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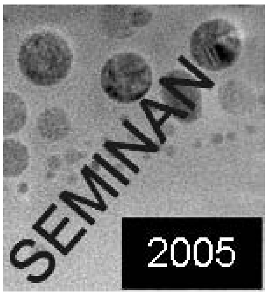

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Peculiarities of the formation and properties of silicon nanocrystals in sapphire

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The light-emitting and structural properties of R-plane sapphire implanted with 100-keV Si^+ *ions and annealed at 500-1100ºC have been studied. The PL bands observed at 400 and 740 nm are interpreted as related to defect and Ti-impurity centers, respectively. The third PL band is centered at 500 nm which correlates with synthesis of Si nanocrystals. TEM analysis combined with electron diffraction indicates the processes of amorphization of the implanted sapphire layer and its recrystallization along with the nanocrystals orientation at the highest annealing temperature. Depth distribution of silicon has been studied by the method of X-ray photoelectron spectroscopy.*

1. Introduction

Visible luminescence from nanocrystalline silicon attracts considerable interest because of its potential applications in electronic and photonic devices [1]. One of more suitable and controllable methods of Si nanostructuring is ion beam synthesis of Si nanocrystals (nc-Si) in the wide-band dielectrics. Most of research works are devoted to SiO_2 as a host material, for which the processes of nc-Si formation and corresponding luminescence have been studied in detail [2]. However, it is also important to synthesize nc-Si in other matrices because combination of the specific properties of some electronic and optical materials with the unique properties of nanocrystals would greatly expand the range of their possible applications. From the fundamental point of view, it is interesting to know how the change of composition and structure of the host matrix surrounding nc-Si affects their physical and optical properties. Aluminum oxide can be considered as such an alternative host material. It has almost the same energy gap as SiO_2, but has a higher dielectric constant, which allows for a larger density of electrically non-interacting Si quantum dots embedded into this material. The same important properties make Al_2O_3 perspective for substitution of SiO_2 in production of ultra-thin gate dielectric layers. There are several publications where nc-Si have been shown to form in Al_2O_3, but very few studies of light emission have been reported [3,4].

In the present work, to prepare nc-Si embedded into Al_2O_3 thin layers we used Si^+ ion implantation into sapphire and subsequent annealings. The methods of photoluminescence (PL), cross-sectional transmission electron microscopy (TEM) and

X-ray photoelectron spectroscopy (XPS) were employed to study the emission properties, structure and composition of the nanostructured layers.

2. Experimental details

Sapphire substrates of $(1\bar{1}02)$ (*R*-plane) orientation were implanted with 100 keV Si^+ ions to doses of 5×10^{16}-3×10^{17} cm^{-2} and subsequently annealed at 500-1100ºC for 2 h. under the dry nitrogen atmosphere. For comparison, separate sample was implanted with 100 keV Ar^+ ions to the dose of 8×10^{16} cm^{-2} providing the similar radiation damage. Room-temperature PL in the range of 350-900 nm was excited by a 337 line of pulse N_2-laser (mean power of ~1 mW, repetition rate of 25 Hz) and detected by a photomultiplier tube. PL in the range of 600-1000 nm excited by Ar^+-laser (488 nm, ~850 mW) was detected by a CCD array detector. The PL decay time measurements were performed using excitation with 488 nm light of optical parametric oscillator pumped by a Nd:YAG laser (pulse duration of 6 ns, repetition rate of 10 Hz, and mean power of 2.9 mW). The cross-sectional TEM micrographs and diffraction patterns were obtained by using JEOL 2000FX transmission electron microscope and 200 keV electrons focused on areas about 100 nm thick. XPS measurements with energy resolution better than 0.6 eV were performed on the ESCALAB MK2 (VG) spectrometer using Al K_α X-ray monochromatized source.

3. Results and discussion

Fig. 1a shows typical PL spectra of the initial sapphire samples and samples implanted with Si^+ and Ar^+ and subsequently annealed to 700ºC. Both the initial and Ar^+-implanted sapphire display a PL band centered at 400 nm and originated from the well known *F*-centers (oxygen vacancies trapping two electrons) [5]. Another PL peak at 740 nm is excited only by the 488 nm light. Although the position of this peak coincides well with emission from Si nanocrystals in SiO_2 [2], such an interpretation is problematic as this PL observed either for the initial or implanted sapphire. Moreover, this PL peak is very similar to that of Ti^{3+}-doped Al_2O_3 produced by direct excitation into the crystal field band of absorption centered at ~490 nm [6]. In order to elucidate its nature we performed measurements of the PL decay time. The plots presented in Fig. 1b were obtained with integration on wavelength in a spectral range 90 nm wide, centered at 740 nm. The PL lifetimes of 3.4 and 3.5 µs for Si^+ and Ar^+-implanted sapphire samples were estimated using the stretched exponential function and are in good agreement with the values reported for

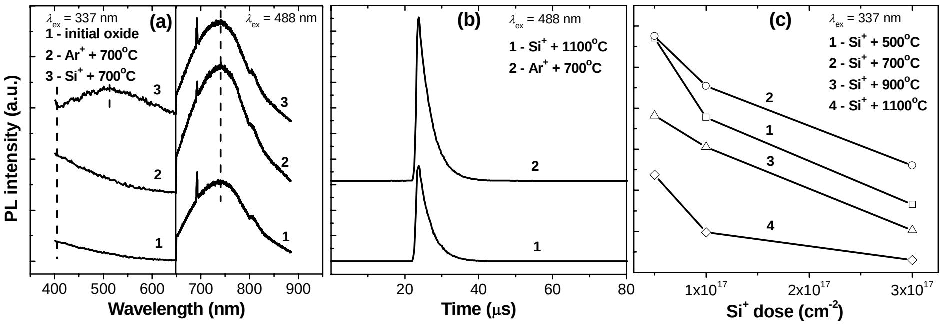

Fig. 1. PL spectra of the initial sapphire and sapphire implanted with Si^+ (1×10^{17} cm^{-2}), Ar^+ (8×10^{16} cm^{-2}) and annealed (a), 740-nm PL decay curves of sapphire implanted with Si^+ (1×10^{17} cm^{-2}) and annealed (b), dose dependencies of the PL intensity at 500 nm of Si^+-implanted sapphire annealed to various temperatures.

Ti^{3+} radiative transition in Al_2O_3 [6]. The sharp PL structures observed around 690 nm (Fig. 1a) are caused by the Cr^{3+}-centers [7] also presented in our sapphire.

PL band with a maximum at 500 nm appears only after annealing of Si^+-implanted Al_2O_3. A similar cathodoluminescence peak at 570 nm has been recently reported for sapphire layers containing Si nanocrystals [4]. It is reasonable to relate this emission to Si nanocrystals. However, this band is drastically blue-shifted from that of Si nanocrystals in SiO_2. The reason for this is unclear at the moment. We can speculate that we observe emission from very small Si nanocrystals or “non-phase” [8] (chain or ring-like) Si clusters or that mechanical stresses which nanocrystals undergo in crystalline matrix lead to an enlargement of the energy gap of Si quantum dots and to the corresponding shift of the PL peak. Another possibility consists in the direct radiative transition in the Si nanocrystal core without the charge trapping into radiative interface states or the contribution of the local interface vibrations, which provide large Stokes shift of the luminescence in case of SiO_2 matrix [2]. Intensity of the observed “orange” PL reaches its maximal value after annealing at 700ºC and monotonically falls down with rising the Si dose (Fig. 1c). Assuming quantum size effect, this behavior can be explained by the corresponding increase of Si nanocrystal size or the transformation of the “non-phase” clusters.

A cross-sectional TEM micrograph of the sample implanted with the highest Si dose (3×10^{17} cm^{-2}) after annealing at 900°C is shown in Fig. 2a. The Al_2O_3 becomes amorphous by the implantation, and the annealing is not sufficient to recrystallize the lattice. Nevertheless, the implanted Si has precipitated out in the amorphous layer as random oriented nanocrystals, as clearly seen from the diffraction pattern displayed in Fig. 2b. After annealing at 1100°C for 2 h the Al_2O_3 has recrystallized, but contains many defects as seen from the TEM picture in Fig. 2c. Si nanocrystals are located about 50-80 nm from surface, tend to be faceted and have a particular relationship to the orientation of the Al_2O_3 lattice as seen from the diffraction spots in Fig. 2d. The orientation relationships are $[01\bar{1}](111)\mathrm{Si} \parallel [210](00\bar{6})\mathrm{Al_2O_3}$. The characteristic Si nanocrystal size is roughly 10 nm. The relatively

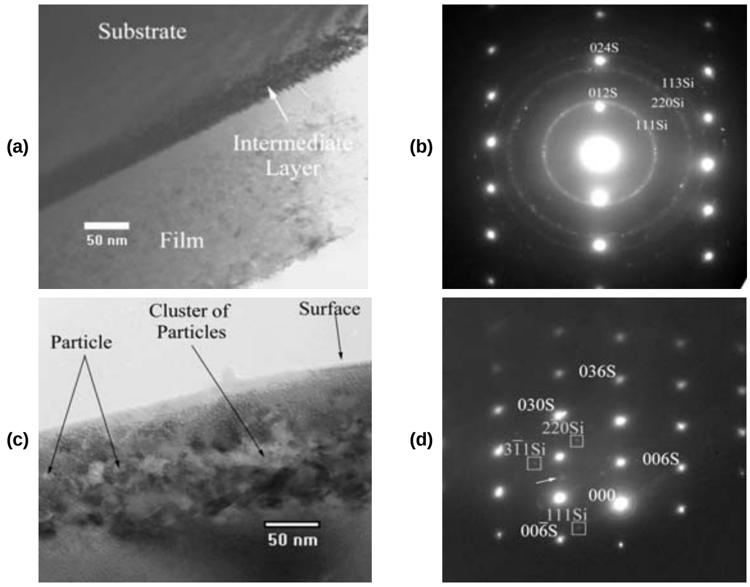

Fig. 2. TEM micrographs (a, c) and electron diffraction patterns (b, d) sapphire samples implanted with Si^+ (3×10^{17} cm^{-2}) and annealed to 900ºC (a, b) and 1100ºC (c, d).

large nanocrystal size for this Si dose correlates with the decrease in intensity of the PL at 500 nm (Fig. 1c).

XPS depth profiling performed by Ar^+-ion etching confirms TEM data on the non-uniform distribution of Si nanocrystals in the implanted sapphire layer. Typical XPS spectra of Si^+-implanted and annealed sapphire samples are presented in the Fig. 3a. The ratio of Si 2s and Al 2s peak intensities represents the relative Si concentration (Fig. 3b). Si distribution has a maximum at the depth of about 80 nm (close to projected ion range calculated by TRIM code) and remains unchanged with the annealing temperature increase at least to 900°C.

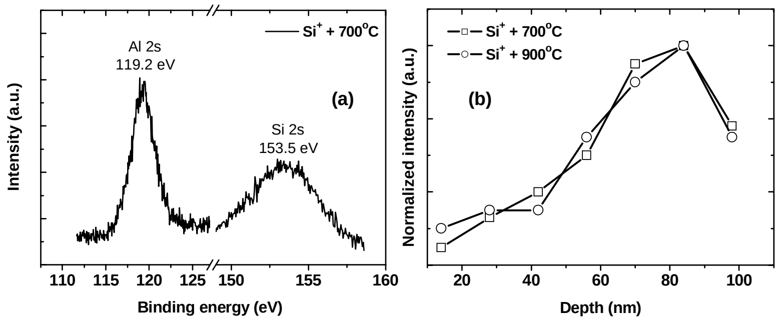

Fig .3. Typical XPS spectra (a) and Si depth distributions represented by the Si2s/Al2s intensity ratio of the Si^+-implanted (5×10^{16} cm^{-2}) and annealed sapphire samples.

4. Conclusions

In summary, three photoluminescence peaks are observed in Si^+-implanted and subsequently annealed sapphire. Among these peaks, only one at ~500 nm can be associated with Si precipitation, and its intensity is maximal after annealing at 700°C. The results of structural analysis have shown that at least a part of introduced silicon atoms forms Si nanocrystals. However, to have a comprehensive model of photoluminescence and its relation to Si nanocrystals further work is needed.

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