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Experimental and theoretical investigations of electronic and atomic structure of Si-nanocrystals formed in sapphire by ion implantation

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Abstract. The semiconductor nanocomposites based on Si nanocrystals in dielectric matrices attract a great amount of attention due to their ability for luminescence in visible and near-IR part of the electromagnetic spectrum. Si nanocrystals in sapphire matrix were formed by Si^+ ion implantation with doses from $5x10^{16}$ to $3x10^{17}$ cm^{-2} at an accelerating voltage 100 kV and post-implantation annealing at 500 - 1100 ^oC for 2 hours. Depth distribution of lattice defects, impurities and Si nanocrystals, the peculiarities of interband electronic transitions were investigated by XPS and HREELS. The molecular orbitals and local electronic structure of the Al_2O_3 matrix with Si nanocrystals was calculated using an atomistic pseudopotential technique. The electronic structure of Si nanocrystals as determined from HREELS measurements is in good agreement with the theoretically calculated electronic structure for Si nanocrystals.

1. Introduction

Development of the silicon-based optoelectronics (including light-emitting devices) is now a very important scientific and technology task. One of the ways for the introduction of silicon into the family of the light-emitting (optoelectronic) materials is using the remarkable property of nanocrystals (quantum dots): the possibility of the quasi-direct radiative transitions of electrons instead of indirect band–gap transition in bulk silicon. This property is caused by the effect of so-called quantum confinement. It was shown that if silicon nanocrystals with the size of 2 –5 nm are embedded into the SiO_2 matrix (SiO_2:Si), rather strong luminescence in the visible range of spectrum is observed at room temperature [1]. The development of nanocomposites on basis of Al_2O_3 matrix allows to fabricate heat resistant and radiation resistant semiconductors.

The ion implantation is one of the best methods for the fabrication of Al_2O_3:Si composites due to its excellent compatibility with usual planar microelectronic technology. The significant success is already achieved in the obtaining visible luminescence in SiO_2:Si produced by this method [2-3]. However, important scientific problems arise on the way to wide employment of the ion implantation for the Al_2O_3:Si fabrication.

One of the primary goals in the studying size-confined systems is to understand the evolution of electronic structure with size. As a result, much effort has gone into measuring the electronic structure

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of nanocrystals by electron spectroscopy, which has been successful in yielding extremely sophisticated information about transitions at or near the energy gap. XPS and HREELS techniques have the potential of acquiring information about the bands of a different nature, namely, the density of occupied and unoccupied states. Here we present an experimental and theoretical study of light emitting Si-NC embedded in Al_2O_3.

2. Experimental details

Materials. The polished sapphire single crystal samples R(1102) orientation, 10x5x1 mm were implanted 100 keV by Si^+ with doses from $5x10^{16}$ to $3x10^{17}$ cm^{-2}. The samples were annealed at 500 — 1100 ^oC for 2 hours in N_2 atmosphere to form Si nanoinclusions in surface layers.

Methods. The research was carried out on the electron spectrometer ESCALAB MK2 (VG) with Al K_α X-ray monochromatized source ($h\nu$ = 1486.6 eV) in vacuum of $1x10^{-8}$ Pa. As prepared samples and samples that were multiple etched with an Ar^+ gun were investigated.

The High Resolution Electron Energy Losses Spectroscopy (HREELS) was used for investigation of interband transitions between the conducting band and the valence band of nanocrystals and estimation of Si nanocrystal electronic structure features. The HREEL spectra were recorded at primary beam energy 30.0 eV, at 50^o angle of incidence with respect to the surface normal.

3. Theoretical details

An atomistic pseudopotential technique is developed [4] to study the electronic structure and interband transitions of Si-nc embedded in Al_2O_3 matrix. Any imperfections in the crystalline order in both the core and matrix are ignored as well as strain effects. This enables us to identify features due to such imperfections like F-centers that are only present in the experimental spectra. The electronic structure, density of states are obtained for several NC diameters. The imaginary part of the optical dielectric function, $Im\{\varepsilon(\omega)\}$ is computed within the independent particle approximation. This is in turn used to calculate its real part through the Kramers-Kronig relation which then yields the energy loss function, $Im\{-1/\varepsilon(\omega)\}$. This theoretical study becomes instrumental in the interpretation of the HREELS data.

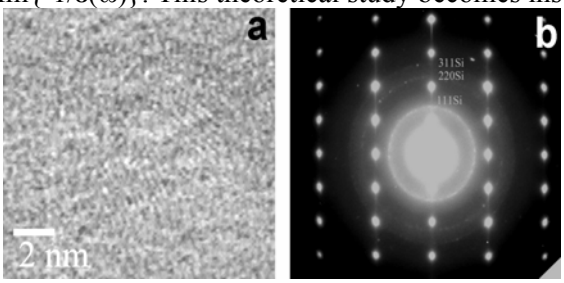

Figure 1. High resolution TEM image and SAD of Si nanocrystals in Al_2O_3 synthesized by implantation with 100 keV Si^+ ions to a dose of $5x10^{16}$ cm^{-2}. Precipitation was carried out by annealing in N_2 at 700 °C (a, b) for 2 hr.

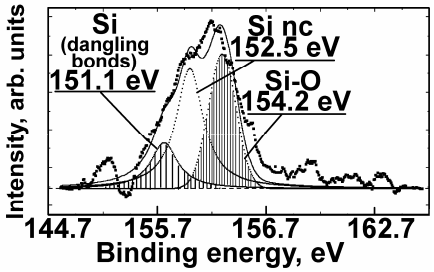

Figure 2. Al 2s and Si 2s photoelectron spectra from Si-nc/Al_2O_3 nanocomposite annealed at 1100 ^oC (b).The spectrum were recorded after Ar^+ ion etching down to depth with medium concentration of Si-NC (56 nm).

4. Results and Discussion

The detailed information about the structure of Si-nc/Al_2O_3 nanocomposite was obtained by high resolution TEM. A complex Si-NC in Al_2O_3 structure appears from the analysis of the high resolution image (Figure 1). In particular, the presence of the Si (111) reflection on diffraction patterns of Figure 1, b and visible (111) planes on TEM indicate the presence of a crystalline particle. Furthermore, this nanocrystal is surrounded by an external shell about 1 nm thick with the absence of reticular planes. The sapphire matrix has a partly amorphous structure under 700 ^oC annealing, and it is recrystallized after heating to 1050 ^oC. Size of Si nanocrystals grows from 2 nm to 4-5 nm when annealing temperature changes from 700 to 1050 ^oC. The PL from Si nanocrystals was observed at 780 nm

(λ_{ex}=337 nm) after Si^+ ion implantation with dose $5 \cdot 10^{16}$ cm^{-2} at 100 kV. The intensity of this peak was decreased with increasing of dose and accelerating voltage of Si ion implantation.

XPS depth profiling performed by Ar^+-ion etching found the non-uniform distribution of Si in the implanted sapphire layer. Si distribution has a maximum at the depth of about 84-100 nm and remains unchanged with the annealing temperature increase at least to 1100 ^oC.

The XPS spectrum of Si^+-implanted ($5 \cdot 10^{16}$ cm^{-2}) sapphire samples after annealing at 1100 ^oC is presented on the Figure 2. It was recorded after Ar^+ ion etching to 56 nm depths. The position of the Si 2s line at 151.7 eV and its additional component at 154.2 eV are shifted from the binding energy value of bulk Si = 151.0 eV evidences the presence of Si nanocrystals and partial oxidation of Si atoms at interfaces. We observed the size-dependent shift +0.7 eV of the Si nanocrystal component of the Si 2s photoelectron line that was described in [5].

Analysis of Si oxidized atom concentration follows the estimation of the fraction of nanocrystal surface atoms. Assuming the spherical shape of the crystals, we can calculate the dependence of its diameter from the etching depth (Table 1).

Table 1. Dependence of Si-NC diameter as a function of depth in Si-NC/Al_2O_3 sample after annealing at 1100 ^oC (on base of XPS depth profiling).

Depth, nm	28	42	56	70	84	98
Si-NC diameter, nm	2.0	2.6	3.8	4.5	5.5	4.5

The interband transition analysis is very important for investigations of band gap features in semiconductors and density of states above Fermi level. The peak at energy 3.0-3.5 eV in Figure 3 is connected with F-centers in Al_2O_3 matrix. The F-center is an oxygen vacancy occupied by two electrons. It is formed due to implantation of Si^+ ions into crystalline lattice of sapphire. Intensity of the 3.0 eV peak does not change at all depths of etching, for samples annealed at 500 ^oC. But annealing at higher temperatures results in decreasing point defect concentration. So the peak at 3.0 – 3.5 eV associated with F-centers presented on Figures 3, a-b decreases with elevation of annealing temperature, and it practically disappears after an 1100 ^oC annealing.

The peaks at 4.0-9.0 eV are associated with excitation of electron transitions through the band gap. Comparing experimental HREEL spectra with the theoretical analysis, we can attribute the individual loss peaks on spectra of Figure 3, a - b with the Si nanocrystals and the Al_2O_3 matrix.

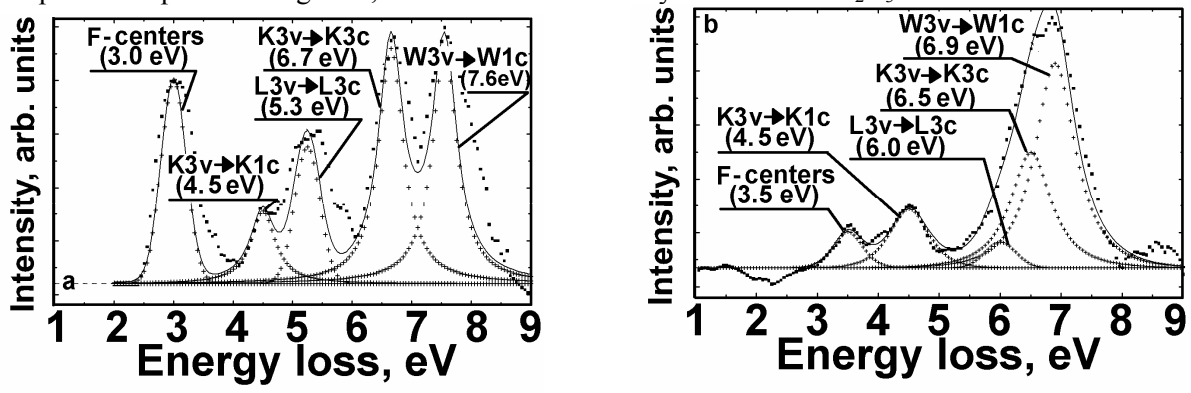

Figure 3. HREEL spectra from Si-NC/Al_2O_3 nanocomposite annealed at 1100 ^oC .The spectra were recorded after Ar^+ ion etching on depth with maximal concentration of Si-nanocrystals (84 nm). a - annealing at 700 ^oC; diameter of Si NC is 2.0 nm (TEM); b - annealing at 900 ^oC; diameter of Si NC is 3.5 nm (XPS).

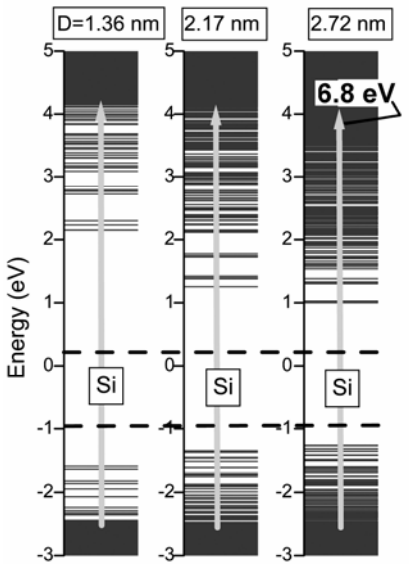

Fig.4. Molecular orbital levels of Si NC at three different diameters. The dotted lines are marked as the band gap of bulk Si

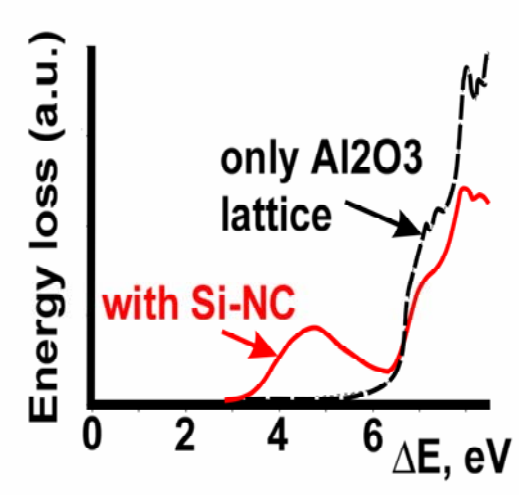

Fig. 5. Calculated energy loss function for 3.5 nm Si nanocrystals in Al_2O_3 matrix; the dashed line shows the case without the presence of NCs.

Figure 4 shows the variation of the Si NC states with respect to size; the band gap gradually approaches to that of the bulk as the diameter increases. This theoretical value correlates very well with the highest peak registered in the EEL data in Figure 4, b. The most conclusive evidence comes from Figure 5 that shows the theoretical prediction of EEL for a 3.5 nm Si NC embedded in a perfect Al_2O_3 lattice. The peak around 4.5 eV is unambiguously due to NCs, as it disappears in their absence as indicated by the dashed line. The other main peak around 7 eV is clearly due to Al_2O_3 matrix which is reproduced by the NC-free curve. It should be stressed that there is no fitting parameter in our theory, hence the agreement with experiment is quite meaningful.

5. Conclusions.

The electronic structure of inner and outer shells of Si nanocrystals in sapphire depends from NCs size. These data were obtained by complex investigations using TEM, XPS, HREELS, EELFS and electronic structure calculations. The theoretical calculations are in very good agreement with experimental results.

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