Photoluminescence from 20 MeV electron beam irradiated homogeneous SiO\(_x\) and composite Si-SiO\(_x\) films

D Nesheva\(^1\), M Šćepanović\(^2\), M Grujić-Brojčin\(^2\), V Dzhurkov\(^4\), S Kaschieva\(^1\), I Bineva\(^1\), S N Dmitriev\(^3\) and Z V Popović\(^2\)

\(^1\) Institute of Solid State Physics, Bulgarian Academy of Sciences, 72 Tzarigradsko Chaussee Blvd, 1784 Sofia, Bulgaria
\(^2\) Center for Solid State Physics and New Materials, Institute of Physics, University of Belgrade, Pregrevica 118, Belgrade 11080, Serbia
\(^3\) Joint Institute for Nuclear Research, Flerov Laboratory of Nuclear Reactions, Dubna, Moskow region 141980, Russia

E-mail: nesheva@issp.bas.bg

Abstract. The effect of 20 MeV electron irradiation on the room temperature photoluminescence from homogeneous SiO\(_x\) and composite Si-SiO\(_x\) films, containing amorphous or crystalline Si nanoparticles, is studied. Layers with \(x = 1.5\) and \(1.7\) and thickness of 200 nm were deposited on crystalline silicon substrates by thermal evaporation of SiO in vacuum. Film annealing in an inert atmosphere at 700 °C or 1000 °C for 60 min was applied to grow amorphous or crystalline silicon nanoparticles, respectively, in a SiO\(_x\) matrix. Samples from all types of films were irradiated with 20 MeV electrons at close to room temperature and a fluence of \(2.4 \times 10^{14}\) e.l.cm\(^{-2}\). Photoluminescence was measured under excitation with the 488 nm line of an Ar\(^+\) laser. The electron irradiation causes a decrease of the integrated photoluminescence intensity in composite samples with initial \(x = 1.7\) samples with Si nanocrystals. The electron irradiation of \(x = 1.5\) samples with amorphous nanoparticles slightly increases the photoluminescence intensity. The obtained results are discussed in terms of electron beam induced phase separation and Si nanoparticle size increase.

1. Introduction
Electron irradiation of solids creates defects and may cause an electronic device or system to fail. It may also cause formation of amorphous or crystalline nanosized domains by decomposition of the target material [1,2]. Therefore during the last few decades there was significant activity to explore the influence of electron irradiation on various types of semiconductor devices, in particular in metal-oxide-silicon (MOS) structures [3,4].

Photoluminescence (PL) spectroscopy has been successfully used to obtain important information about changes in the defect structure upon electron irradiation of light emitting materials [5-7]. For example, the observation that the PL intensity of irradiated TiO\(_2\) nanocrystals was much larger as compared to the PL from non-irradiated samples, has been attributed to irradiation induced defects and particle size variation [7]. Photoluminescence, Hall and X-ray photoelectron spectroscopy measurements carried out on 0.8 MeV electron beam irradiated indium-gallium-zinc oxide films have allowed to conclude that n-type conductivity was preserved in films irradiated with a low dose up to \(10^{14}\) electrons/cm\(^2\) while the conductivity was converted to p-type with further dose increase [5].
These observations were attributed to strong reduction of donor-like oxygen vacancy defects as a result of formation of either oxygen interstitial or zinc vacancy acceptor defects.

Due to the modification of the energy structure afforded by charge carrier confinement, silicon nanocrystals are good candidates for photonic applications involving efficient radiation recombination. The emission from silicon nanocrystals has characteristic features: PL intensity increases and shows a “blue-shift” with decreasing crystallite size. Photoluminescence spectroscopy has been applied in a study of silicon nanocrystals’ growth in amorphous silicon films by assistance of a 200 keV electron beam. Various localized states’ emission was measured [8,9]. It has been

Electron irradiation is most frequently carried out in high voltage transmission electron microscopes with electrons having energy of around or less than 1 MeV [10-12] but the information on the effect of high energy electrons (> 10 MeV) on the processes of the nanoparticle growth in silicon oxide matrices is very limited [1]. Our previous Raman scattering investigations of 20 MeV electron irradiation effects on homogeneous SiOₓ films (initial x = 1.3) and composite Si-SiOₓ films (x = 1.8), containing amorphous silicon nanoparticles, have indicated appearance of amorphous silicon phase and some structural changes in the oxide matrix of the homogeneous SiOₓ films. An electron beam stimulated decrease of the defects at the a-Si/SiOₓ interface in the composite films has been assumed, as well [13].

In this work, the effect of 20 MeV electron irradiation (with a fluence of 2.4×10¹⁴ el⋅cm⁻²) on homogeneous SiOₓ and composite films, containing amorphous/crystalline silicon nanoparticles (a/cSi NPs, a/cSi-SiOₓ composite films), is studied by photoluminescence spectroscopy and Raman scattering measurements. Layers with initial x = 1.5 and 1.7 deposited on crystalline silicon substrate are investigated since they show much stronger photoluminescence at room temperature than the previously studied films with initial x = 1.3. The obtained results are discussed in terms of electron beam stimulation of phase separation and changes in the Si nanoparticle size.

2. Experimental details

Silicon suboxide SiOₓ layers with an initial composition of x = 1.5 and 1.7 and thickness of 200 nm were prepared by thermal evaporation of SiO at a vacuum of 1×10⁻³ Pa on p- or n-type (100) crystalline silicon (c-Si) substrates ((7.2-10) and (4-6) Ω⋅cm for p or n-type Si, respectively) maintained at room temperature [14]. Prior to film deposition the silicon wafers were cleaned chemically using a standard procedure for the microelectronics industry. The deposition rate and film thickness were monitored by a calibrated quartz microbalance system. All as-deposited layers were annealed at 250 °C for 30 min in an Ar atmosphere to keep them stable at ambient conditions. This annealing procedure does not lead to formation of pure silicon phase [14]. In a part of the SiOₓ samples amorphous/crystalline Si nanoparticles were grown in a SiOₓ matrix with x = 1.9, 2.0 (for films with initial x = 1.5, 1.7, respectively [16]) by an additional furnace annealing at 700 / 1000 °C in an argon atmosphere for 60 min [14,15].

Both kinds of films (homogeneous SiOₓ films and composite a/cSi-SiOₓ films) were irradiated with 20 MeV electrons with a fluence of 2.4×10¹⁴ el⋅cm⁻². The irradiation was carried out in Microtron MT-25 in FLNR, Joint Institute for Nuclear Research, Dubna. The beam current was Iₑ ≈ 5 µA. The sample temperature was controlled during the entire irradiation process and kept close to room temperature.

Photoluminescence measurements were carried out using the 488-nm line of an Ar⁺ laser, Jobin–Yvon U1000 double monochromator and a photomultiplier as detector. Micro-Raman scattering measurements were performed in the backscattering geometry by a Jobin-Yvon T64000 triple spectrometer system, equipped with a confocal microscope and a nitrogen-cooled CCD detector. Raman spectra were collected by using Verdi™ G-Series Optically Pumped Semiconductor Laser operating at 532 ± 2 nm. Both PL and Raman scattering measurements were performed at room temperature in air.

3. Results and Discussion
Raman scattering measurements were carried out to get information about the pure silicon phase in the different kind of samples. The spectra collected on non-irradiated and irradiated homogeneous SiO_x (initial x = 1.7) and the corresponding composite a/c-Si-SiO_x films are shown in figure 1. In all spectra the strong band situated at ~ 521 cm^{-1} is due to Raman scattering from 1TO phonons of the c-Si substrate. The low intensity feature at around 300 cm^{-1} (well seen in figure 1(a)) is also due to light scattering from the c-Si substrate. The weak band at ~ 430 cm^{-1} is normally related to scattering in amorphous SiO_x [17]. The wide band located between 930 and 1030 cm^{-1} is assigned to multi-phonon scattering in the c-Si substrate [18,19].

![Figure 1](image_url)

Figure 1. Raman spectra of non-irradiated and 20 MeV electron beam irradiated samples with initial x = 1.7: (a) – homogeneous SiO_x film, (b) - aSi-SiO_x composite film containing amorphous Si NPs and (c) - cSi-SiO_2 composite film containing crystalline Si NPs; in (a) and (c) the spectra of non-irradiated and irradiated samples practically coincide while in (b) they have significantly different PL background. Each pair of spectra corresponds to the same y-scale but the y-scale in (a) is 40 times enlarged when compared with the y-scale in (b) and (c) to ensure better presentation of the bands observed in the Raman spectrum.

The Raman spectra of the composite films shown in figure 1(b) and (c) are strongly up-shifted with respect to the spectra of homogeneous ones (figure 1(a)) due to presence of photoluminescence background [15]. It should be noted that the Raman spectra obtained for the samples with initial x = 1.5 are very similar to those from figure 1, but with less intense background. Unfortunately the PL background makes difficult to draw reliable conclusions about the pure silicon phase, but it indicated that the photoluminescence spectroscopy could be applied to investigate the effect of high energy electron beam irradiation.

Photoluminescence spectra of non-irradiated and 20 MeV electron beam irradiated homogeneous and composite films with initial x = 1.7 and x = 1.5 are shown in figure 2 and figure 3, respectively. The maximum PL intensity from the x = 1.5 samples is more than three times lower than the intensity from the corresponding films with x = 1.7 and the PL from non-irradiated and irradiated homogeneous x = 1.5 samples is negligible. The electron beam irradiation causes some increase of the integrated PL intensity from homogeneous x = 1.7 film (figure 2(a)), whereas a decrease of the integrated PL intensity is observed for the aSi-SiO_x (figure 2(b)) and a/cSi-SiO (figure 2(c))
Figure 2. Photoluminescence spectra of non-irradiated and 20 MeV electron beam irradiated samples with initial $x = 1.7$: (a) - homogeneous SiO$_x$ films, (b) - aSi-SiO$_x$ composite films containing amorphous Si NPs and (c) - cSi-SiO$_2$ composite films containing crystalline Si NPs. Each pair of spectra corresponds to the same y-scale but the y-scale in (a) is 4 times enlarged when compared with the same y-scale in (b) and (c) in order to ensure better presentation of the PL bands.

Figure 3. Photoluminescence spectra of non-irradiated and 20 MeV electron beam irradiated samples with initial $x = 1.5$: (a) - aSi-SiO$_x$ composite films containing amorphous Si NPs and (b) - cSi-SiO$_2$ composite films containing crystalline Si NPs. All spectra correspond to the same y-scale.
composite films, being stronger for the films with crystalline Si nanoparticles. In the $x = 1.5$ samples the electron beam induced changes are weak; in the samples with aSi NPs the electron irradiation causes slight PL intensity increase (figure 3(a)), whereas the spectra of non-irradiated and irradiated cSi-SiO$_2$ composite films with nanocrystals are quite similar (figure 3(b)).

Our previous investigations on non-irradiated samples have shown [15,20] that when exciting with the 488 nm line, the PL spectrum consists of two bands: a band related to radiative recombination via defects in the oxide or at the Si/SiO$_2$ interface (band 1 peaked in the range 2.2-2.3 eV) and a second band related to radiative recombination of electrons and holes localized in Si nanoparticles (band 2). Normally band 1 is related to radiative recombination in non-bridging oxygen hole center (NBOHC, PL centered at ~2 eV) and/or positively charged oxygen vacancy (E' center, PL centered at ~ 2.3 eV) [21,22]. For the aSi-SiO$_2$ films band 2 (i.e. PL from Si NPs) has maximum in the ‘orange-red’ spectral range which moves from ~ 2.1 to ~ 1.7 eV [15, 20] with changing NP size while for the cSi-SiO$_2$ the band 2 maximum moves from ~ 2.0 to ~ 1.6 eV [15]. It has been shown that the intensity of PL from Si NPs strongly decreases with increasing nanoparticle size [15,20]. Keeping in mind all those results, the PL spectra of both non-irradiated and electron irradiated samples have been deconvoluted into two Gaussian bands and the results obtained for the composite films with initial $x = 1.7$ are shown in figure 4. As seen from the figure, in both types of composite films the intensity of the PL from NPs (the band at ~ 2.15 eV (compare figure 4(a) and (b)) and the band at ~ 2.0 eV (compare figure 4(c) and (d)) decreases upon electron irradiation. The result is similar for the cSi-SiO$_2$ $x = 1.5$ films (figure 3(b)). Only in the aSi-SiO$_2$ films a slight increase of the band 2 intensity is observed (figure 3(a)).

The electron beam irradiation could cause: (i) phase separation or rearrangement of the defect structure in the homogeneous films; (ii) further phase separation in aSi-SiO$_2$ composite films with keeping NP size constant and only increasing the amount of the pure aSi phase; (iii) NP size increase in composite films which results in an intensity decrease and some red shift; (iv) improvement of the interface between the nanoparticles and oxide matrix, as assumed in Ref. [13]. The mechanism (ii) is not expected in composite films with cSi NPs since a complete phase separation takes place upon 60 min annealing at 1000°C [14]. The mechanisms (ii) and (iv) should cause a PL intensity increase. Hence in all films with the irradiation induced PL intensity reduction most likely the electron beam irradiation causes some nanoparticle size increase (mechanism (iii)). This could be easy understood since the matrix composition in all those films is $x ~ 2.0$ [14, 16]. Only in the aSi-SiO$_2$ films with initial $x = 1.5$, in which the oxygen matrix content is $x < 2.0$, further phase separation (mechanism (ii)) could take place and could have more pronounced effect than the effect of the nanoparticle growth, thus causing the observed slight PL intensity increase. We notice that the Raman scattering increase observed in aSi-SiO$_2$ films with initial $x = 1.3$ [13] can be also due to electron beam induced phase separation (at least partially, together with the annealing effect). Finally, the PL increase found for the $x = 1.7$ homogeneous films (figure 2 (a)) could be related to electron induced formation of few very small aSi clusters but it could be also due to some increase of the NBOHC or E’ defects.

Upon electron irradiation the intensity of the PL from the oxide matrix (band 1) shows an increase in the aSi-SiO$_2$ films (figure 4 (a), (b)) and a decrease in the cSi-SiO$_2$ films (figure 4 (c), (d)). However in the $x = 1.5$ samples (the fit results are not shown) the intensity of band 1 strongly decreases in the aSi-SiO$_2$ films and does not change cSi-SiO$_2$ films. Hence, no clear tendency is observed with changing the film composition and annealing temperature. Probably both the initial composition and the annealing temperature considerably affect the density of the defects in the oxide matrix and the observed various PL intensity changes are result of a specific contribution of both effects. Because of this the band 1 behaviour was not helpful for clarifying the origin of the PL from irradiated $x = 1.7$ homogeneous films.

4. Conclusions
Homogeneous 200 nm thick SiO$_x$ films ($x = 1.5$ and 1.7) on c-Si substrate and composite a/cSi-SiO$_x$ films containing amorphous/crystalline Si nanoparticles have been irradiated with 20 MeV electrons
Figure 4. Deconvolution of the photoluminescence spectra of 20 MeV electron beam irradiated composite samples with initial $x = 1.7$: (a), (b) – non-irradiated and irradiated aSi-SiO$_x$ films, respectively, and (c), (d) - non-irradiated and irradiated cSi-SiO$_2$ films, respectively. All spectra correspond to the same y-scale.

at a fluence of $2.4 \times 10^{14}$ el.cm$^{-2}$. The results from photoluminescence measurements under excitation with the 488 nm of an Ar$^+$ laser have revealed an electron beam induced intensity increase of PL from the $x = 1.7$ homogenous samples. The PL increase has been related to appearance of small amount of aSi nanoparticles due to electron beam induced initial phase separation and/or an increase of the NBOHC/E' defect density. An increase of the PL from the $x = 1.5$ composite films containing aSi NPs has been found and ascribed to increase of the total amount of the pure aSi phase due to further phase separation stimulated by the electron beam irradiation in samples with under stoichiometric oxide matrix. The observed intensity decrease of the PL from composite films with nearly stoichiometric oxide matrix (initial $x = 1.7$ containing a/cSi NPs and composite films with initial $x = 1.5$ containing cSi NPs) has been attributed to electron beam induced increase of nanoparticle size.

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References
[1] Kaschieva S and Dmitriev S N 2010 Radiation Defects in Ion Implanted and/of High-Energy Irradiated MOS Structures (New York: Nova Science Publishers)
[2] Krasheninnikov V and Nordlund K 2010 J. Appl. Phys. 107 071301 and references therein
[3] Fourches N T and Nenoi M 2012 Current Topics in Ionizing Radiation Research 32 741 (Rijeka: InTech)
[4] Oldham T R 2003, IEEE Trans. Nuclear Sci. 50 483
[5] Jung S H, Moon H J, Ryu M K, Cho K I, Bae B S and Yun E -J 2012 Journal of Ceramic Processing Research 13 Special. 2 246
[6] Egilsson T, Henning A, Ivanov I G, Lindström J L and Janzén E 1999 Phys. Rev. B 59, 8008
[7] Priyanka K P, Sunny J, Anu T S, Jaseenthara O P and Varghese T 2012 International Journal of Emerging Technology and Advanced Engineering 2 130
[8] Huang W-Q, Liu S-R, Huang Z-M, Dong T-G, Wang G and Qin C-J 2015 Sci. Rep. 5 9932
[9] Huang W-Q, Liu S-R, Huang Z-M, Dong T-G, Wang G and Qin C-J 2015 Sci. Rep. 5 16682
[10] Takeguchi M, Tanaka M and K. Furuya 1999 Appl. Surf. Sci. 146 257
[11] Chen G S, Boothroyd C B and Humphreys C J 1998 Phil. Mag. A 78 491
[12] Du X-W, Takeguchi M, Tanaka M and Furuya K 2003 Appl. Phys. Lett. 82 1108
[13] Nesheva D, Dzhurkov V, Šćepanović M, Bineva I, Manolov E, Kaschieva S, Nedev N, Dmitriev S N and Popović Z V 2016 J. Phys.: Conf. Series 682 012012
[14] Nesheva D, Bineva I, Levi Z, Aneva Z, Merdzhanova T and Pivin J C 2003 Vacuum 68 1
[15] Nesheva D, Raptis C, Perakis A, Bineva I, Aneva Z, Levi Z, Alexandrova S and Hofmeister H 2002 J. Appl. Phys. 92 4678
[16] Donchev V, Nesheva D, Todorova D, Germanova K and Valcheva E 2012 Thin Solid Films 520 2085
[17] Rahmani A, Benoit M and Benoit C 2003 Phys. Rev. B 68 184202
[18] Temple P A and Hathaway C E 1973 Phys. Rev. B 7 3685
[19] Borowiec P, Latko M, Rzodkiewicz W, Łaszcz A, Czerwinski A and Ratajczak J 2012 Adv. Nat. Sci.: Nanosci. Nanotechnol. 3 045003
[20] Bineva I, Nesheva D, Aneva Z and Z. Levi Z 2007 126, 497
[21] Vázquez-Valerdi D E, Luna-López J A, Carrillo-López J, García-Salgado G, Benítez-Lara A and Espinosa-Torres N D 2014 Nanoscale Research Letters 9 422
[22] Lin C-J and Lin G-R 2005 IEEE J. Quantum Electronics 41 441