Emission and structure investigations of Si nano-crystals embedded in amorphous silicon

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Abstract. The influence of oxygen flow at the hot-wire-CVD process on light-emission and structural properties of Si nano-crystallites embedded in amorphous silicon has been investigated. It was shown that increasing of an oxygen flow is accompanied by the Si nanocrystallite size variation and by the appearance of some new photoluminescence bands. Using of X-ray diffraction and photoluminescence methods the dependence of photoluminescence properties on the size of Si nanocrystallites was shown. The nature of light emission centers is discussed as well.

1. Introduction

The strong interest to the Si nanocrystallites (NC) is motivated by a potential application of such material in silicon based electronics: light emission diodes [1], photodetectors [2] and memory devices [3]. The interest to this system in optoelectronics was connected primarily with observation of the intense visible photoluminescence (PL) in Si NCs at room temperature. It was established that blue and green photoluminescence (PL) are caused by various emitting centers in silicon oxide on the Si NC interface [4, 5], while the nature of more intensive orange, red and infrared (IR) PL bands are still discussed [6]. When Si NCs are embedded in silicon oxide matrix, the several PL bands exist in PL spectra, as a rule, and both SiO₂ and Si NCs are considered as the sources of light emission. It is clear that the substitution of SiO₂ matrix by amorphous silicon one (α-Si) allow to avoid the influence of SiO₂ related light emission centers on PL spectra as well as to separate and confirm the nature of some PL bands. Moreover the special addition of an oxygen flow at α-Si preparation process can give the additional information for the analysis of the emission center origin.

This paper presents the results of photoluminescence and X-ray diffraction studies on amorphous Si films with embedded Si NCs. Amorphous Si films were prepared at the different level of oxygen flow. We combined PL spectroscopy with X-ray diffraction method with the aim to investigate the PL spectra variation in dependence on the size of Si nanocrystallites as well as on the oxygen flow level.

2. Experimental procedure.

The amorphous silicon films were grown by a hot wire-CVD technique in a high vacuum deposition system with a background pressure of ~ 10⁻⁴ Pa. The gases flowed through the 0.75 mm diameter and 13 cm long coiled tungsten filament. All films were deposited at 10 Pa on boron-doped crystalline silicon substrates with <100> orientation and resistivity of 10⁻¹² ohm-cm. At the sample preparation
process a mixture of silane /hydrogen \([\text{SiH}_4]/\text{[H}_2]\) gas sources with 7/15 flow ratio was used with the filament temperature of \(~1950\degree\text{C}\), the heated substrate temperature of 200\degree\text{C} and the different oxygen flows: 0, 4, 10 and 20 sccm. The tungsten filament temperature was monitored during the deposition processes using Chino’s IR-AHU infrared sensor collimated with close-up lens.

PL spectra were measured at 300 K by spectrometer of model ORIEL Instruments MS257 with Hamamatsu R5108 photo-detector and lock-in amplifier. The PL spectra were corrected to the spectral response of the setup. The 150 mW Ar laser line (488 nm) focused to \(~200\ \mu\text{m}\) spot was used as the excitation source. The X-ray diffraction experiments were made using the XRD equipment model of Siemens D5000. The measurements have been made under a glancing angle of 1\degree.

3. Experimental results and discussion

The X-ray diffraction (XRD) spectra of the samples prepared at different oxygen flows are presented in Fig. 1a. It is seen that the oxygen flow effects on structural properties of the films. The samples grown without oxygen in a chamber are characterized by a set of intensive X-ray peaks at the angles \(2\theta = 28.40, 47.38, 56.08\) corresponding to (111), (220) and (311) silicon crystal planes (Fig. 1a) [7]. XRD data prove that these films consisted of Si NCs with preferential (111) orientation. The small additional peaks around the \(2\theta =26.12, 42.52, 76.33\) and 88.27 (Fig.1a, curve a) can be connected with \(\text{SiO}_2\) inclusions or some metastable Si states. With increasing of an oxygen flow in a CVD chamber the size of Si NCs monotonically decreases (Fig.1a, curves b, c and d) as it follows from the dropping down of the X-ray peak intensity and of enlargement of a peak half-width. Sometimes the samples exhibit weak (111) peak only (Fig.1a, curve d), suggesting growth of the concentration of small size Si NCs dispersed in \(\alpha\)-Si matrix. The size of Si NCs was estimated using Scherrer’s formula [8]. Deconvolution procedure was applied to X-ray diffraction spectra (Fig.1b), which gives three types of Si NCs with the XRD intensities and average sizes presented in Table 1.

![Fig. 1 (a)](image1)

**Fig. 1 (a)** X-ray diffraction spectra for amorphous silicon films with Si nano-crystallites prepared at the different oxygen flows: 0 (a), 4(b), 10(c) and 20(d) sccm. **(b)** presents the XRD spectrum deconvolution on three bands for the curve (a).

It is clear that the process of Si NC growth at CVD is multi-modal with three average sizes 0.55 (I) 3.19-3.95 (2) and 10.12-16.00 (3) nm dominated in NC ensemble. The NC size of the first group equal to 0.55 nm (5.50\AA) is typical for amorphous Si. This size is very close to the bulk Si crystal lattice parameter (5.43-5.67 \AA). The intensity of XRD signals, which is proportional to the volume of Si NCs, changes with the increase of oxygen flow for three types of NCs by different way. The XRD peak intensity and the size of large NCs (3) monotonically decrease as presented in Fig.1a and Table 1. The
size of Si NCs of the second group decreases monotonically, but the size of NCs for the first group practically does not change (Table 1). The concentration of the first and second group NCs (XRD peak intensity) changes non monotonically versus oxygen flow: at low oxygen flow (4-10 sccm) their concentration decreases and at high flow (20 sccm) it increases (Table 1).

| Oxygen flow (sccm) | Nanocrystal 1 | Nanocrystal 2 | Nanocrystal 3 |
|---------------------|---------------|---------------|---------------|
|                     | Size 1 (nm)   | Intensity (arb. un.) | Size 2 (nm)   | Intensity (arb. un.) | Size 3 (nm)   | Intensity (arb. un.) |
| 0                   | 0.55          | 3450          | 3.78          | 130              | 16.00         | 170              |
| 4                   | 0.55          | 2950          | 3.95          | 97               | 14.00         | 95               |
| 10                  | 0.55          | 2800          | 3.30          | 97               | 11.53         | 60               |
| 20                  | 0.55          | 3600          | 3.19          | 130              | 10.12         | 22               |

PL spectra measured at 300 K for the studied samples are shown in Fig. 2. It is seen that PL spectra contain non elementary PL bands. The intensity of these PL bands rises with Si NC concentration increase and the size decreasing (Fig.1 and 2). Deconvolution procedure on Gaussian components was applied to these spectra, which gives eight elementary PL bands with the maxima at 1.21-1.26 (I), 1.34-1.38 (II), 1.43-1.53 (III), 1.63-1.68 (IV), 1.77 (V), 1.87 (VI), 1.97 (VII) and 2.06 (VIII) eV. As an example the deconvolution results for the PL spectrum (curve 3) are shown in Fig.2 as well.

Fig. 2 PL spectra measured at 300 K for amorphous Si films prepared at substrate temperature 200 °C and hot-wire temperature 1950 °C and different oxygen flows: 0 (1), 4(2), 10(3) and 20(4) sccm. Dashed lines present the result of deconvolution of the PL spectrum (curve 3) on elementary PL bands. All elementary PL bands can be attributed to amorphous silicon and embedded Si NCs as well as to surface related centers in some silicon or silicon oxide inclusions. Note that the intensity of four last PL bands (1.77, 1.87, 1.97 and 2.06 eV) increases in PL spectra when the oxygen flow increases at α-Si film preparation (Fig.2). The peak positions of these PL bands do not change with Si NC size variations. The integrated intensity variation of 1.21-1.26, 1.34-1.38, 1.43-1.55 and 1.63-1.68 eV PL bands correlates with the variation of Si NC concentrations of small (0.55nm) and middle (3.19-3.95nm) sizes as it is shown in Fig.3. At the same time these PL peak positions shift into the high energy side (Fig. 4) with NS size decreasing.

Si nano-crystallites with the size less than 4.8 nm are characterized by a quantum confinement effect and named as quantum dots (QDs). PL bands of Si QDs have peak energies higher than Si band gap at 300K (1.12 eV), which allows attributing them to radiative transitions between quantum confined levels localized inside of Si NCs. We suppose that the 1.21-1.26, 1.34-1.38, 1.43-1.55 and 1.63-1.68 eV PL bands characterize the set of Si NCs with four different average sizes which are smaller than 4.8 nm (Si QDs).
The change of the PL integrated intensities for four elementary PL bands (a) and XRD peak intensities for small and middle size Si QDs (b) versus oxygen flows.

Note that PL band with the maxima at 1.42-1.58 eV at 300K was previously observed in Si QDs embedded into silicon oxide as well [9, 10]. The peak position of this PL band depended on Si crystallite sizes. It was shown that PL peak position shifts into high energy side from 1.42 eV up to 1.58 eV with decreasing of Si NC sizes from 4.2 nm up to 2.7 nm [9, 10]. This shift of PL peak positions versus Si NC sizes was much slower than predicted by quantum confinement theory [11]. As a rule in theoretical papers the shift of PL peak positions from 1.5 up to 3.3 eV has been predicted for the Si QDs with the size decreasing from 4 nm up to 1.2 nm [11].

The date presented in this paper indicate that in studied Si QD samples there are two dominated groups of Si QDs with the average sizes 0.55 nm and 3.19-3.95 nm (Table 1). The set of PL bands at 1.21-1.26, 1.34-1.38, 1.43-1.55 and 1.63-1.68 eV can be assigned to the middle size Si QDs (2.8-3.7 nm). The role of small size Si QDs is necessary to discuss additionally.

It was shown earlier [12] when Si QDs are in contact with oxygen the surface state which involved Si=O bonds can be formed on Si QD surface. These surface states capture the electron or/and hole, where they recombine radiatively. In this case the PL peak position for small size QDs does not shift as predicted quantum confinement theory. The electronic states associated with such type of surface Si=O bonds appear inside the band gap if the dot size is small enough. When this situation realizes PL
peak energy increases much more slowly than the band gap energy with decreasing of QD sizes and even can saturates [12].

In presented paper we specially introduce the oxygen flow in the system and Si QDs in a-Si matrix were formed actually in the condition of oxygen atmosphere. So, we can suppose that the surface state deals with Si=O bonds can appear on the Si QD surface as well. The PL bands with the peaks at 1.77, 1.87, 1.97 and 2.06eV in this case can be attributed to the surface states on small size Si QDs (0.55 nm).

4. Conclusions

We investigated the photoluminescence of amorphous Si films with embedded Si NCs in correlation with X-ray diffraction spectra. Eight elementary PL bands with the maxima at 1.21-1.26 (I), 1.34-1.38 (II), 1.43-1.53 (III), 1.63-1.68 (IV), 1.77 (V), 1.87 (VI), 1.97 (VII) and 2.06 (VIII) eV have been revealed. It was shown that four former PL bands can be explained as a radiative transition between quantum confined levels within Si QDs of a middle size (3.19-3.95 nm) embedded into the a-Si matrix. The four last PL bands are attributed to the surface state involved Si=O bonds on the small size Si QD surface (0.55nm).

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