Spectroscopic studies of SiO$_x$ films irradiated with high energy electrons

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Abstract. The effect of 20 MeV electron irradiation on the vibrational properties of homogeneous SiO$_x$ films and SiO$_x$ films containing amorphous or crystalline Si nanoparticles is studied. Layers with $x = 1.15$ and 1.3 and two different thicknesses, 200 nm and 1000 nm, were deposited on crystalline silicon substrates and annealed at 250 ^{o}C for stabilization. No nanoparticle growth occurs at this temperature. A part of the films were annealed in an inert atmosphere at 700 ^{o}C or 1000 ^{o}C for 60 min in order to grow amorphous (a-Si) or crystalline (nc-Si) silicon nanoparticles, respectively. Samples from all types of the films were irradiated with 20 MeV electrons at close to room temperature and a fluence of 2.4×10^{14} el.cm^{-2}. The effect of the irradiation was investigated by means of Fourier Transform Infrared Absorption (FTIR) and Raman scattering spectroscopy. The FTIR results show no appreciable changes in the composition of the homogeneous SiO$_x$ films and the oxygen content in the matrix of a-Si-SiO$_x$ composite films. The electron irradiation causes an increase of the intensity of the light scattered from the pure silicon phase. The results obtained are discussed in terms of disorder decrease in the Si nanoparticles stimulated by MeV electron beam irradiation.

1. Introduction

The radiation induced changes of electrical properties of solid-state materials and devices are well-known phenomena. Such changes may cause an electronic device or system to fail and therefore during the last few decades considerable activity has taken place to explore such alterations in various types of semiconductor devices and in particular in those based on metal-oxide-silicon structures [1]. The nature of the interaction between the impinging particle and the target depends on the particle mass, charge, and kinetic energy. Target properties of importance are mass, charge, impurity and density. When electrons pass through matter, several possible processes occur, including ionization in which moving particle loses energy in small steps through interactions with the electrons in the material through which it passes. Once the particle loses enough energy, such that it no longer has sufficient energy to excite an electron, then it may lose energy by nuclear collisions. Further, creation

of X-rays from Bremsstrahlung (electron deceleration) and elastic scattering from nuclear and electronic interactions take place. The path of an electron is zigzagged i.e. it is not well defined and an energy of MeV is high enough for electrons to penetrate through the whole Si - SiO_2 samples and to create radiation defects (electrons and holes) in the oxide, at the Si - SiO_2 interface and in the Si wafers [2, 3]. Annealing of ion-irradiation created defects has also been observed [4].

After creating defects the intense electron beam irradiation of solid state dielectrics and semiconductors can further form nanoclusters. The interest in formation of such nanosized particles in silicon oxide films is conditioned by the prospect of development of new functional materials and devices suitable for usage in intense radiation fields in spacecraft, medicine, nuclear power plants, etc. It has been reported that the electron beam in the transmission and scanning electron microscopes (TEMs and SEMs) can induce formation of nanostructures [5, 6]. Formation of Si nanocrystals (NCs) in a SiO_2 thin film matrix at 560 ^{o}C by irradiation of a high intensity convergent electron beam in an ultrahigh vacuum field emission transmission electron microscope using acceleration voltage of 100 kV has been reported in [7]. For Ge it was demonstrated that nanocluster formation occurs at room temperature under irradiation with 400 kV electrons and a fluence higher than 3.75×10^{22} el.cm^{-2}. [8]. The authors have also demonstrated that ripening takes place at temperatures far below the activation threshold of the corresponding thermal process, which is about 1000 K. Phase separation in SiO_x films [9] as well as defect production and annealing in high energy ion-irradiated Si nanocrystals [10] have also been investigated under irradiation with high-energy (50 MeV) ion beams. To the best of our knowledge, the information on the effect of MeV electrons on the lattice structure of Si nanoparticles (crystallization/amorphization, level of disorder) is exiguous.

In this work SiOx films with x = 1.15 and 1.3 were deposited on crystalline silicon substrates and then annealed at high temperatures to prepare composite films containing amorphous or crystalline Si nanoparticles in a SiOy matrix; y = 1.8 - 1.9 or 2, respectively. Both types of films were irradiated with 20 MeV electrons in vacuum and the effect of the film irradiation on the vibrational properties of the film matrix and Si nanoparticles was investigated by means of Fourier Transform Infrared (FTIR) absorption and Raman scattering spectroscopy, respectively. The obtained results are discussed in terms of MeV electron beam stimulated ordering of the Si nanoparticles.

2. Experimental details

SiOx layers with an initial composition of x = 1.15 and 1.3 and thickness of 200 and 1000 nm were prepared by thermal evaporation of SiO at a vacuum of $1 \times 10{-3}$ Pa on p-type (100) c-Si substrates ((7.2 – 10) Ω×cm) maintained at room temperature. The film composition has been set by the applied preparation conditions and proven by means of Rutherford Back Scattering [11]. The SiO evaporation was carried out from a tantalum crucible situated at the base of a molybdenum cylindrical screen [11]. The film thickness and deposition rate were monitored by a calibrated quartz microbalance system. Prior to film deposition the silicon wafers were cleaned chemically using a standard procedure for the microelectronics industry. All as-deposited layers were annealed at 250 oC for 30 min in an Ar atmosphere to keep them stable at room conditions. No formation of pure silicon phase occurs during this annealing procedure [11]. In order to grow Si nanoparticles an additional furnace annealing at 700 ^{o}C in Ar or 1000 ^{o}C in N_2 atmosphere for 60 min was carried out. Previous high resolution electron microscopy and Raman scattering measurements have shown the formation of amorphous silicon (a-Si) nanoparticles in films annealed at 700 ^{o}C and Si nanocrystals (nc-Si) in films annealed at 1000 ^{o}C [12, 13].

Both homogeneous SiO_x and composite films (a(nc)-Si-SiOx) containing nanosized amorphous or crystalline particles were irradiated with 20 MeV electrons at approximately 30 ^{o}C. Electron irradiation with a fluence of 2.4×10^{14} el.cm^{-2} was carried out in Microtron MT-25 in FLNR, Joint Institute for Nuclear Research, Dubna. No significant temperature increase was observed during irradiation.

The Raman scattering measurements of non-irradiated and electron irradiated films were performed in the backscattering geometry at room temperature in the air using a TriVista T557 triple

spectrometer with a 900∕900∕1800 grooves∕mm gratings combination. The spectrometer was equipped with a confocal microscope and a nitrogen-cooled charge coupled device detector. Two lines of a mixed Ar^+/Kr^+ gas laser with wavelengths of 514.5 or 488 nm and output power of about 50 mW were used for excitation. Fourier Transform infrared Transmission (FTIR) spectra of the films were measured using a Perkin Elmer Spectrum One FTIR spectrometer in transmission mode in the $450 - 4000$ cm^{-1} range with a resolution of 2 cm^{-1}.

3. Results and Discussion

Experimental FTIR spectra of non-irradiated and 20 MeV electron irradiated 200 and 1000 nm thick SiO_x films with $x = 1.3$ annealed at 250 ^oC (not containing Si nanoparticles) are shown in figure 1. The stretching vibration band of the 1000 nm films is significantly broader than that of the 200 nm ones which is most likely due to some compositional variations in the film depth. Similar IR spectra were recorded from the $x = 1.15$ films. It is known that the main band in the IR spectra of SiO_2 is observed at ~ 1080 cm^{-1}. It is due to an asymmetric stretching vibration of the Si–O–Si bridge and consists of one transverse optical (TO) mode at 1080 cm^{-1} and others longitudinal optical (LO) modes in the range 1200 - 1300 cm^{-1} [14, 15]. With a decrease of the oxygen content ($x < 2$) the position of the peak is shifted to lower frequencies ('red' shift) with respect to silica, the characteristic LO shoulder at the high-frequency side of the band disappears and the full-width at half maximum (FWHM) of the band increases. The band position (~ 1014 cm^{-1}) seen in figure 1 is in good agreement with our previous results for $x = 1.3$ films [11]. No significant electron beam induced alterations in the band position and shape are observed which indicates that the film composition has not been changed upon the applied electron irradiation of $2.4×10^{14}$ el.cm^{-2}. Hence based on the IR transmission data one can conclude that though the energy of irradiating electrons is rather high no appreciable electron beam induced phase separation occurs in the homogeneous SiO_x films. This observation differs from the result reported in [9] showing that it takes a fluence of about 10^{14} ions.cm^{-2} 50 MeV Cu ions to obtain a Si-O-Si infrared absorption spectrum characteristic for a $Si-SiO_2$ composite film structure. Rather, our result is in line with the data of other authors for keV electrons in TEMs showing that high electron fluencies and an increased film temperature (above 500 ^oC) are required during irradiation [7, 8] to cause phase separation in Si-rich silicon oxide films and formation of pure silicon phase.

Figure 2 shows IR transmission spectra of a homogeneous x = 1.3 film annealed at 250 ^oC and a pair of non-irradiated and 20 MeV electron irradiated composite films with the same initial composition containing a-Si nanoparticles. The film thickness is 200 nm. As expected [11] the furnace annealing at 700 ^oC causes both a "blue" shift of the stretching vibrational band from ~ 1014 cm^{-1} to ~ 1060 cm^{-1} and a FWHM decrease; the shoulder at ~ 1200 cm^{-1} is also better seen. This indicates an increase in the oxygen content of the matrix due to formation of pure silicon phase but the oxygen content in the matrix is still below the stoichiometric proportion. No appreciable changes in the band position and FWHM related to the electron irradiation are observed in figure 2. The $x = 1.15$ films showed the same behavior thus implying that the electron irradiation does not cause further phase separation in the composite films and does not create a high defect density in the matrix which should result in FWHM increase.

The described IR transmission data give information mainly about the composition and the lattice disorder in the silicon oxide films but they do not provide information about the relatively small amount of pure silicon phase formed due to phase separation in SiO_x films. Raman spectroscopy can provide a fast and nondestructive method to detect the existence of silicon phase and to determine whether silicon particles are amorphous or crystalline [16, 17]. The ''finite size effects,'' which destroy the full translation symmetry of a crystalline material, result in a "red shift" and low-frequency asymmetric broadening of the most intensive silicon Raman band at about 520 cm^{-1} [18].

All experimental Raman spectra presented in this paper have been normalized with respect to the band located between 930 and 1030 cm^{-1} after subtraction of a linear baseline. This band was assigned to multi-phonon scattering coming from the c-Si silicon substrate [19, 20] and it was assumed that its intensity had almost the same value for the films with a given thickness and composition (which
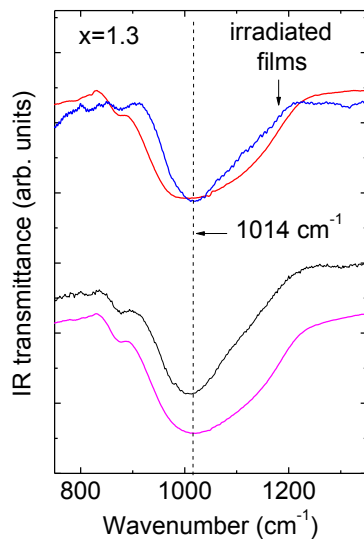
Figure 1. IR transmission spectra of pairs of 200 nm (the spectra with narrower band) and 1000 nm thick SiO$_x$ films with $x = 1.3$. All films were annealed at 250 ^{o}C for 30 min in argon and a film from each pair was then irradiated with 20 MeV electrons.
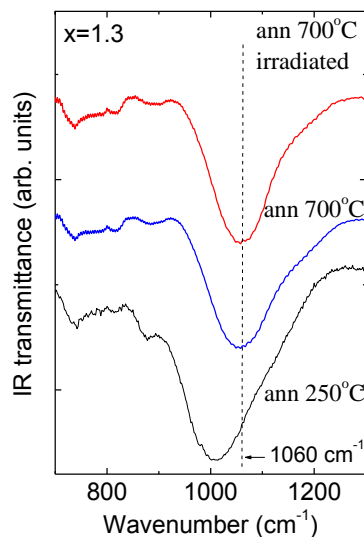

Figure 2. IR transmission spectra of a homogeneous $x = 1.3$ film and a pair of non-irradiated and 20 MeV electron irradiated composite films with the same initial composition but furnace annealed at 700 ^{o}C for 60 min and containing a-Si nanoparticles.

determine the exciting light absorption). Normalized Raman spectra of three non-irradiated 200 nm thick films with $x = 1.3$ annealed at different temperatures are shown in figure 3 on an enlarged scale applied to reveal better the low intense features in the spectra. The inset in figure 3 depicts the same spectra in a scale in which only a very strong band situated at ~ 521 cm^{-1} is well seen; this band can be assigned to Raman scattering from 1TO phonons of the c-Si substrate. A low intensity feature at around 300 cm^{-1} also can be ascribed to the substrate, whereas the weak band at ~ 430 cm^{-1} can be related [21] to scattering in amorphous SiO$_2$. It is seen from figure 3 that only bands originating from the crystalline Si substrate are well resolved in the spectrum of the homogeneous SiO$_x$ film annealed at 250 ^{o}C. In the spectrum of the film annealed at 700 ^{o}C two additional broad bands, centered at ~ 150 cm^{-1} and 480 cm^{-1} are observed. These bands are typical for a-Si [16, 17] and indicate existence of amorphous silicon phase in the film. A weak asymmetry at the low frequencies side of the c-Si band at ~ 521 cm^{-1} is observed in the spectrum of the film annealed at 1000 ^{o}C. It can be related to the presence of Si NCs whose formation has been proven by TEM investigations [12, 13].

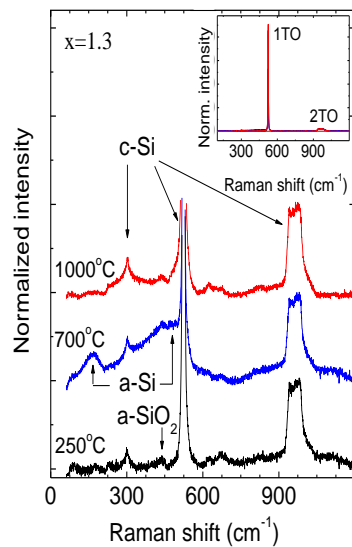Figure 4 depicts normalized Raman spectra of three pairs of $x = 1.3$ non-irradiated and MeV

Figure 3. Normalized Raman spectra of three non-irradiated $x = 1.3$ films annealed at different temperatures denoted in the figure. The spectra of the films annealed at 700 ^{o}C and 1000 ^{o}C are vertically shifted for clarity. Inset: The same spectra shown in a 10 times compressed scale.

electron irradiated films annealed at the temperature denoted in the corresponding figure (a), (b) and (c). It is seen that the electron irradiation did not cause appreciable changes in the Raman spectrum of the homogeneous film annealed at 250 ^{o}C (figure 4 (a)), i.e. no bands due to scattering from pure Si phase in the SiO_x film appeared. This observation is in agreement with the FTIR result (figure 1) and confirms that there was no electron induced phase separation in homogeneous films. However the irradiation of the composite film annealed at 700 ^{o}C (figure 4 (b)), containing amorphous silicon phase, has caused an increase of the light scattering from this phase. Namely, the intensity of the band at ∼ 480 cm^{-1} is significantly higher than the intensity of the multiphonon scattering from the c-Si substrate in the Raman spectrum of the electron irradiated sample. Figure 5 shows normalized Raman spectra of three MeV electron irradiated $x = 1.15$ films annealed at different temperatures. Again, no new features in the 250 ^{o}C spectrum are seen whereas the intensity of the band at ∼ 480 cm^{-1} is significantly higher than the intensity of the c-Si multiphonon scattering band in the 700°C spectrum. In the Raman spectra of the films annealed at 1000 ^{o}C (figure 4 (c) and figure 5) for both compositions the asymmetry of the 521 cm^{-1} c-Si band at the low frequencies side is better distinguished after MeV electron irradiation.

Our previous studies [11] as well as the results in figure 2 have shown that the phase separation process in the films annealed at 700 ^{o}C is not completed and a-Si nanoparticles in a SiO_y ($y < 2$) matrix are formed. The observed electron irradiation increase of the scattering from the a-Si phase could be ascribed to an increase of its amount upon irradiation. Should this be the case an increase of the oxygen content y in the SiO_y matrix would take place, which was not observed. In fact the IR transmission (figure 2) as well as the Raman scattering spectra (figures 4 and 5) of the homogeneous films from both compositions have not given indications for electron induced phase separation. No appreciable change in the matrix oxygen content and appearance of Raman bands characteristic for a-Si have been observed. Therefore we suppose that the applied electron irradiation does not cause formation of Si nanoclusters. Our previous investigations have shown silicon nanoparticle formation in Si-SiO_2 structures upon 20 MeV electron irradiation and a fluence of 1.2×10^{15} el.cm^{-2} [2, 22]. Perhaps the lack of nanoparticle formation in this study is due to the relative low irradiation dose (2.4×10^{14} el.cm^{-2}) applied; maybe it is less than a required critical dose and experiments with higher doses are planned.

The furnace annealing at 1000 ^{o}C causes a complete phase separation in SiO_x films (and formation of Si NCs in a SiO_2 matrix) and no electron stimulated phase separation is expected in such films. The observed low frequency asymmetry increase of the 1TO c-Si band in the electron irradiated films with
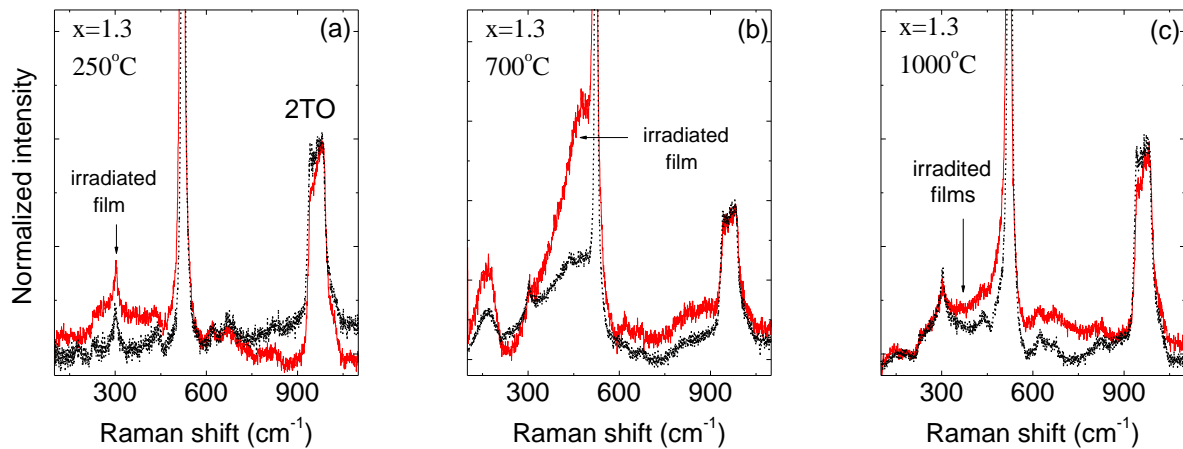
Figure 4. Normalized Raman spectra of three pairs of $x = 1.3$ films. Each pair was annealed at the temperature denoted in the corresponding figure and then a sample of each pair was 20 MeV electron irradiated.
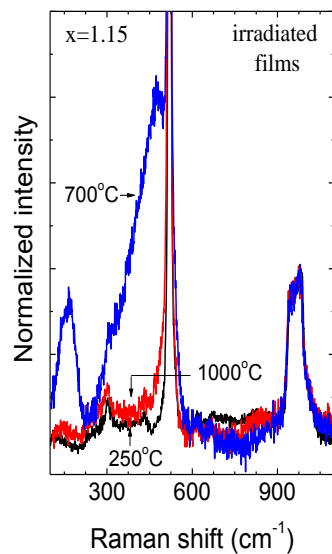

Figure 5. Normalized Raman spectra of three 20 MeV electron irradiated $x = 1.15$ films annealed at different temperatures denoted in the figure.

Si NCs and the a-Si Raman bands increase give us basis to assume that the electron irradiation reduces the structural disorder in the both types of nanoparticles. This could happen: (i) if an electron induced annealing takes place or (ii) due to a nanoparticle size increase caused by electron stimulated Ostwald ripening (small particles dissolve and redeposit onto larger particles).

The radiation effect on the nanoparticle crystallinity is an important point. The results on irradiation with electrons having energy < 1 MeV speak about rather weak effects. Very high fluencies (400 keV electrons of up to 1.7×10^{24} el.cm^{-2}) were required to amorphize 5 nm Si NCs [23]. Crystallization of Ge nanoclusters in a SiO_2 matrix has been observed under irradiation with 400 keV electrons at room temperature and a fluence above 4×10^4 C.cm^{-2} (2.5×10^{23} el.cm^{-2}) but ripening has been observed at temperatures far below the activation threshold of the corresponding thermal process, which is about 730 ^{o}C [8]. It has been suggested that the Ge diffusion in SiO_2 necessary for the cluster formation is a secondary process and that it is induced by the displacement of O and Si atoms due to electron nucleus collision [8]. However, it has been observed that the irradiation of Si-SiO_2 samples with high energy electrons (> 10 MeV) caused radiation assisted annealing at relative low dose (3×10^{16}

el.cm^{-2}) [2, 4]. This observation implies that the irradiation with > 10 MeV electrons at room temperature stimulates processes that normally occur in the Si-SiO$_2$ structures at high temperature (> 800 ^{o}C). Although the detailed mechanism is still unclear this result gives some support to the above assumption for electron stimulated annealing. Nevertheless, at this stage we cannot distinguish between the electrons induced nanoparticle annealing and Ostwald ripening process. High resolution TEM investigations on 1000 ^{o}C annealed films are planned whose results can favor one of the assumptions.

4. Conclusions

Homogeneous SiO$_x$ films with $x = 1.15$ and 1.3 as well as composite films containing amorphous or crystalline Si nanoparticles in a SiO$_y$ matrix ($y = 1.8 - 2$) were irradiated at room temperature with 20 MeV electrons and a fluence of 2.4×10^{14} el.cm^{-2}. The Fourier transform infrared absorption data have shown that no appreciable electron induced changes in the composition of both the homogeneous films and the oxide matrix of the composite films occurred thus indicating that no phase separation was initiated by the electron irradiation. It has been concluded that the applied electron irradiation does not cause formation of Si nanoclusters in the films studied; higher fluences are required.

A significant increase of the Raman scattering from the pure silicon phase has been seen in the films containing amorphous Si nanoparticles. In the electron irradiated films with Si NCs the low frequency asymmetry of the 1TO c-Si Raman band, caused by the finite size effect in NCs, also increased. The observed intensity increase has been related to disorder decrease in the Si nanoparticles stimulated by the MeV electron irradiation. It has been assumed that either an annealing or a nanoparticle size increase caused by Ostwald ripening take place during electron irradiation.

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