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Investigation of electronic structure of Si nanocrystals and their interface with host matrix in P-doped SiO_2:Si and Al_2O_3:Si nanocomposites

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Abstract

The system of the nanoinclusions of Si in the SiO_2 and Al_2O_3 matrix (SiO_2:Si, Al_2O_3:Si) attracts great attention due to its ability of the luminescence in visible and near-IR range of spectrum. The influence of the P ion alloying on the electronic structure of nanocomposites was investigated. The P ion doping and post-annealed at $T=1000$ °C (2 h) results in the enhancement of the photoluminescence (PL) peak connected with the Si nanocrystals. The electronic structure was investigated by X-ray photoelectron spectroscopy (XPS) and high-resolution electron energy losses spectroscopy (HREELS) methods. Ion surface modification and annealing forms the special nanostructure with Si nanocrystals in SiO_2 and Al_2O_3 matrix having high density of interfaces with special atomic structure and various degree of oxidation of Si atoms on the boundaries. HREELS investigations show that the P ion doping increases the probability of interband transitions in SiO_2:Si and Al_2O_3:Si composites.

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Keywords: P ion doping; Si nanocrystals; Sapphire; Optoelectronics; XPS; HREELS

1. Introduction

The systems of Si nanocrystals in SiO_2 and Al_2O_3 matrix (SiO_2:Si, Al_2O_3:Si) show photoluminescence (PL) in the red and near-IR spectrum ranges (750–900 nm) at room temperature. These nanocomposites could be used for production of light-emitting diodes (LEDs) integrated in Si-based chips and for elements of high-density memory devices. Due to higher permittivity and thermal stability of Al_2O_3, the Al_2O_3:Si system seems prospective for high power and high temperature applications. The dispersion of Si particles significantly increases the luminescence of non-direct band semiconductors. It was found earlier that ion doping of the nanocrystalline Si by donor elements gives additional increase of PL and changes its electronic structure [1]. However, up to present time, the influence of doping was investigated insufficiently and present data have discordance. The present paper deals with influence of P doping on electronic structure and properties of the (SiO_2:Si) and (Al_2O_3:Si) nanocomposites and interfaces. Al_2O_3 is promising a matrix for Si nanocrystals formation due to its higher permittivity and thermal stability so it allows building thinner layers in semiconductor devices.

2. Experimental details

The samples of Si(100) with thermally grown SiO_2 films ≈ 0.6 μm thick and sapphire ($1\bar{1}02$) single crystals as thin plates $10 \times 10 \times 2$ mm were used as targets for Si implantation.

Si^+ ions implantation into the plates was made with dose 10^{17} cm^{-2} at an accelerating voltage of 150 kV. After Si ion implantation the samples were annealed at 1000 °C for during 2 h and than ion doped by P with a dose of 3×10^{16} cm^{-2}, 100 kV and annealed at 700, 900 and 1100 °C for 2 h. Annealing was done in N_2 atmosphere. After Si implantation in SiO_2 or sapphire matrixes and annealing of samples, the nanoinclusions (quantum dots) were formed in surface layers. During P ion doping and annealing this dopant is redistributed between matrix and Si nanocrystals and forms segregation on the interface.

The samples were investigated in the spectrometer ESCALAB MK2 (VG) at vacuum 1×10^{-8} Pa after short preliminary Ar^+ ion etching. The electron spectroscopy was done using X-ray monochromatic Al K_α ($h\nu=1486.6$ eV) and low energy electrons EMU-50 (beam energy, $E_0=7.0$ eV and 39.0 eV)

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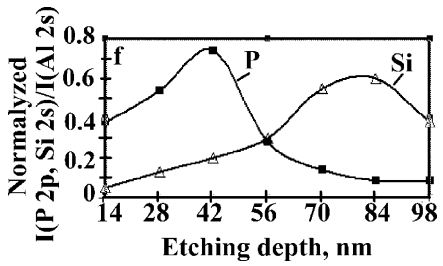

Fig. 1. Dependence of normalized I(P 2p), I(Si 2s)/I(Al 2s) from etching depth (f). The intensities of the photoelectron lines were divided on photoelectron cross-section (sensitivity factor) of each element.

sources. The spectrometer was adjusted using gold reference. The acquisition settings were selected in the way to provide the best energy resolution of the spectrometer. The HREEL spectra were recorded at the same spectrometer settings at primary beam energies of 7.0 eV and 39.0 eV, at an angle of incidence of 50° to the surface normal. The nominal resolution of the spectrometer was 17 meV using the graphite standard. The spectra were recorded with 33–35 meV FWHM of the elastic peak depending on the state of the sample at 0.002 eV/s with 50 scans of signal accumulation.

3. Results and discussion

3.1. Al_2O_3: Si system

3.1.1. XPS investigation of depth chemical composition

The depth distribution of P and Si was investigated by XPS. The Ar^+ ion etching speed was approximately 1 monolayer/s. The intensities of Al 2s and P 2p photoelectron lines in the P-doped Al_2O_3:Si were changed with etching time. The distribution of P and Si (Fig. 1) is non-uniform, and these elements have maximal concentrations at 42 and 84 nm, respectively.

3.1.2. HREELS investigation of interband transitions

The interband transition analysis is very important for investigation of band gap features in semiconductors and density of states above the Fermi level. Fig. 2 presents the well defined peak on HREELS spectra of P-doped Al_2O_3:Si after annealing at 700 °C and several Ar^+ ion etching times. This peak at 6.95, 6.55 and 6.50 eV is associated with the excitation of electrons transitions through the band gap. Its intensity depends on P concentration in the layer and its influence on density of sates (DOS) over the band gap. These features are in good agreement with depth profiles of P and Si in this sample (Fig. 1). So the intensity of HOMO–LUMO transitions (integral intensity of the losses peak) arises (Fig. 2b). Moreover, the width of energy loss peaks essentially grows with increasing depth of analyzed layer due to a size effect: the diameter of Si nanocrystals rises on a depth of 84 nm comparing to ones at subsurface, and space non-uniformity of band gap for these "roughly" disperse nanocrystals increases (Table 1).

The fine structure of spectra also changes under the influence of P doping. Fig. 3 shows differential HREELS spectrum obtained as a result of subtraction of spectra before and after P doping. The P doping increases both interband transitions with energies of 6.28, 5.70 and 5.10 eV and transitions between bottom of conducting band and electronic levels of lattice imperfections (3.99 and 3.21 eV).

3.2. SiO_2:Si system

3.2.1. Investigation of HREEL spectra: vibrational spectra

Fig. 4 shows the spectrum from the initial SiO_2:Si nanocomposite and calculated positions of phonon peaks for various Si suboxides. The spectrum was obtained in analogous mode without signal accumulation on computer. The FWHM of the elastic peak was 35 meV. Even on the scale of this figure, one can see that all peaks exhibit considerable fine

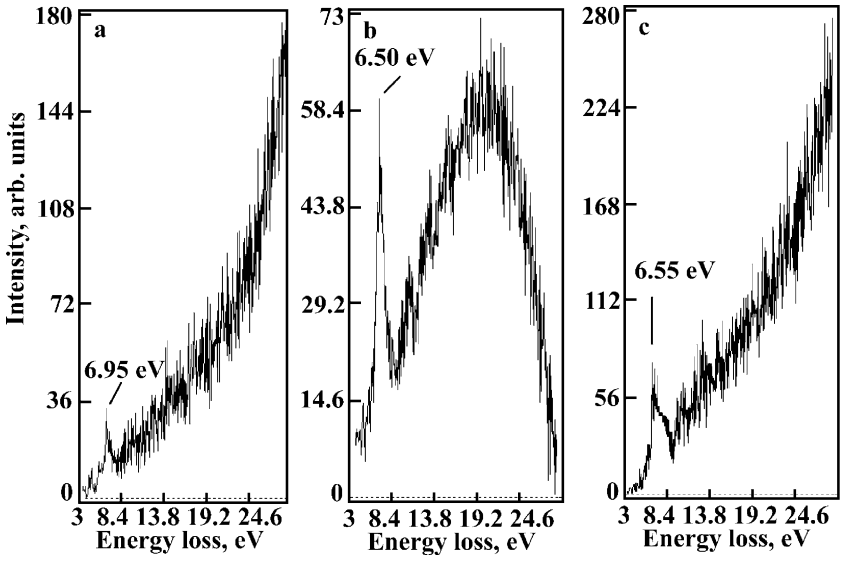

Fig. 2. HREELS spectra of P-doped Al_2O_3:Si nanocomposite after annealing at 700 °C and Ar^+ ion etching at depth of 14 nm (a), 42 nm (b) and 84 nm (c).