Investigation of Swift Heavy I-ion Irradiation Effects on Damage in Silicon Dioxide Thin Film

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ABSTRACT

Silicon dioxide (SiO_2) is a next-generation dielectric material for semiconductor processing. In particular, a thin film of amorphous-SiO_2 (a-SiO_2) on silicon wafers has many technological applications in microelectronics. However, a-SiO_2/Si structures can be severely degraded in the presence of radiation, due to the formation of defects in SiO_2 and its interface. In this study, we investigated the irradiation-induced defects of SiO_2 by swift I-ions. Thermally a-SiO_2 film was grown on Si wafer and subsequently irradiated with swift I-ions at energies of 10, 20 and 30 MeV at low or high fluences and at room or high temperatures. The effects of the irradiation were investigated following the changing of the infrared transmittance properties of the samples. From the measurements, we concluded that the energy, fluence and substrate temperature during irradiation greatly affected defects in the film. The electronic energy loss mechanism of the tens-MeV I-ion irradiation of a-SiO_2/Si structure plays a major role in the structure destruction.

Keywords: Silicon dioxide, Thin film, Ion irradiation, Swift heavy ions, Infrared spectroscopy

INTRODUCTION

A thin film of amorphous SiO_2 (a-SiO_2) on silicon wafers has many technological applications, especially in fabricating semiconductor devices. These applications include (Van Ommen, 1988) passivating the silicon surface for preventing uncontrolled potential fluctuations; acting as a diffusion barrier against the diffusion of impurities; acting as an insulating film between the metalization pattern, interconnecting devices and silicon substrate; and acting as a dielectric, insulating the gate from the substrate in field-effect devices. The effects of radiation on SiO_2/Si structures have been studied for many years. This steady interest reflects the importance of their practical applications. For example, Si integrated circuits

can be severely degraded in the presence of nuclear radiation due to formation of defects in SiO_2 and its interface (Ma and Dressendorfer. 1989). Several studies have investigated the defects induced by γ- and x-rays, electron or proton irradiation of SiO_2/Si structures (Mclean, 1980; Antonini et al., 1982).

With ion irradiation, low-energy (E < 1 MeV/u) incident particles mainly transfer their kinetic energies to the target nuclei (nuclear stopping). The primary elastic knock-on collisions produce cascades of secondary atomic displacements, resulting in the creation of vacancy-interstitial pairs. In the high-energy range (E > 1 MeV/u), the incident ion collides with the target electrons and thus induces in its trail a localized high density of excited and ionized target atoms, also causing the emission of secondary electrons (electronic stopping). In most insulators, part of the energy transferred initially to the electrons is subsequently passed to the atoms, causing some anisotropic permanent damage (the so-called ion latent track). Large, high-energy accelerators dominated the early investigation of irradiation-induced defects in SiO_2. However, heavy ions with energies below 1 MeV/u may deposit a high enough energy density to create continuous latent tracks of short length or at small depth, e.g., in thin films.

Therefore, it is important from both a fundamental and application point of view to systematically study radiation-induced damage in thin films of SiO_2 by ions delivered from smaller accelerators. Thus, this paper investigated the effects of such ions on the radiation damage to SiO_2 thin film deposited on Si-substrate by thermal process. The experiments are limited by the investigation of irradiation-induced defects of 10 – 30 MeV iodine ions (^{127}I-ions), which have energy of about 0.08 – 0.25 MeV/u, in a-SiO_2.

MATERIALS AND METHODS

Amorphous SiO_2 films were thermally grown on (100) n-type silicon wafers of 525 μm thickness in a water vapor environment at 1050 °C. The thickness of the film was determined by the exposure time to be ~600 nm. After SiO_2 growth, the silicon wafers were cut into pieces with a size of ~1 x 1 cm^2 and subsequently treated by ion bombardment.

The samples were irradiated at the Tandem Laboratory, Uppsala University. Heavy ions were delivered by a 5-MV NEC pelletron accelerator. The absolute ion fluence was determined from the irradiation time and the beam current, which was measured using a set of three Faraday cups with 1.0 cm^2 apertures located behind the sample holder. The irradiations were performed with an electrostatically rastered beam and the Faraday cups were thus used to measure the fluence homogeneity over the scanned area of 2x2 cm^2. The samples were bombarded at normal incidence with I-ions of 10, 20 or 30 MeV. The irradiations were done at room temperature (RT) or 800 °C (HT) to fluences of $1x10^{12}$ ions/cm^2 (low fluence = LF) or $2x10^{12}$ ion/cm^2 (high fluence = HF) and at a pressure of ~10^{-6} mbar.

SRIM 2008 simulation program was used to estimate the values of nuclear $(dE/dx)_n$ and electronic stopping power $(dE/dx)_e$ and the range (R_p) of the iodine ion in the SiO_2 substrate, as summarized in Table 1. The density of SiO_2 was

given from SRIM to be that of bulk vitreous silica (ρ = 2.20 g/cm^3 (Sze, 1981)). It is clear from the table that the iodine ions passed through the film and finally stopped deep inside the silicon substrate.

Table 1. Parameters for the iodine ion irradiations: projected range (R_p), nuclear $(dE/dx)_n$ and electronic stopping power $(dE/dx)_e$ at the incident energy (E).

E (MeV)	R_p (μm)	$(dE/dx)_n$ (keV/nm)	$(dE/dx)_e$ (keV/nm)	$\frac{(dE/dx)_e}{(dE/dx)_n}$
10	3.9	0.46	2.5	5.4
20	6.3	0.28	4.7	16.8
30	8.0	0.21	6.3	30.0

Measuring infrared (IR) transmittance provides information about the vibronic and structural properties of SiO_2 film on an Si-substrate. The vibrations detected by IR spectroscopy are those that produce a change in a molecule's dipole moment (Lin-Vien et al., 1991). Due to varied properties of SiO_2 film, such as distortions in the film composition and differences in both the Si-O bond angle and the Si-O bond length, the frequency and the width of the IR absorption peak vary significantly. The information about SiO_2 film properties, therefore, can be obtained by analyzing the peak shape of the Si-O absorption mode; a narrower and stronger peak is considered here as an indicator of better crystallographic quality of SiO_2 (Ay, 2000). In this study, the IR spectra were obtained using a Perkin Elmer FT-Infrared spectrometer in the range of 200-2000 cm^{-1} with a resolution of 4 cm^{-1}.

RESULTS

In the IR spectrum of as-prepared sample, three main vibrations of SiO_2 were clearly observed as strong peaks at 457, 817 and 1095 cm^{-1}, which are ascribed to the vibrations of Si-O-Si bond rocking, O-Si-O bond bending and Si-O bond symmetric stretching modes, respectively (Bhan and Ashokan, 1992; Wolfe et al., 1999). The mode at 1095 cm^{-1} was the dominant mode observed in the IR spectra of SiO_2. This vibration has been described as a rigid sublattice mode in which oxygen atoms and silicon atoms move in opposite directions (Galeener and Lucovsky, 1976). The in-phase oxygen motion accompanied by silicon motion gives rise to the peak around 1095 cm^{-1} and the high-frequency shoulder is due to the out-of-phase oxygen motion, where there is very little associated silicon motion (Pai et al., 1986). We noticed that the three peaks of SiO_2 showed the same trend of modification upon irradiation. Therefore, only the Si-O stretching mode at the peak around 1095 cm^{-1}, as shown in Figure 1, was fully characterized and summarized in Table 2.

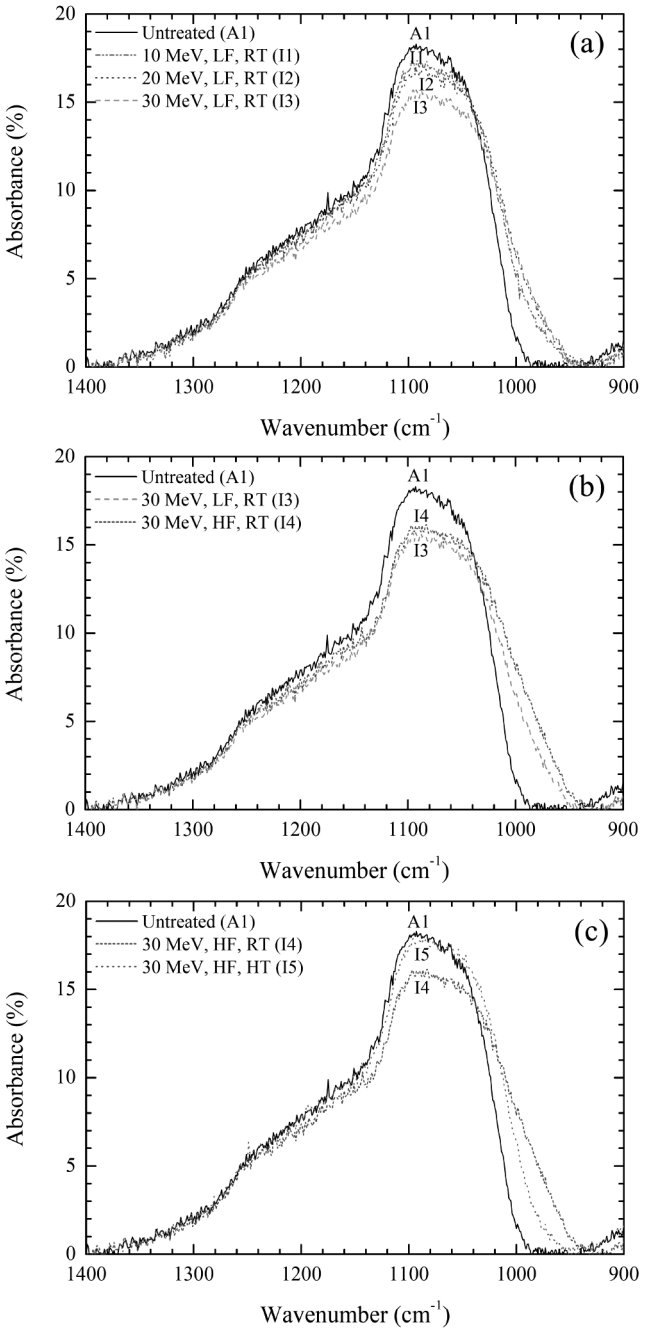

Figure 1. Deconvolution of the Si-O stretching mode of IR-spectra of all investigated samples; (a) energy dependence, (b) fluence dependence and (c) substrate temperature dependence.

Note: LF = low fluence; HF = high fluence; RT = room temperature; HT = high temperature.

Table 2. Samples details and their IR peak characteristics.

Samples	Peak characteristics			
	Position (cm^{-1})	Height (a.u.)	FWHM (cm^{-1})	Area (a.u.)
A1 *(untreated)*	1093	18.3	153	3083
I1 *(10, LF, RT)*	1097	17.4	163	3129
I2 *(20, LF, RT)*	1087	17.0	169	3158
I3 *(30, LF, RT)*	1093	15.7	176	2961
I4 *(30, HF, RT)*	1083	16.2	183	3174
I5 *(30, HF, HT)*	1083	17.9	172	3288

Note: 10, 20, 30 = ion energy in MeV; LF = low fluence; HF = high fluence; RT = room temperature; HT = high temperature.

As seen in Figure 1, energy, fluence and substrate temperature during irradiation greatly affected the damage in the film. The ion energy strongly affected the damage of SiO_2, as seen in Figure 1 (a). The peak height decreased, while the peak width increased, for increasing energy. It is very interesting that in our case, the FWHM of IR-peak was linearly dependent to the electronics stopping power $(dE/dx)_e$, as seen in Figure 2. Therefore, this finding indicated that the electronics stopping mechanism dominated the nuclear stopping mechanism for heavy ions with energies between 0.08 – 0.25 MeV/u.

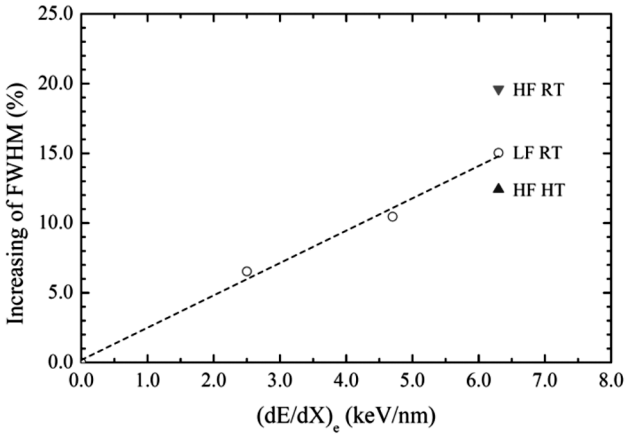

Figure 2. Increasing FWHMs after irradiation for selected Infrared bands as a function of electronic stopping power $(dE/dx)_e$. Trends are similar for all bands. The lines represent linear fits to the data.

As the energy was kept constant at 30 MeV, the irradiation fluence showed strong effects on the damage of SiO_2, as seen in Figure 1 (b). The peak height decreased, while the peak width increased, for increasing fluence. Thus, a higher fluence enhanced the destruction of Si-O bonding. This observation makes sense, as higher fluences cause heavier damage, until the damage is saturated.

In comparing irradiation temperatures, the IR peak height increased, while the IR peak width decreased, following the rise of the target temperature, as seen in Figure 1 (c). This indicates that the amount of SiO_2 increased with increasing irradiation temperature, while the quality of the structure was well preserved. It seems that oxygen is more activated by higher temperatures to form Si oxide.

DISCUSSION

Chaudhari et al. (2003) reported that when a SiO_2 matrix is irradiated with swift ions, the oxygen diffuses away from the ion tracks, leaving Si nanostructures whenever quenching of the melted zone is slower than the oxygen diffusion. The observed phenomena might originate from chemical reactions induced by high-energy ion irradiation; $SiO_2 \rightarrow Si + 2O$. The oxygen molecule will be pumped out from the samples. Carlotti et al. (2006) reported silicon bumps growth, induced by swift heavy ions at the silicon oxide-silicon interface. According to these authors' suggestions, the phase separation assists the Si bump growth at the SiO_2/Si interface, and consequently recrystallized silicon nanostructures can be generated inside the ion-irradiation damaged volume in the silicon-rich region close to the interface. The underlying silicon single crystal substrate is quickly rebuilt due to the intrinsic properties of that material: high thermal conduction and high diffusion of excited electrons. Then the structure of the silicon substrate and the near-interfacial silicon-rich oxide can provide favorable seeds for silicon nanostructure growth. Saint Martin et al. (2007) proposed that for lower-energy swift irradiation, where the track did not reach the SiO_2/Si interface, a Si local concentration increased into the track-damaged material region, associated with oxygen diffusion away from the ion track. Discontinuous silicon nanostructures may be growing inside SiO_2 tracks even for distances far away from the favorable site at the SiO_2/Si interface. This nanostructure should be responsible for the modification of the IR-peak characteristics in our experiments.

When an energetic ion enters a solid, it loses energy by two processes: (i) by elastic or nuclear collisions with the matrix atoms, causing direct atom displacements and disorder and (ii) by inelastic or electronic processes in which the electrons of the solid are excited (Dearnaley et al., 1973). In semiconductors, only elastic collisions usually generate lattice damage, whereas in insulators, both processes can induce atomic displacements (Kelly, 1981). The collisional or direct displacement processes that occur during the collision cascade take place in a very short time. After that, the cascade is quenched and, if the resulting discrete defects are immobile and stable, disorder will be preserved. However, if defects, such as vacancies and interstitials, are mobile at the implantation temperature, then significant dynamic annealing and annihilation of damage can occur during implantation (Williams, 1986).

Oxidation can be achieved by annealing in dry oxygen at 800 °C (Ourmazd et al., 1988). Besides, Yano et al. (2007) demonstrated that the damage of neutron irradiated crystalline and non-crystalline SiO_2 was 80-90 % recovered by subsequent annealing at a temperature of about 800 °C. They believed that

the irradiation-induced thermal spike was responsible for the effects. Some parts of the spike regions were rapidly quenched, leaving a slightly denser and more disordered state than the original glass state. After annealing, dense and disordered portions were relaxed into an ordinary state and restored to the same state as the non-irradiated one. Moreover, Arnoldbik et al. (2004) proposed the following model for the behavior of O in SiO_2 under ~MeV/u. heavy ion irradiation: O_2 molecules are produced in and/or along the ion track in the SiO_2 film, via bond breaking and recombination, presumably by energetic electrons that are produced as a result of the passage of the ions. These molecules are considered volatile, but not inert, except in a perfect SiO_2 matrix. Therefore, only in the beginning of irradiation can O_2 escape from the entire bulk of the film. Already at a low fluence, the irradiation brings about a structural change in the oxide. This structural change and/or the removal of O may bring oxygen-trapping centers into existence, causing the process of bulk loss of oxygen to be self-limiting. Only in the surface region are O_2 molecules able to desorb from a typical depth of 5 nm. So, a typical O_2 diffusion length of about 5 nm is deduced. Therefore, we believe that in our case, most of the oxygen relieved from the irradiation sites is trapped and induced to bond back to silicon under high temperatures. This is because the pumping speed is slower than the bonding mechanism. Additionally, the residual oxygen in the vacuum chamber (even very low in quantity) is also induced to oxide the silicon surface at this temperature.

CONCLUSION

We investigated irradiation-induced defects of SiO_2 by swift I-ions. Thermally a-SiO_2 film was grown on Si wafer and was subsequently irradiated with swift I-ions at energy of 10, 20 and 30 MeV at low or high fluence and at room or high temperature. The effects of the irradiation were investigated following the changing of the infrared transmittance properties of the samples. From the measurements, we concluded that the energy, fluence and substrate temperature during irradiation greatly affect the damage in the film. The higher energy and fluence irradiations induce more dissociation of the Si oxide and leave Si nanostructure growing in the ion tracks. The high irradiation temperature plays a compensatory effect to the high energy and fluence irradiation effects, as relieved oxygen is activated to recombine silicon to form more Si oxide.

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