5 [min], the thickness of the SiO_2 film is calculated to be 4.9 [nm], for 10 [min], 5.2 [nm], and for 15 [min], 6.5 [nm], respectively. From these results, as the oxidation time increased it can be seen that the insulating film thickness increased. Figure 5 shows I-V characteristics for each oxidation time. It is clearly shown that the leakage current level decreases as the oxidation time increases. It is considered that the reduction of the leakage current level

was mainly due to the increase of the insulator film thickness as the oxidation time was increased.

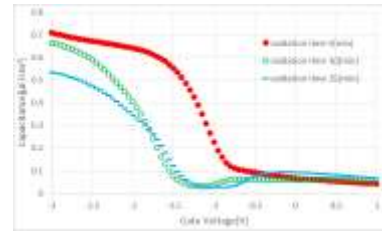


Fig.4 C-V characteristics of SiO_2 /Si structure for each oxidation time

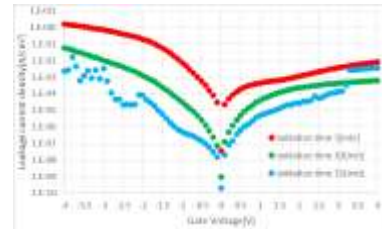


Fig.5 J-V characteristics of SiO_2 /Si structure for each oxidation time

B. HfO_2 formation on Si wafers by various oxidation method

Figure 6 (a) shows C-V characteristics for each oxidation time using piranha solution at a temperature of 100 degree of C (sample (1)). Since the thickness of initial deposited metal Hf layer was as thick as 30[nm], only the surface region of the metal Hf layer was oxidized even though oxidation time was 15[min]. Therefore, all samples have MIM (Metal Insulator Metal) structures and it has the same value of C with respect to the change of the voltage as is shown in the figure. The thickness of the HfO_2 film can be calculated from the C value. For the oxidation time of 5 [min], the thickness of the HfO_2 film is calculated to be 20.8 [nm], for 10 [min], 25.3 [nm], and for 15 [min], 21.3 [nm], respectively. So, we can conclude that the oxidation mechanism of metal Hf layer was as follows. (1) For initial stage of oxidation, the metal Hf layer was oxidized rapidly and higher oxidation rate could be obtained. (2) For 2nd stage of oxidation from 5[min] to 10[min], additional HfO_2 layer had been indeed formed, but the etching from the surface region occurred by the piranha solution. So the oxidation rate was shown to be decreased. (3) For the next stage from 10[min] to 15[min], since the rate of etching mentioned above was higher than that of oxidation rate, the thickness of HfO_2 layer would be decreased.

To achieve HfO_2 on Si directly for the fabrication of MOS structure, metal Hf with the thickness of 10 [nm] on Si has been prepared as shown in figure 3 (2). In this case, the thickness of Hf layer was determined by the assumption that the volume expansion of Hf to HfO_2 would be about twice during the oxidation process. Figure 6 (b) shows C-V characteristics for each oxidation time using 10[nm] thick Hf/Si structure. The oxidation process was the same as that shown in figure 3 (1). It is clearly shown that the insulator/Si directly stacked structure could be formed using 10[nm] thick Hf/Si structure because typical C-V curves have been obtained. For 5[min] oxidation sample, HfO_2 /Si structure would be formed because it shows higher value of accumulation capacitance. For 10[min] oxidation sample, additional oxidation of Si occurred and the capacitance value had been decreased. For 15[min] oxidation, however,

the etching from the surface region occurred by the piranha solution and the thickness of insulator film would be decreased. These trend of oxidation and etching mechanism still hold in figure 6(a) and (b). Figure 7 shows J-E characteristics from the sample(2) as the function of oxidation time. In case of 5[min] oxidation sample, which had HfO₂/Si structure, lower leakage level could be achieved. For longer oxidation sample however, leakage level tends to be higher because the etching occur and the film thickness tends to be thinner.

For comparison, the C-V characteristics of HfO₂/Si structure using conventional thermal oxidation process at 400 degree of C for 40[min] is shown in figure 8. From the figure, it might have quite low interface defects and/or traps close to the interface. The C-V characteristics of HfO₂/Si structure using conventional thermal oxidation process might become one aim for that formed by the chemical solution oxidation method.

IV. Conclusion

An oxidation method using chemical solution has been proposed to form thin oxide film such as SiO₂, HfO₂ for the fabrication of MOS structure on large diameter of Si wafers. For the formation of SiO₂ on Si wafers, piranha solution with 130 degree of C for 5[min] was suitable to achieve good interface properties. For the formation of HfO₂ on Si wafers to fabricate MOS structure, initial thickness of deposited metal Hf layer was very important under the oxidation condition using piranha solution with 100 degree of C. The piranha solution causes both oxidation of metal Hf and etching of HfO₂. Precise control of oxidation time was essential to achieve high quality HfO₂ on Si wafer for the fabrication of MOS structure.

References

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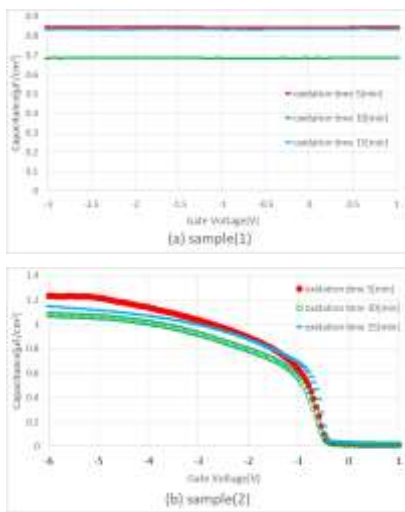


Fig.6 C-V characteristics of (a) sample(1) : oxidation of 30[nm] thick Hf. (b) sample(2) : oxidation of 10[nm] thick Hf.

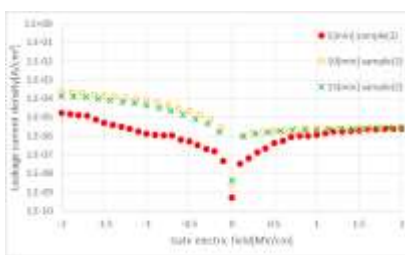


Fig.7 J-E characteristics of sample(2)

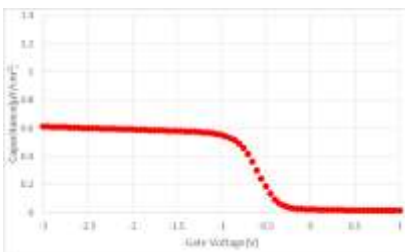


Fig.8 C-V characteristics of sample(3)