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Mechanism of E' Center Generation in SiO_2 Film by Ion and Neutral Beam Bombardment

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The radiation damage in SiO_2 films thermally grown on silicon and bombarded by ion and neutral beams has been studied by electron spin resonance (ESR). It is found that the E' center generation yield is much higher for ion bombardment than for neutral bombardment in spite of the same kinds of atoms and the same incident energy. The generation yield of ion-induced E' centers depends on the incident energy and ionization energy of the parent atom. On the other hand, for neutral bombardment, it depends only on the incident energy. These results indicate that the neutral-induced E' centers are created by bond breaking due to a collision cascade. However, ion-induced E' centers are generated by both collision cascades and carriers (electrons and holes) induced in the SiO_2 film by ion neutralization.

KEYWORDS: radiation damage, ion beam, neutral beam, ESR, SiO_2, E' center, collision cascade, ion neutralization

§1. Introduction

Plasma processes are key technologies in ultra-LSI (ULSI) fabrication processes, particularly for fine pattern delineation and thin-film deposition. However, radiation damage induced in devices during plasma processes must be minimized in future ULSIs. Damage-inducing factors in plasma are forms of ionizing radiation such as ions, electrons, and vacuum ultraviolet (VUV) photons.[1,2] It is necessary to clarify how the damage is caused by such radiation in order to develop low-damage surface processes.

There are several kinds of damage which degrade devices. Damage to thin SiO_2 films, especially gate oxides, is the most serious problem in metal-oxide-semiconductor (MOS) devices with SiO_2/Si structures. We have previously characterized the damage in SiO_2/Si induced by VUV irradiation.[3] After VUV irradiation, E' centers were observed by ESR measurements. It is argued that the generation mechanism of this E' center is bond breaking due to direct photoionization.

The purpose of this study is to determine the defect generation mechanism in a SiO_2/Si structure, especially the generation of point defects in SiO_2 film by energetic ions and neutrals which, as well as UVU photons, are expected to create defects. For this purpose, ESR measurements have been carried out on ion- and neutral-beam-irradiated SiO_2/Si samples. This study concentrates on the effect of particle charges by comparing ion-induced defects with neutral-bombardment-induced defects.

§2. Experimental

The samples in this study were 76-mm-diameter silicon wafers with (111) surface orientation and a high resistivity (>1000 Ω·cm). A SiO_2 film about 120 nm thick was grown in dry oxygen at 1000°C. No postoxidation annealing was performed.

The samples were irradiated with ion or neutral beams extracted from a rare gas (He, Ne, Ar, Xe) plasma using the magneto-microwave plasma apparatus shown in Fig. 1. The background gas pressure of this chamber was 6.5×10^{-2} Pa. The beam path length from the extraction electrode to the sample surface was 13 cm.

Ion beam energy was chosen between 300 and 800 eV. Ion beam flux was 5×10^{13}–$2\times10^{14}/cm^2$ s depending on the energy and ion species.

The neutral beam was produced by a charge exchange reaction between the extracted ion beam and background thermal neutrals. The cross section of charge exchange reaction without energy transfer was much larger than the cross section of collisions with energy transfer (momentum transfer)[4] for the case of rare gas ions. Therefore, the kinetic energy of most of the atoms in the neutral beam was the same as that of the ion beam before neutralization. The neutralization probability was about 20–40% depending on the ion species, its energy, gas pressure, and beam path length. The neutralization

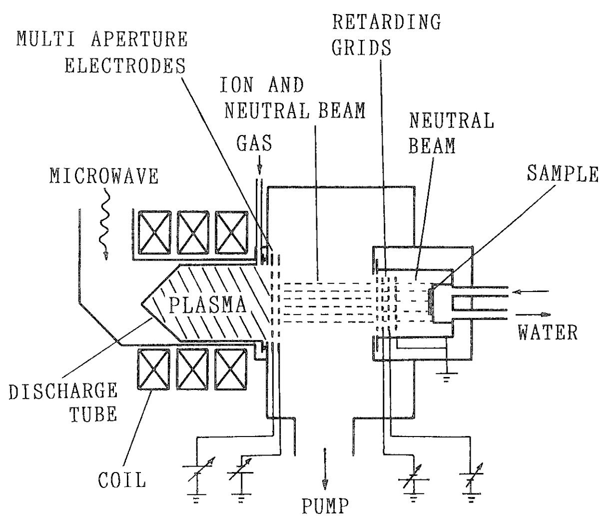

Fig. 1. Magneto-microwave plasma apparatus for ion and neutral beam irradiation.

probability was determined by measuring the sputter etch rate of Cu film.[5] Retarding potential grids were set up in front of the sample to eliminate residual ions and electrons from the beam, and thus the sample was irradiated only by the neutral beam.

After irradiation, the sample wafer was cut into bar-shaped pieces of 3×30 mm. Then they were dipped into an aqueous solution of hydrazine to terminate the Si dangling bonds at the edges of the pieces.

The ESR measurements were carried out under the temperature of 10 ± 0.2 K using a JEOL-JES-RE2X spectrometer (X-band). The microwave power was 0.01 mW. At this low power, a linear relationship between microwave power and signal intensity was maintained. The modulation width of the magnetic field was 0.2 Gauss. The g value and spin densities were determined by comparing the observed spectra with those of reference samples, i.e., Mn^{2+} in MgO and TEMPOL (4-hydroxy-2,2,6,6-tetramethyl-piperidine-1-oxyl) in benzene.

A buffered HF (5% HF, 95% NH_4F) solution was used for step etching of the SiO_2 film in order to determine the distribution of the generated defects. The thickness of the remainig SiO_2 film was measured using a thin film thickness meter (Nanospec-SDP-2000T).

§3. Results

After Ne ion (Ne^+) or Ne neutral (Ne^0) beam irradiation, ESR signals were observed. The observed ESR spectra are shown in Fig. 2. These spectra show the same characteristics except for intensity. The g-value obtained from these spectra is about 2.001. The nonsymmetric line shape of these spectra corresponds to axially symmetrical defects which are arranged in random directions in amorphous SiO_2. These results indicate that the observed spectra correspond to E' centers. The E' center is an oxygen-deficient "trivalent silicon" in the silicon dioxide. The E' center peak disappeared after etching the SiO_2 in buffered HF to a depth of 10 nm. Therefore, these E' centers exist only in the top SiO_2 surface layer.

Figure 3 shows the E' center densities as a function of

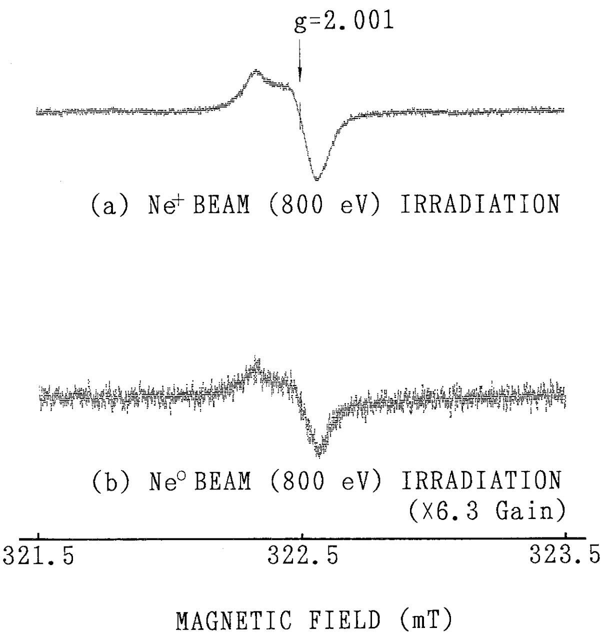

Fig. 2. ESR spectra of SiO_2/Si samples after (a) Ne^+ beam, and (b) Ne^0 beam irradiation.

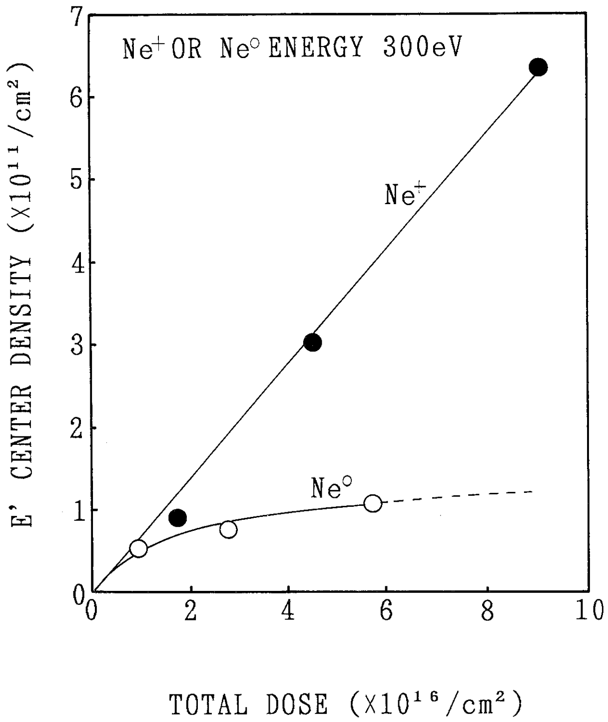

Fig. 3. E' center densities as a function of total dose of Ne^+ and Ne^0 beams. The incident energy of these beams is 300 eV.

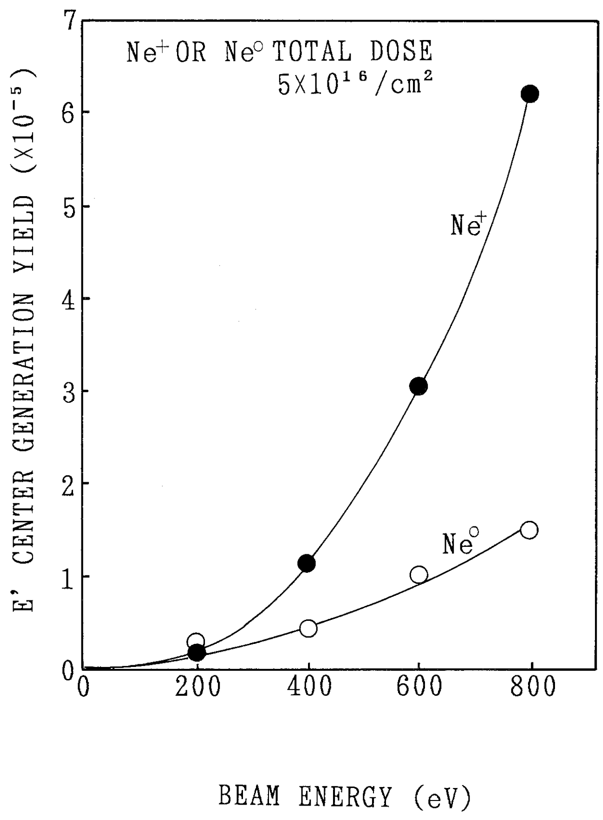

Fig. 4. E' center generation yield as a function of the kinetic energy of Ne^+ and Ne^0 beams.

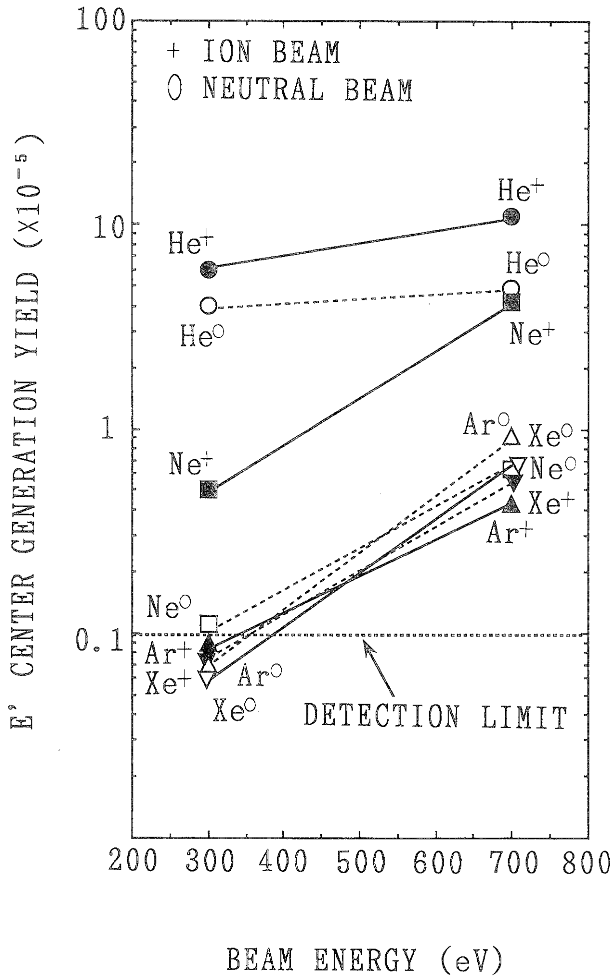

Fig. 5. E' center generation yields with respect to ions and neutrals of several kinds of atoms.

the total dose of Ne^+ and Ne^0 beams (at an incident energy of 300 eV). The Ne^0-beam-induced E' center density increases with the total dose of incident Ne^0 and seems to saturate at about $2\times10^{16}/cm^2$. In comparison, the Ne^+-beam-induced E' center density increases monotonically without saturation.

Figure 4 shows the E' center generation yield as a function of the kinetic energy of Ne^+ and Ne^0 beams. Both Ne^+- and Ne^0-induced E' center generation yields increase with the kinetic energy. However, the slope for the Ne^+ beam is larger than that for the Ne^0 beam.

Figure 5 shows the E' center generation yields for ions and neutrals of several kinds of atoms. The E' center generation yields depend on the kind of atom as well as on whether the incident particle is an ion or neutral. The E' center generation yields for He^+ and Ne^+ are very high. However, the yields for Ar^+ and Xe^+ ions are low and nearly equal to the yields for neutrals of the same elements.

§4. Discussion

The E' center is a trivalent silicon in SiO_2 which has several structures denoted as E'_1, E'_2, E'_4.[6-8] Any of these E' centers have a dangling bond, i.e., an unpaired electron on the Si atom. When the Si–O bond is broken by particle bombardment, there is always a possibility of E' center generation. In addition, if a hole comes to reside on the broken bond site, the unpaired electron on the Si atom at the bond-broken site (trivalent Si structure) is stabilized as an E' center.

As regards the E' center generation, two conclusions can be drawn from the results in Fig. 4. One is that the E' center generation yield by ion bombardment is more than twice that by an identical neutral bombardment. The other conclusion is that the E' center generation yields increase with bombardment energy (for ions and neutrals). These results mean that energetic bombardment by itself can produce E' centers but the ionization energy of the ion increases the E' center generation yield.

To show how much the ionization energy contributes to the E' center generation yield, we compared the generation yields with various ions and their parent neutrals. As shown in Fig. 5, the E' center generation yields with He^+ (ionization energy E_i=24.58 eV) and Ne^+ (E_i=21.56 eV) are much larger than those with He^0 and Ne^0, whereas the yields with Ar^+ (E_i=15.96 eV) and Xe^+ (E_i=12.08 eV) are about the same as those with Ar^0 and Xe^0. From these results, we conclude that the ionization energy plays an important role in E' center generation through some electronic processes.

It is possible that ions are neutralized before reaching the SiO_2 surface. In particular, high-ionization-energy ions, He^+ and Ne^+, may be neutralized through Auger neutralization,[9] generating holes in SiO_2. Thus, the generated holes will be captured at the broken bond site to stabilize the Si dangling bonds, forming E' centers.

Another possible reason why the high ionization energy contributes to the E' center generation is that core ionization of oxygen (in SiO_2) induced by ion incidence through interatomic Auger decay[10] leads to release of oxygen from the SiO_2 network forming on oxygen vacancy (with E' centers).

We have recently shown that preferential sputtering of oxygen from SiO_2 can be done by ion bombardment but not by neutral bombardment.[11] It can be argued that this preferential oxygen release is caused by the above electronic process. This partly explains the higher E' center generation yield with ion bombardment.

Of course, a collision cascade generated by particle bombardment may give higher energies to lighter atoms (oxygen in SiO_2) than to heavier atoms, and preferential sputtering of oxygen from SiO_2 may be caused only by kinetic energy being transferred from a particle.[12] This will bring about the oxygen vacancy and the Si dangling bond. The role of the electric charge on ions will be to enhance the preferential sputtering of oxygen and to provide holes to reside at oxygen vacancy site and thus to stabilize the unpaired electron on a Si atom.

The above model of E' center generation suggests that the profile of ion-beam-induced E' centers is deeper than the profile of neutral-beam-induced E' centers. This should be because the ion-beam-induced E' centers are created by the carriers which can diffuse in SiO_2 film. This agrees with the results in Fig. 3. The saturation of Ne^0-beam-induced E' center density is probably due to the competition between the generation of E' centers in SiO_2 film and the etching of SiO_2 film by physical sputtering. On the other hand, the Ne^+-beam-induced E' center density shows no saturation. This indicates that the generation region of Ne^+-beam-induced E' centers is deeper than the estimated depth of sputtering, 1–5 nm.

The high yield of E' center generation in the case of the He^0 beam is also explained by this suggestion. The sputtering yield for He atoms is much smaller than that for heavier projectiles. The E' center induced by the He^0 beam can remain in the SiO_2 surface layer without being etched off.

§5. Conclusions

Radiation damage in SiO_2 film irradiated with rare-gas ion and neutral beams has been studied by ESR measurements. Following results were obtained:

(1) The E' center generation yield is much larger for ion bombardment than for neutral bombardment.

(2) The E' centers both for ion and neutral bombardments are generated in the SiO_2 layer within a depth of 10 nm.

(3) The E' center generation yield induced by ion bombardment is larger for lighter atoms, i.e., for He and Ne than for heavier atoms, i.e., Ar and Xe. This means that the E' center generation yield for ion bombardment depends on the ionization energy of the parent atoms as well as on the incident energy.

(4) The E' center generation yield for neutral bombardment depends only on the incident energy.

(5) These results indicate that neutral-beam-induced E' centers are generated by bond breaking due to a collision cascade. On the other hand, ion-beam-induced E' centers are generated by both this bond breaking and carriers induced in the SiO_2 film by ion neutralization.

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