

# The formation of Si nanocrystal in SiO<sub>2</sub> matrix after ion beam mixing and heat treatment

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## INTRODUCTION

Photoluminescence (PL) from silicon nanocrystals embedded in SiO<sub>2</sub> has attracted wide interest due to its potential application in Si-based optoelectronic devices. According to the quantum confinement model, PL is sensitive to the nanocrystal shape and size distribution [1]. Among different techniques to produce Si nanocrystals such as selective-size precipitation, spark erosion, ion implantation and chemical vapor deposition, ion implantation technique has been widely used because its various parameters can be modified and controlled easily. However, high concentrations of Si nanocrystals are difficult to achieve by ion implantation due to its sputtering effect. Ion beam mixing (IBM) process can produce higher Si concentrations because the deposited films are intermixed by heavy ions with high kinetic energies, leading to the formation of homogeneously mixed layers.

In this study we present the results of photoluminescence (PL) and soft x-ray emission spectroscopy (XES) measurements of Si monolayers in SiO<sub>2</sub> films and SiO<sub>2</sub>/Si multilayers in order to study the formation of Si nanocrystals depending on different treatments of the samples.

## EXPERIMENTAL

Amorphous SiO<sub>2</sub> (a-SiO<sub>2</sub>) and amorphous Si (a-Si) layers were deposited by ion sputtering at room temperature (RT) on a Si (001) substrate in the order 100 nm SiO<sub>2</sub>, 3 nm Si, and 60 nm SiO<sub>2</sub> (SiO<sub>2</sub>/Si/SiO<sub>2</sub> film). For comparison, SiO<sub>2</sub>/Si multilayered films with 5 periods were also prepared on Si (001) substrate. The sublayer thickness of SiO<sub>2</sub> and Si was 10 and 3 nm, respectively [[SiO<sub>2</sub>(10 nm)/Si(3 nm)] $\times$ 5/SiO<sub>2</sub>(5 nm)]. Table 1 gives an overview of the samples we studied, labeled 1 through 9. All multilayers were irradiated by Ar<sup>+</sup> ions of 80 keV energy with a dose of 5 $\times$ 10<sup>15</sup> ions/cm<sup>2</sup> at room temperature (RT). Then, the samples were annealed to a temperature of 1100 °C for various periods in order to remove defects induced by ion irradiation and produce silicon nanocrystals. All thermal annealing was performed under N<sub>2</sub> atmosphere.

The photon excited Si *L*<sub>2,3</sub> XES spectra (3*s*3*d*  $\rightarrow$  2*p* transition) were measured at ALS using the Rowland circle spectrometer with an energy resolution of about 0.3 eV. The spectra were excited with 120 eV photons, well above the Si *L* absorption edge. The energies of the Si *L*<sub>2,3</sub> emission spectra were calibrated with reference samples of crystalline silicon.

Table 1.

Label	Composition of Si-multilayers	Treatment	Description
1	SiO <sub>2</sub> (60 nm)/Si(5 nm)/SiO <sub>2</sub> (100 nm)	Annealed (1100 °C, 2 hrs) after IBM at RT	Si nanocrystalline in SiO <sub>2</sub>
2	SiO <sub>2</sub> (60 nm)/Si(5 nm)/SiO <sub>2</sub> (100 nm)	Annealed (1100 °C, 2 hrs) without IBM	Si grain formation
3	SiO <sub>2</sub> (60 nm)/Si(5 nm)/SiO <sub>2</sub> (100 nm)	IBM at RT	Randomly distributed Si in SiO <sub>2</sub>
4	SiO <sub>2</sub> (60 nm)/Si(5 nm)/SiO <sub>2</sub> (100 nm)	No treatment	Si monolayer in SiO <sub>2</sub>
5	Si implanted SiO <sub>2</sub> (100 nm)	Annealed (1100 °C, 2 hrs) after Si implantation	Si nanocrystalline in SiO <sub>2</sub>
6	[SiO <sub>2</sub> (10 nm)/Si(3 nm)]×5/SiO <sub>2</sub> (5 nm)	Annealed (1100 °C, 2 hrs) after IBM at RT	Si nanocrystalline in SiO <sub>2</sub>
7	[SiO <sub>2</sub> (10 nm)/Si(3 nm)]×5/SiO <sub>2</sub> (5 nm)	Annealed (1100 °C, 2 hrs) without IBM	Si grain formation
8	[SiO <sub>2</sub> (10 nm)/Si(3 nm)]×5/SiO <sub>2</sub> (5 nm)	IBM at RT	Randomly distributed Si in SiO <sub>2</sub>
9	[SiO <sub>2</sub> (10 nm)/Si(3 nm)]×5/SiO <sub>2</sub> (5 nm)	No treatment	Si monolayer in SiO <sub>2</sub>

## RESULTS AND DISCUSSION

Figure 1 shows the PL spectra of the samples 1 through 9. Both the ion beam mixed film (sample 3) and the film without any treatment (sample 4) do not show any photoluminescent (PL) behavior, most likely because Si and SiO<sub>2</sub> layers are amorphous with high densities of defects. On the other hand sample 2 annealed at 1000 °C for 2 hours without IBM shows a broad PL peak centered at 730 nm even with a weaker intensity than sample 1. It is supposed that the PL peak in the spectrum of sample 2 is caused by silicon nanocrystals smaller than the exciton Bohr diameter formed during high temperature annealing. Sample 1 annealed at 1100 °C (for 2 hours after IBM) shows a broad PL peak centered at 720 nm at room temperature with strong intensity. We suggest that this is due to the high density of Si nanocrystals of the ion beam mixed sample (compared to the Si implanted sample). Fig 1b shows that there is almost no photoluminescence for the SiO<sub>2</sub>/Si multilayered samples (samples 6 to 9). This may be due to formation of Si grains with larger diameter than the exciton Bohr diameter. In this case the diffusion length of Si atoms recoiled by IBM is larger than the interlayer spacing of the adjacent Si layer and could result in formation of Si grains with excessive diameters resembling the physical property of a bulk Si sample.

We have performed x-ray fluorescence measurements in order to verify some of the assumptions made about the origin of the high PL intensity in those SiO<sub>2</sub>/Si/SiO<sub>2</sub> films, which were annealed at 1100 °C after IBM at RT. The results of fluorescence measurements of SiO<sub>2</sub>/Si/SiO<sub>2</sub> films (samples 1 through 4) are shown in Fig. 2. In order to estimate the penetration depth of the photons in SiO<sub>2</sub> we have calculated the attenuation length using Henke's atomic scattering factors. We have estimated the attenuation length to be about 60 nm for 120 eV photons impinging under an angle of 70 degrees (to the sample surface). This means that only the top SiO<sub>2</sub> layer (60 nm) of SiO<sub>2</sub>/Si/SiO<sub>2</sub> film is probed by the exciting photons. Slight differences between the Si L<sub>2,3</sub> emission spectra of samples 1 and 2 to those of samples 3 and 4 are found. The ratio of the peak heights in the subbands and the degree of their overlapping differ. An additional feature at the high-energy end is found in samples 3 and 4 (Fig. 2).

The similar differences were found in Si  $L_{2,3}$  XES spectra of a-SiO<sub>1.70</sub> and a-SiO<sub>1.30</sub>. The changes in Si  $L_{2,3}$  XES spectrum of a-SiO<sub>1.30</sub> with respect to that of a-SiO<sub>1.70</sub> have been attributed to the formation of a-Si in a-SiO<sub>2</sub>. Therefore the same explanation can be stressed in order to explain the similar differences in the emission features of samples 1 and 2 to those of samples 3 and 4. The differences are due to the formation of Si nanocrystals embedded in the SiO<sub>2</sub> matrix induced by annealing of the Si monolayer in SiO<sub>2</sub> films without IBM (sample 2) and after IBM treatment at RT (sample 1). Thus we have received direct spectroscopic evidence for the formation of Si nanoparticles in a SiO<sub>2</sub> matrix.

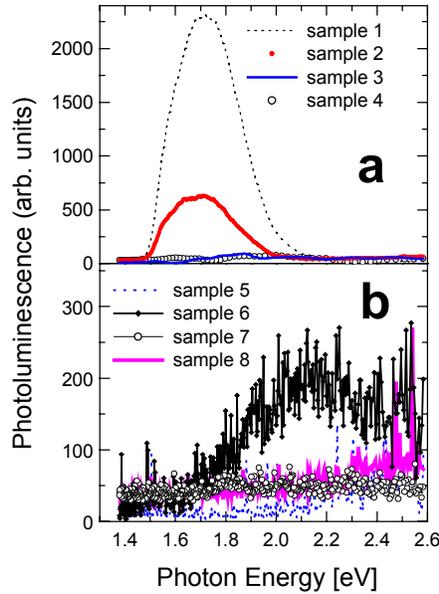


Fig.1. Photoluminescence spectra .

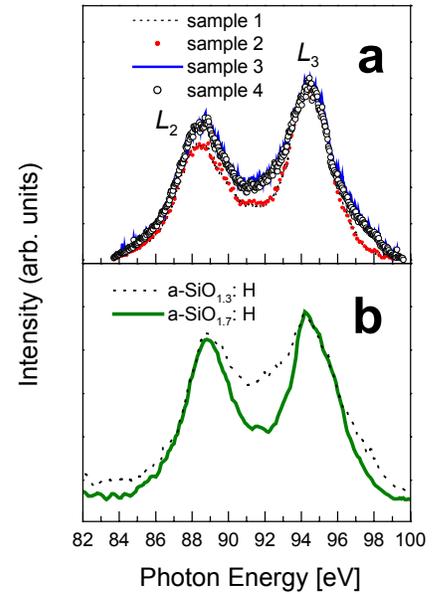


Fig.2. Photon-excited Si  $L_{2,3}$  soft-x-ray emission spectra of samples 1 through 4 (a) and electron excited Si  $L_{2,3}$  spectra of amorphous SiO<sub>1.3</sub>:H and SiO<sub>1.7</sub>:H.

## REFERENCES

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