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Characterization of $CoSi_2$ Gate MOS Structure Formed by Ion Irradiation

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Abstract: $CoSi_2$ gate MOS structures were formed by 20, 30, and 40 keV Si^{2+} Focused Ion Beam (FIB) irradiation to the 14/50 and 21/75 nm Co/Si layers on 20 nm SiO_2 films, and electrical properties of the structures were investigated. The results of the C-V measurement show that the flat-band shift increases with increasing the irradiation damage in SiO_2 films. The leak current was also investigated by the I-V measurement, and it is concluded that the leak current was caused by the irradiation damage in SiO_2 films and the Si-rich layers near the silicide/SiO_2 interface formed by insufficient mixing of Co and Si atoms. In order to optimize the fabrication process of the $CoSi_2$ gate MOS structures by the irradiation, the irradiation damage induced in SiO_2 films should be minimized, and the sufficient energy should be deposited in Co/Si layers to induce the mixing of Co and Si atoms. For the 21/75 nm Co/Si sample irradiated with 40 keV Si^{2+} to $5\times10^{15}\,cm^{-2}$, the Fowler-Nordheim tunneling current was observed, and flat-band shift was 1.6 V.

Keywords: $CoSi_2$, MOS, Beam, Ion mixing, SiO_2

1. Introduction

Recent years, there are VLSI chips with more than 1 G devices per chip, and the number of the devices will increase in the future. The increase contributes to improvement of the system performance such as operation speed, power dissipation, and fabrication cost. However, the speed of the miniaturization of devices has been slowing down, owing to degradation of performance of the miniaturized devices. In order to maintain the miniaturization trend, some approaches are required to improve the miniaturized device performance.

$CoSi_2$ is expected to be an alternative gate material for the Si based devices, because of its low resistivity and chemical and thermal stability. Many researchers have investigated the formation methods of $CoSi_2$.[1),2),3),4),5),6),7)] One of the promising methods utilizes ion irradiation to the Co/Si stacked layers. Co and Si layers in unirradiated regions can be removed by an appropriate selective wet etching against the irradiated regions.[8)] If the ion irradiation is performed selectively by Focused Ion beam (FIB), fine cobalt silicide structures can be formed without any mask processes.[8)] Although narrow fine structures of cobalt silicide can be obtained by this procedure, irradiation may cause some damage in the underlying layers. Although the creation of the damage is the serious problem in the device application, especially to gate electrodes of MOS devices, the effects of the damage to the MOS devices have not been investigated.

In the present study, we formed the $CoSi_2$ gate MOS structures by irradiation to the Co/Si/SiO_2/Si structures, and irradiation effects to the MOS properties were evaluated. The relation between irradiation condition and the MOS properties is discussed, and the guideline for the optimized process condition is proposed.

2. Experimental Procedure

In the experiment, P-doped n-type CZ-Si(100) wafers with 8-12 Ω cm were used. The wafers were cut into the chips about 5×10 mm. These chips were chemically cleaned by the standard RCA procedure. Immediately after the cleaning, the chips were loaded into the oxidation furnace. Dry oxidation was performed at 900 °C for 75 min with O_2 flow rate of 500 sccm. SiO_2 films with 20 nm thickness were formed on the substrates. After the oxidation, the chips were transferred into the molecular beam evaporation chamber equipped with the K-cells. Si and Co were sequentially deposited on SiO_2 films at room temperature in a vacuum below 5×10^{-8} Torr. The Co/Si layer thickness was 14/50 and 21/75 nm. The ratio of the thickness corresponded to the atomic ratio of Co:Si=1:2. The sam-

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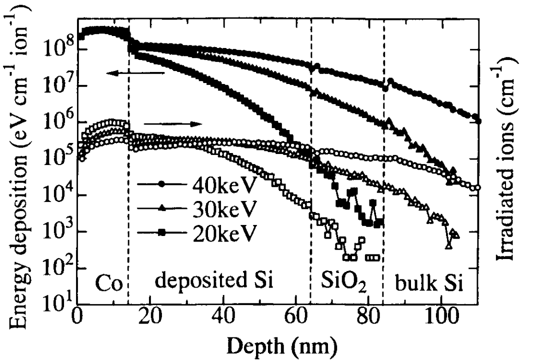


Fig.1 Energy deposition rate for 20, 30, and 40 keV Si^{2+} irradiation to 14/50/20 nm $Co/Si/SiO_2$ layers on Si calculated using the SRIM96 code.

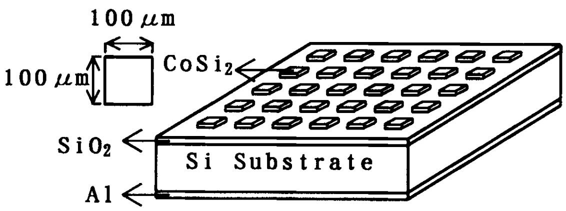


Fig.2 Schematic of the $CoSi_2$ gate MOS structures. The gate area is 100×100 μm square.

ples were selectively irradiated in the 100×100 μm square with Si^{2+} FIB to doses between 2×10^{14} and $5\times10^{15}\,cm^{-2}$ at room temperature.

The irradiation energies were 20, 30, and 40 keV. Energy deposition by 40 keV irradiation is the maximum at 14/50 nm Co/Si interface as shown in **Fig. 1**. After the irradiation, unreacted Co layers remaining on the surface were removed by dipping the samples into the solution of HNO_3:H_2O_2=1:3 for 30 s, and unreacted Si layers were removed with H_3PO_4 at 160 °C for several minutes. After the etching, the samples were heat treated at 700 °C for 20 min, in order to convert the irradiated regions into $CoSi_2$.[9] Al electrodes for the ohmic contact were formed on the backside of the samples. **Figure 2** shows the schematic of the MOS structures formed by the present method. Electrical properties of the MOS structures were evaluated by the *C-V* and the *I-V* measurements.

3. Results and Discussion

The *C-V* curves for the 14/50 nm Co/Si samples irradiated with 40 keV Si^{2+} ions to various doses at room temperature are shown in **Fig. 3**. The differ-

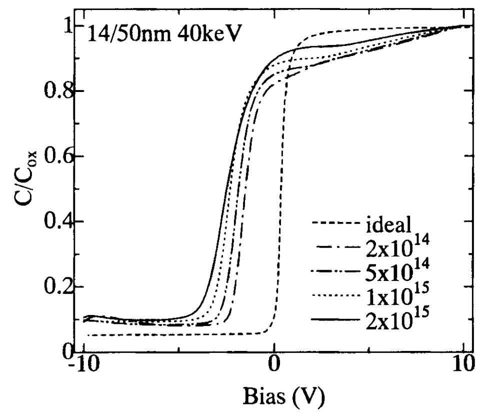


Fig.3 *C-V* curves for samples irradiated with 40 keV Si^{2+} ions to doses between 2×10^{14} and $2\times10^{15}\,cm^{-2}$ at room temperature. The Co/Si layer thickness is 14/50 nm.

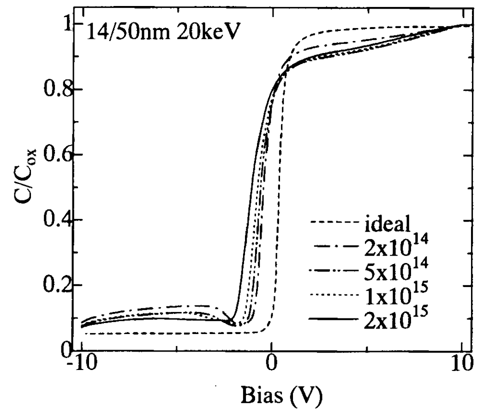
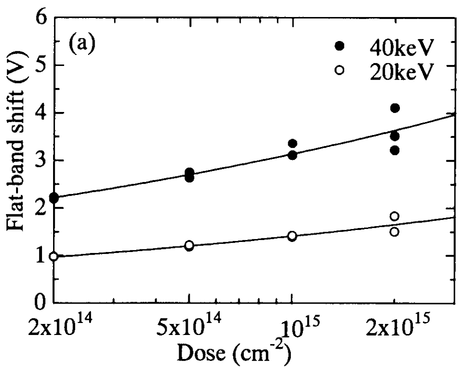


Fig.4 *C-V* curves for samples irradiated with 20 keV Si^{2+} ions to doses between 2×10^{14} and $2\times10^{15}\,cm^{-2}$ at room temperature. The Co/Si layer thickness is 14/50 nm.

ence in the shape of the *C-V* curves from that for the ideal curve increases with increasing the dose, and the flat-band shift also increases with increasing the dose. Thus, it is suggested that the irradiation damage induces charged traps in the SiO_2 films, and the amount of the traps increases with the dose. Moreover, the gradient of the curves at the frat-band voltage decreases with increasing the dose. The decrease can be attributed to the increase of the SiO_2/Si interface states. Thus, it can be concluded that the irradiation induces the SiO_2/Si interface states and the charged traps in the SiO_2 films, and they increase with increasing the dose. The dose of $2\times10^{14}\,cm^{-2}$ corresponded to the minimum value



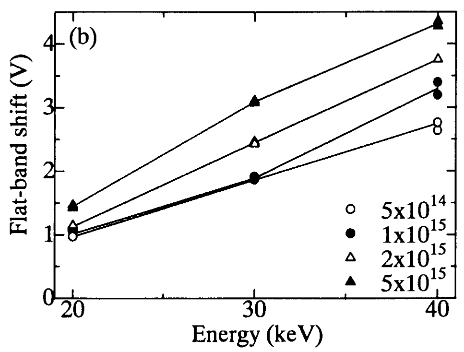


Fig.5 Dose dependence (a) and energy dependence (b) of flat-band shift for samples with 14/50 nm Co/Si layers.

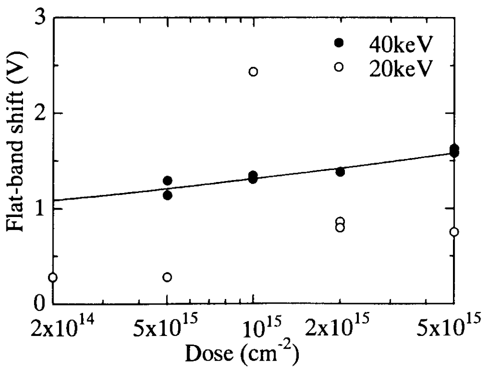


Fig.6 Dose dependence of flat-band shift for samples irradiated with 20 and 40 keV Si^{2+} ions. The thickness of Co/Si layers is 21/75 nm.

to obtain the etching selectivity in the present process, and the mixed layers irradiated with a dose less than $2\times10^{14}\,cm^{-2}$ were etched out during the etching of the unreacted Si. While the irradiation damage can be decreased by decreasing the dose, the irradiation over the minimum dose is necessary to perform the selective etching.

Figure 4 shows the *C-V* curves for the 14/50 nm Co/Si samples irradiated with 20 keV ions to various doses at room temperature. The curves show the similar trend to those for the 40 keV irradiation, shown in **Fig. 3**. With increasing the dose, the flat-band shift increases, and the gradient of the curves at the flat-band voltage decreases. However, the increase in the flat-band shift and the decrease in the gradient is rather small compared with that for the irradiation at 40 keV. The energy deposition at the SiO_2 films by a 20 keV Si^{2+} ion is smaller by about 2 order of magnitude than that by a 40 keV Si^{2+} ion, as shown in **Fig. 1**, and thus, the energy dependence of the *C-V* curves is caused by the difference in the energy deposition.

The dose dependence and the energy dependence of the flat-band shift are shown in **Figs. 5(a)** and **5(b)**, respectively. The flat-band shift increases with increasing the dose and the irradiation energy. The solid lines in **Fig. 5(a)** show the results of least-square fit of the experimental data to the equation for a power law,

$$\Delta V_{FB} = AN^b, \qquad (1)$$

where ΔV_{FB} is the flat-band shift, N the dose, and A and b fitting parameters. The parameter b corresponds to the reaction order. The fit of the data to the curves is good for all irradiation energies. A similar power law dependence of the flat-band shift on the dose has been reported by Kim *et al.* for SiO_2 films irradiated with electron beams,[10] and it is suggested that the same process governs the dynamics of the damage formation during the irradiation with ions and electrons.

From these results, it is found that the damages in the SiO_2 layers should be decreased to suppress the degradation of SiO_2 layers, and the irradiation with lower energy and lower dose, but sufficient to obtain the etching selectivity, is required. Another promising approach to reduce the damage in the SiO_2 films is the use of more thick Co/Si layers. Thus, we next performed the irradiation to the 21/75 nm Co/Si layers and evaluated the electrical properties.

Figure 6 shows the dose dependence of the flat-band shift for samples with 20 and 40 keV Si^{2+} ions. The flat-band shift for samples irradiated with 40 keV ions is quite small compared with the 14/50 nm Co/Si layer samples irradiated with the

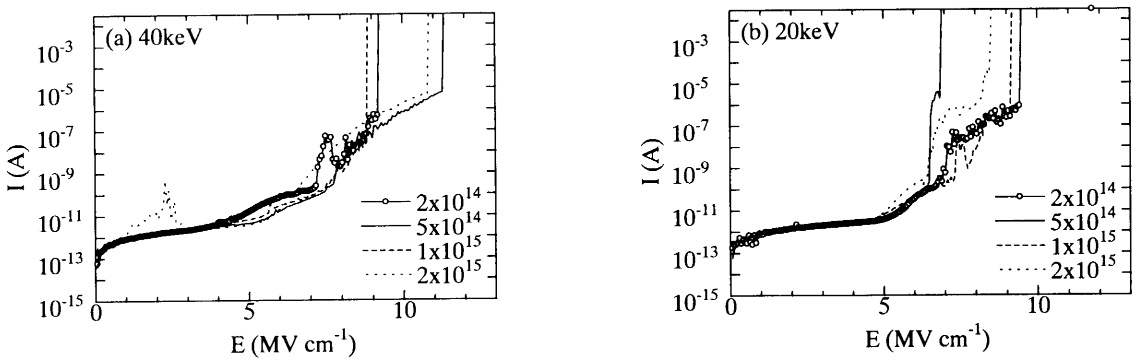


Fig.7 *I-E* curves for samples irradiated with 40 keV (a) and 20 keV (b) Si^{2+} ions to doses between 2×10^{14} and 2×10^{15} cm^{-2} at room temperature. The Co/Si thickness is 14/50 nm.

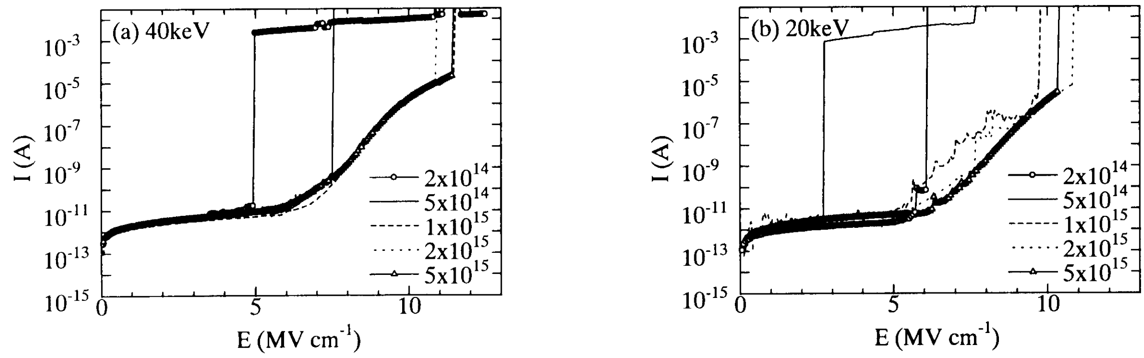


Fig.8 *I-E* curves for samples irradiated with 40 keV (a) and 20 keV (b) Si^{2+} ions to the dose between 2×10^{14} and 5×10^{15} cm^{-2} at room temperature. The Co/Si layer thickness is 21/75 nm.

same energy. The dose dependence of the flat-band shift also obeys the power law. The SRIM simulation showed that the energy deposition in the SiO_2 films of the 21/75 nm Co/Si layers was lower than that of the 14/50 nm Co/Si layers by 2 orders of magnitude.

On the other hand, the flat-band shift for samples irradiated with 20 keV shows large deviation from the power law. The leak current for the samples was large as described later, and the reason for the deviation will be discussed later.

The *I-E* characteristics for samples irradiated with 40 and 20 keV Si^{2+} ions are shown in **Figs. 7(a)** and **7(b)**, respectively. The thickness of Co/Si layers was 14/50 nm. For the samples irradiated with 40 keV ions shown in **Fig. 7(a)**, large leak current is observed. The leak current can be classified into three groups, *i.e.*, the leak current observed at electric field ranging from 1 to 3 MV cm^{-1}, that from 4 to 7 MV cm^{-1}, and that from 7 to 10 MV cm^{-1}. The leak current at the electric field above 7 MV cm^{-1} is significant for samples with lower doses. From the Fowler-Nordheim plots of the data at the electric field 7–10 MV cm^{-1}, it was found that only the sample irradiated with 2×10^{15} cm^{-2} showed the Fowler-Nordheim tunneling characteristics.

The samples irradiated at 20 keV in **Fig. 7(b)** show the smaller leak current at 4–7 MV cm^{-1} than that for samples irradiated at 40 keV. This decrease in the leak current is due to the reduction of the damage in the SiO_2 films caused by the decrease of the irradiation energy. However, the leak current at the electric field 7–10 MV cm^{-1} is larger, and no samples showed the Fowler-Nordheim tunneling characteristics. In order to clarify the reason for the increase in the leak current at 7-10 MV cm^{-1}, the statistical investigation with more samples will be needed.

The *I-E* characteristics for samples with 21/75 nm Co/Si layers have been also investigated. **Figures 8(a)** and **8(b)** show the results for the samples irradiated with 40 and 20 keV ions, respectively. For both irradiation energies, the leak current at the electric field 4 7 MV cm^{-1} is smaller compared with that for samples with 14/50 nm Co/Si layers. Moreover, the current for the samples irradiated at 40 keV with doses above 1×10^{15} cm^{-2} showed the Fowler-Nordheim tunneling characteristics. This suggests that the damage introduced in the SiO_2 films has been significantly reduced by increasing the layer thickness. On the other hand, the breakdown voltage for samples irradiated with 2×10^{14} and 5×10^{14} cm^{-2} decreased to less than 8 MV cm^{-1}. For the samples irradiated at 20 keV, the leak current is larger than that at 40 keV , and only the sample irradiated with 5×10^{15} cm^{-2} indicated the Fowler-Nordheim tunneling characteristics.

These results show that the SiO_2 layers degrade with decreasing the dose below 5×10^{14} cm^{-2}, which can be explained as follows. If the mixing of Co and Si atoms is not sufficient, excess Si atoms exist in the silicide region near the silicide/SiO_2 interface. It is reported that excess Si atoms in $CoSi_2$ layers degrade the electrical properties of the SiO_2 films.[11)] Thus, we speculate that the degradation of SiO_2 films observed for samples with smaller dose is due to the excess Si atom regions on the SiO_2 films.

In order to optimize the formation process of the $CoSi_2$ gate MOS structures by ion irradiation, the irradiation conditions have to be selected to minimize the induced damages in SiO_2 films and simultaneously to maximize the mixing efficiency of Co and Si atoms.

4. Conclusion

The $CoSi_2$ gate MOS structures were formed by the ion irradiation to the Co/Si layers on SiO_2 films, and the relation between the MOS properties and the irradiation conditions has been investigated. The irradiation was performed with 20, 30 and 40 keV Si^{2+} FIB to doses ranging from 2×10^{14} to 5×10^{15} cm^{-2} at room temperature. After the selective etching, the silicidation of the irradiated regions was induced by heat treatment at 700 °C for 20 min.

The result of the *C-V* measurement showed that the flat-band shift increased with increasing the dose and the irradiation energy, and it decreased with increasing the Co/Si layer thickness. This trend is explained by the amount of the damage in SiO_2 films induced by the irradiation. The dose dependence of the flat-band shift obeys the power law.

The *I-V* measurement for the samples was performed, and the leak current was investigated. For the 21/75 nm Co/Si samples irradiated with doses above 1×10^{15} cm^{-2}, the leak current at the electric field 4 7 MV cm^{-1} was smaller compared with that for the 14/50 nm Co/Si samples, and the Fowler-Nordheim tunneling current was observed. However, for the 21/75 nm samples irradiated with doses below 5×10^{14} cm^{-2}, the breakdown field was less than 8 MV cm^{-1}. The smaller breakdown field has been attributed to the excess Si atoms in the silicide layers near the silicide/SiO_2 interface.

In order to optimize the formation process of the $CoSi_2$ gate MOS structures using ion irradiation, the irradiation conditions have to satisfy the next two requirements: (I) irradiation damages induced in SiO_2 layers should be minimized, and (II) sufficient energy should be deposited in Co/Si layers to induce the mixing of Co and Si atoms. For the 21/75 nm Co/Si sample irradiated with 40 keV Si^{2+} to 5×10^{15} cm^{-2}, the Fowler-Nordheim tunneling current was observed, and flat-band shift was 1.6 V and minimum under the present experimented conditions.

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