The electron and crystalline structure features of ion-
synthesized nanocomposite of Si nanocrystals in Al₂O₃ matrix
revealed by electron spectroscopy

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Abstract. The luminescence yield depends on structure of Si nanocrystals embedded into
Al₂O₃ matrix, matrix lattice defects, chemistry, and accommodation discordance at the
interfaces. The physical ground of this phenomenon is connected with a competition between
radiative and nonradiative transitions. The Si-NC were formed in the C-cut sapphire wafers,
and electron-gun deposited Al₂O₃ films on Si substrate by Si⁺ by ion implantation and post-
implantation annealing at 500-1100 °C. XPS depth profiling allowed revealing electron and
crystalline structure of Si⁺-implanted sapphire layers, depth distribution of Si nanocrystals,
matrix defects, accommodation stresses, and electron transitions. The presence of defects at the
Si nanocrystal/Al₂O₃ interfaces originated from the accommodation discordance leads to severe
degradation of light-emitting properties of Si nanocrystals in sapphire.

1. Introduction
Silicon nanocrystals (nc-Si) embedded in SiO₂ and other dielectrics have attracted much attention
because quantum phenomena are realized in these systems, which have potential applications in
optoelectronic and electronic devices [1, 2]. The origin of visible luminescence from the ion-beam
synthesized Si nanocrystals has not so far been clear enough, primarily due to a lack of distinction
between luminescence originating from matrix defects and luminescence originating from
nanocrystals [3]. It is well known that defects in SiO₂ display luminescence at various energies
including the visible range, so the interpretation of luminescence spectra without differentiation of the
contribution from defects can be very misleading [4]. The developments of nanocomposites on base of
Al₂O₃ matrix will allow fabricate heat- and radiation resistant semiconductor devices. However, the
great scientific problems are rising on this way. The nanocomposites should have highly stable and
well passivated interfaces. Structural defects are the sources of both radiative and nonradiative
electronic transitions which can enhance or weaken the luminescence.

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The investigation of structure, electronic and luminescent properties of Si nanocrystals embedded in Al₂O₃ allow to clear a fundamental question about amplification or quenching of luminescence under influence of defects.

2. Experimental details
Si nanocrystals were fabricated in C-cut sapphire wafers and amorphous alumina films (~ 300 nm) deposited on Si substrate by electron-gun evaporation of Al₂O₃ powder. Si⁺ ions were implanted at 100 keV with doses from 5·10¹⁶ to 3·10¹⁷ cm⁻². The samples were finally annealed at 500-1100 °C during 2 hours in dry N₂. The nanocrystals are formed by the precipitation of Si in matrix during annealing. Photoluminescence (PL) measurements at room temperature in the range of 350-900 nm were performed by using a 337 nm line of pulse N₂-laser (mean power ~ 1 mW, pulse rate – 25 Hz, pulse duration ~ 10 ns) for excitation, an Acton SP-150 grating monochromator and a Hamamatsu R-928 photomultiplier. X-ray photoelectron spectroscopy (XPS) was performed using an ESCALAB MK2 system (VG) with monochromatized Al Kα X-ray source (hν = 1486.6 eV).

Extended Energy Loss Fine Spectroscopy (EELFS) was used for investigation of nc-Si accommodation in Al₂O₃ matrix. It is a novel surface technique to study the local atomic structure in terms of radial distribution function (coordination numbers vs. interatomic distances) [5]. High resolution electron energy loss spectroscopy (HREELS) was used for investigation of interband transitions in nanocomposites, estimation of lattice defects and features of Si nanocrystals electronic structure. The spectra were recorded at primary beam energy 30.0 eV (FWHM = 0.035 eV).

3. Results and Discussion
The XPS depth profiling of Si⁺-implanted (5·10¹⁶ cm⁻²) sapphire samples after annealing at 900 °C and Ar ion etching is presented on the Figure 1. The non-uniform distribution of Si in the implanted sapphire layer was found, and its maximum was at the depth about 84-100 nm. The Si 2s components at 152.5 – 152.9 eV and additional component at 154.2 eV are shifted from the binding energy for bulk Si - 151.0 eV. It speaks in favor of Si nanocrystals presence and partial oxidation of Si atoms at interfaces. The components at 151.0-151.2 eV shall be connected with Si dangling bonds. Assuming the spherical form of crystals, we can calculate the dependence of their diameter from etching depth. Non-monotonous dependence of the Si-nc size (curve 2) from depth is caused by change of implanted silicon concentration (curve 1). The relative concentration Si-O bonds in comparison of bulk Si-Si bonds in nanocrystals (curve 3) decreases with increasing of nanocrystal size. Small concentration of implanted silicon resulting to long diffusion paths provides formation of 1-2 nm particles in Al₂O₃ on depths about 20-40 nm. On depths more than 40 nm concentration of Si increases, and nanocrystals become bigger. The Al₂O₃ passivates the interface of the Si nanocrystals thereby reducing the number of surface defects. However, low concentration of dangling bonds defect exists at interfaces.

Figure 1. XPS depth profiling of sapphire layer implanted with Si⁺ (5·10¹⁶ cm⁻²) and annealed at 900 °C.

Figure 2. Fourier transforms of the Al₂O₃:nc-Si nanocomposite after ion etching to the depth of approximately 84 nm (a) and the scheme of atomic configuration at the nc-Si/Al₂O₃ interface (b).

Figure 2 presents the Fourier transforms similar to the Radial Distribution Functions in EXAFS that provide the averaged information about atomic structure of nanocomposite Si-nc:Al₂O₃ after annealing at 900 °C during 2 hours at depth of maximal concentration of Si nanocrystals. The scale on the figure top presents the nearest coordination spheres radii in sapphire. Positions of strong peaks on
this figure correlate to interatomic distances on close-packed Si-nc coordination spheres. These positions are close to those for Al₂O₃ matrix. Comparing peaks positions with a scale, one can conclude that Si nanocrystals are well connected to a matrix. Si atoms have 3 bonds with oxygen at interface. The length of nearest Si-O bonds is 1.62 Å, and Si-Si bonds is 2.32 Å, as shown on Figure 2, b. The lengths of matrixes bonds Al-Al (3.20 Å), Al-Al (4.15 Å) and Al-O (5.00 Å) are transformed at the nc-Si/Al₂O₃ interfaces to 3.37, 4.25 and 4.94 Å, correspondingly. The principal reason of this discrepancy is explained by structural accommodation at interfaces between Si-nc and Al₂O₃ matrix. The mismatch between lattices is non-uniform and corresponds to 1 – 4 %.

The interband transition analysis was used for investigation of density of states (DOS) above the Fermi level and lattice defects. Figure 3 provides HREEL spectra obtained from nc-Si/Al₂O₃ sample annealed at 1100 °C with different depths of ion etching and normalized on intensity of E₀ peak.

![Figure 3. HREEL spectra of Al₂O₃:nc-Si nanocomposite formed by Si⁺ implantation to a dose of 5·10¹⁶ cm⁻² and annealing at 900 °C after Ar ion etching(a); fine structures of low energy losses (b) and losses at 4.5-7.6 eV (c).](image)

The spectra contains three different peaks at 0 - 0.34 eV (A), 3.0 - 3.5 eV (B) and 4.5 - 7.6 eV (C). The peak (B) is connected with F-centers in Al₂O₃ matrix. The F-center is an oxygen vacancy occupied by two electrons formed due to implantation of Si⁺ ions into crystalline lattice of sapphire. After excitation of the first electron, a relaxation process goes in several single transitions. The energy loss of scattered primary electrons for excitation of this process is 3.0 eV. Intensity of these transitions essentially weakens on depths 84-100 nm where the layer of silicon nanocrystals is formed. It was established that intensity of characteristic losses observed at energies 0.063 eV (A) and 4.5-7.6 eV (C) are connected with Si nanocrystals, and its increases with growth of Si-nc concentration. The fine structure of peaks (A) and (C) is shown on Figures 3 (b) and (c). The energy losses at 0.140 - 0.330 eV are connected with electrons transitions between conducting band and nearest impurities levels. Its energy is practically unchanged at different etching depths. The fine structure of the region (C) has several components provided by different electronic states in valence band of Si nanocrystals and transitions between the valence and conducting bands. On base of theoretical band structure of bulk Si, we can attribute the individual loss peaks on spectra of Figure 3 (b). These results demonstrate splitting of conducting band and valence band levels. This effect increases with decreasing of nanocrystals size. As the size of Si nanocrystals comes smaller, the continuous energy bands are evolving into discrete levels. As the size of the system is decreased, the nearest-neighbor interactions decrease and the band width of the conduction and valence bands are approaching.

**PL investigations.** The sapphire samples display a luminescence at around 400 nm excited from the F-centers (Figure, 4a). A PL band with a maximum at 500-550 nm appears only after annealing of Si-implanted Al₂O₃. Intensity of “green” PL monotonically falls down with rising of Si dose and annealing temperature over the entire investigated ranges. We can assume that emission is originated from chain or ring-like Si clusters or defects in the oxide matrix. It is worth noting for all the annealing temperatures the absence of typical nanocrystal-related PL in the range 700-900 nm under excitation at 337 nm, which is attributed to the formation of non-radiative defects at the nc-Si/Al₂O₃ interfaces as was shown by EELFS investigations.
Fig. 4. Influence of Si+ ion implantation and post-annealing on PL spectra of sapphire (a) and electron-gun deposited Al2O3 films (b) excited with a 337 nm line of N2 laser.

The PL measurements of the Si+-implanted electron-gun deposited Al2O3 films (Figure 1b) show emission bands in the range of 350-550 nm associated with the F- and aggregate F2+2-centers. In contrast to the sapphire samples, the observed red-infrared PL (at around 760 nm) is typical of Si nanocrystals in SiO2 matrix. The intensity of this band non-monotonically depends on the Si dose. The infrared transmission measurements of the Si+-implanted Al2O3 films (not shown), in addition to the absorption peaks at around 550 and 735 cm⁻¹ originated from the Al2O3 matrix, revealed strong Si-O-Si vibration modes (460, 811, 1080 cm⁻¹) typical of SiO2 phase which become more expressed with increase of Si dose and annealing temperature. These results indicate that Si nanocrystals are surrounded by the SiOx shells. The shells can reduce local stresses and prevent formation of nonradiative dangling bonds as well as provide additional way for radiative recombination through the double Si=O bond formation. The defects produced by Si+ implantation and subsequent high-temperature annealing play important role in luminescence of the synthesized Si nanocrystals.

4. Conclusions

So, the luminescent properties of the nc-Si depend on the kind and origin of Al2O3 matrix: nc-Si do not reveal PL in sapphire, in contrast to the deposited initially amorphous Al2O3 films. The electron spectroscopy points out that the absence of emission from Si nanocrystals ion-beam-synthesized in sapphire is originated from the formation of defects at the nc-Si/Al2O3 interface due to stresses under structural accommodation in the presence of mismatch of interatomic distances in nanocrystals and matrix. In the case of Si nanocrystals synthesized in the deposited alumina films, significant relaxation of the stresses may occur probably due to large free volume, insufficiently high adhesion to the silicon substrate, and the presence of free oxygen that leads to the formation of damping SiOx shells around nc-Si core.

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References

[1] P. Mutti, G. Ghislotti, S. Bertoni, L. Bonoldi, G.F. Cerofolini, L. Meda, E. Grilli, M. Guzzi, Appl. Phys. Lett. 66, 851 (1995).
[2] G.A. Kachurin, A.F. Leier, K.S. Zhuravlev, I.E. Tyschenko, A.K. Gutakovski, V.A. Volodin, W. Skorupa, R.A. Yankov, Semiconductors 32, 1222 (1998).
[3] P.P. Ong, Y. Zhu, Physica E 15 (2002) 118.
[4] K.S. Min, K.V. Shehegov, C.M. Yang, H.A. Atwater, M.L. Brongersma, A. Polman, Appl. Phys. Lett. 69 (1996) 2033.
[5] D.L. Wainstein, A.I. Kovalev, Surf. Interf. Anal. 34 (2002) 230.