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A New Low-Temperature Oxidation Technique by Gas Cluster Ion Beams

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High quality SiO_2 films of the thickness up to 11 nm were grown on Si substrate surfaces at room temperature by O_2 cluster ion irradiation. No damage was observed after N_2 annealing at 400 °C for 30 min on I-V characteristics of the gate oxide irradiated with 5 keV Ar cluster ions. These results indicate that O_2 cluster ions strongly enhanced the oxidation with low irradiation damage.

1. Introduction

Gas cluster ion beams offer new surface modification techniques for shallow implantation, high rate sputtering, surface smoothing, cleaning and film formation [1-3]. The average energy per constituent atom of a 10 keV cluster ion containing 1000 atoms is only 10 eV. As a result, the interactions between cluster and substrate atoms occur at near-surface regions. Moreover, cluster ions can deposit their energy in high density within a very localized surface region. Thus, it can be expected that the irradiation of gas cluster ions enhances the chemical reactions on the substrate surface.

Scaling down of integrated Si devices requires fabrication processes at reduced temperature to prevent a degradation of device performance due to the impurity redistribution and the formation of the stress-induced defects in Si. Though thermal oxidation technique can produce high quality gate oxides, it requires high temperature above 800°C to obtain sufficient thickness. Thus, many kinds of oxidation techniques at reduced temperature, such as plasma oxidation at 600°C [4] and ion-assisted oxidation at 450 °C [5] have been intensively studied. Room temperature oxidation by low-energy oxygen ion beam has also been reported [6]. In this case, the SiO_2 films thicker than 6 nm could not be formed.

We have already found that 9 nm thick SiO_2 films can be formed on Si substrate surfaces at room temperature by irradiation with 10 keV CO_2 cluster ions [3]. In this paper, oxidation of Si substrate surfaces by O_2 cluster ion beam irradiation at low temperatures, mainly at room temperature, is studied in comparison with that by monomer ions.

2. Experiments

Figure 1 shows a schematic diagram of low energy gas cluster ion beam equipment. Cluster beams from gas sources such as O_2, CO_2 and Ar gas can be formed by adiabatic expansion through a Laval nozzle into a vacuum chamber [7]. The clusters ionized by electron bombardment can be accelerated up to 10 kV. The monomer ions and the clusters of smaller sizes are excluded by using retarding potential method [7]. The minimum and mean sizes of O_2 cluster ions used in this experiment were 250 and 2000, respectively. Al gate MOS capacitors of 1.7×10^{-4} cm^2 in area were fabricated on n-type (100) 2-3 Ωcm silicon wafers to examine the electrical characteristics.

3. Results and discussions

3.1 Evaluation of damage caused by Ar cluster ion irradiation

MOS capacitors were used to evaluate the damage caused by gas cluster ion irradiation. 18 nm thick gate oxide films thermally

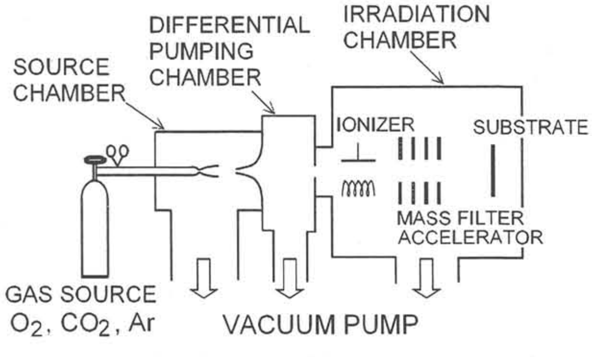

Fig. 1 Schematic diagram of low energy gas cluster ion beam equipment.

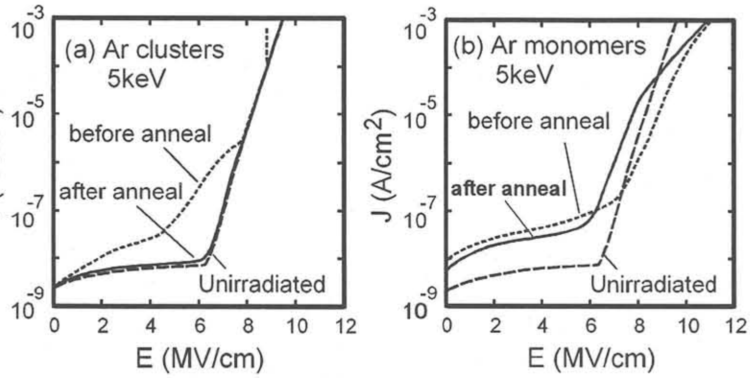

Fig. 2 I-V characteristics of MOS capacitors of which the 18 nm thick gate oxide films thermally grown at 900 °C were irradiated (a) with 5keV Ar cluster ions and (b) with 5keV Ar monomer ions at a dose of 10^{14} ions/cm^2. Annealing at 400 °C in N_2 for 30 min was given to some samples after the ion irradiation.

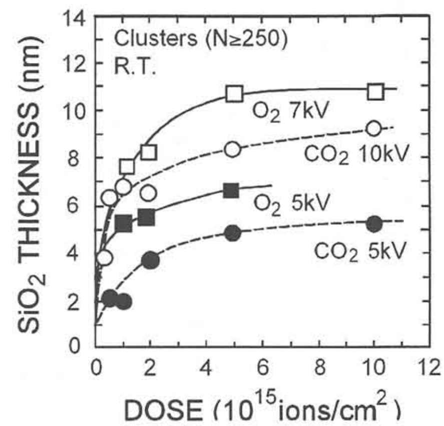

Fig. 3 Dose dependence of SiO_2 film thickness formed by O_2 and CO_2 cluster ion oxidation.

grown at 900 °C were directly irradiated with 5keV Ar cluster and monomer ions. Some samples were annealed at 400°C in N_2 for 30 min after the irradiation. Figure 2 shows the forward I-V characteristics of the Al/SiO_2/Si capacitors. The degradation of I-V characteristics were observed in both oxides before anneal. However, in the case of irradiation with cluster ions the I-V characteristics of the annealed samples coincided with that of the unirradiated samples, which meant that the damage was recovered by the annealing. On the other hand, the damage caused by monomer ion irradiation was not recovered. These results indicate that the type of irradiation damage caused by cluster ion irradiation is different from that by monomer ions and the irradiation process by 5 keV cluster ions might be applicable to the fabrication process of Si LSI devices.

3.2 Oxidation process by O_2 cluster ion beam irradiation

Low temperature oxidation processes by O_2 and CO_2 cluster ion irradiation have been investigated. Figure 3 shows the dose dependence of SiO_2 film thickness. The thickness was measured by X-ray photoelectron spectroscopy. The film thickness exhibited the tendency to saturate at doses above 5×10^{15} ions/cm^2 and could be easily controlled by the cluster ion energy. SiO_2 films of the thickness of 11 nm were formed by irradiation with 7 keV O_2 cluster ions at a dose of 5×10^{15} ions/cm^2. It has been reported that in the case of oxidation by 40-180 eV O_2 monomer ion irradiation at room temperature, SiO_2 film thickness reach a limiting value of 4-6 nm at a dose of approximately 5×10^{17} ions/cm^2 [6]. The 11 nm SiO_2 films formed by irradiation with 7 keV O_2 cluster ions are much thicker than those of monomer ion cases reported before, even though the average energy per atom in the clusters is less than 14 eV.

A preliminary study at elevated substrate temperatures up to 400 °C showed that the activation energy for the O_2 cluster ion oxidation was approximately 0.02 eV. This value is two order of magnitude lower than the activation energy for thermal oxidation, which is 2.0 eV [8]. The activation energy for cluster ion oxidation is rather close to those for the monomer ion oxidation (0.025 eV [5] and 0.007 eV [6]). These results indicate that the irradiation of cluster ions enhances the oxidation.

Figure 4 shows the dependence of SiO_2 film thickness on accerelation voltage of O_2 cluster ions. Formation of the oxide layer had a strong dependence on acceleration voltage. Oxidation started at around 3 kV. In the case

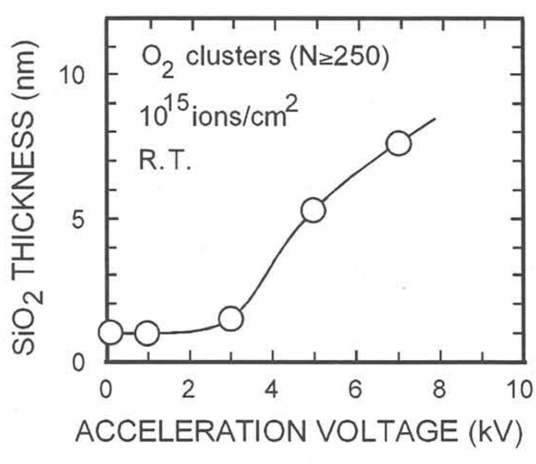

Fig. 4 Dependence of SiO_2 film thickness on the acceleration voltage of O_2 cluster ions.

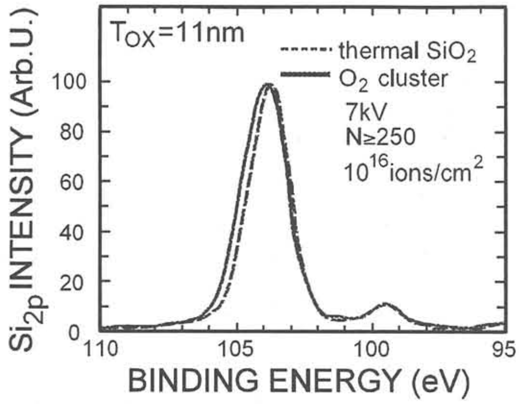

Fig. 5 XPS spectra of 11 nm SiO_2 films formed by irradiation with 7 keV O_2 cluster ions and by thermal oxidation at 900 °C.

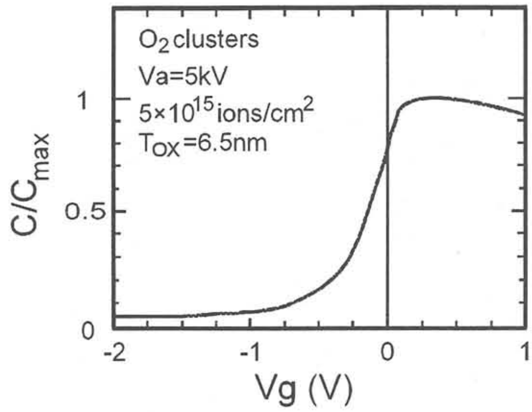

Fig. 6 High frequency C-V curves for a MOS capacitor. The SiO_2 film formed by O_2 cluster ion irradiation at room temperature was used as a gate insulator.

of monomer ion oxidation, the thickness was insensitive to ion energy in the range of 40-180 eV [6]. These results strongly suggest a new oxidation mechanism in the cluster ion oxidation.

According to the molecular dynamics simulations, very high temperature and high pressure region can be produced near substrate surface by a cluster ion irradiation [9]. Enhancement of oxidation processes by O_2 cluster ion irradiation could be explained by the generation of exited atoms around the impact region caused by the high density energy deposition.

SiO_2 film formation by gas cluster ion beam oxidation can be achieved without using any plasma processes. Irradiation dose of cluster ions is 2-3 order of magnitude lower than that of monomer ions. This is important for the minimization of the degradation of semiconductor devices by charge up effects.

3.3 Oxide Film quality

Figure 5 shows the Si2p lines of the X-ray photoelectron spectra for 11 nm SiO_2 films formed by 7 keV O_2 cluster ion irradiation and by thermal oxidation at 900 ° C. The films formed by cluster ion irradiation had similar structures to thermal oxides. It was also found by cross-sectional TEM that the interfaces of SiO_2/Si were very smooth. The carbon content of SiO_2 films formed by O_2 cluster ion irradiation was as low as that of thermal oxide film. Figure 6 shows a high frequency C-V curve for a MOS capacitor which gate oxide was grown to 6.5 nm by irradiation with 5 keV O_2 cluster ions. The curve showed that high quality SiO_2 films could be formed.

4. Conclusions

The damage caused in the gate oxides by 5 keV Ar cluster ion irradiation was recovered after N_2 annealing at 400°C for 30 min. High-quality SiO_2 films of the thickness up to 11 nm were formed at room temperature on Si surfaces by O_2 cluster ion beam irradiation. This should be resulted from high density energy deposition by cluster ion irradiation. Film formation by gas cluster ion beams is a new technique. This technique could be applied to the formation of various kinds of insulators for future semiconductor LSI devices.

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