Nanocrystals growing under irradiation of electron beam

Wei-Qi Huang[a) *], Shi-Rong Liu[b)], Zhong-Mei Huang[a)],
Tai-Ge Dong[a)], Gang Wang[a)], Cao-Jian Qin[b)]
[a)]Institute of Nanophotonic Physics, Guizhou University, Guiyang 550025(China)
[b)]State Key Laboratory of Geochemistry Institute of Geochemistry, Chinese Academy of Science Institute of Geochemistry, Guiyang 550003(China)
[*]E- mail: sci.wqhuang@gzu.edu.cn

Abstract It is interesting that silicon nanocrystal rapidly grows with irradiation of electron beam on amorphous silicon film prepared by pulsed laser deposition in our experiment. It is discovered that the shape of silicon nanocrystal is usually sphere in smaller nanoscale with less irradiation time under electron beam, in which the Si quantum dots are prepared in nanoscale of 2~3nm. It was investigated that the various crystals structures in different orientations occur in same time, and condensed structures of silicon nanocrystal are changed with different impurity atoms so that batter emission is obtained.

Key words: Nanocrystal; Irradiation of electron beam; Different orientations; Impurity atoms

Silicon nanocrystal has been studied intensively over the past decade [1-5]. The popular methods for fabricating silicon nanocrystal are self-assembly from silicon-rich silicon oxide matrices [6–8] and plasma synthesis [9–12]. The interesting method to fabricate silicon nanocrystal is growth under photons interaction [13–15]. In the first case, SiOx (with x < 2) is formed by a thin-film deposition technique such as pulsed laser deposition (PLD). Subsequent high-temperature annealing of the substoichi-metric film (typically 900~1100 ℃) produces a phase separation between Si and SiO_2 with the formation of Si nanoclusters. The dimensions, crystallinity and size distribution of the nanoclusters depend on the Si excess, the temperature and the annealing time [6, 7].

In the letter, the most interesting and simplest method discovered in our experiment for fabricating silicon nanocrystal is self-assembly growth by assistance of electron interaction, in which silicon nanocrystal rapidly grows with irradiation of electron beam on amorphous silicon film prepared by PLD, and shape of silicon nanocrystal is usually sphere when crystal size is smaller with less exposure time of electron beam. The method of electronic irradiation could be used to replace the traditional annealing methods in preparing process of silicon nanocrystal. In the process, it was investigated that the condensed structures of silicon nanocrystal are changed with different impurity atoms in silicon film, for examples oxygen or Er atoms make a stronger condensed trend than doing of nitrogen or Yb atoms in impurity, in which various localized states emission was measured.

It is very interesting that the electronic irradiation promotes the growth of nanocrystal, whose physical mechanism may be from the nanoscale characteristics of electronic de Broglie wave which produces resonance to transfer energy to crystal atoms. In natural sciences many analogous structures and properties occur on different size hierarchy, for example in the nanoscale space related to electronic de Broglie wavelength and in the sub-micrometer scale related to photonic de Broglie wavelength, in which the nanosecond or femtosecond laser is used to fabricate periodic surface structures with 100nm spatial periods on silicon [16, 17], and the electron irradiation is used to prepare silicon nanocrystal.

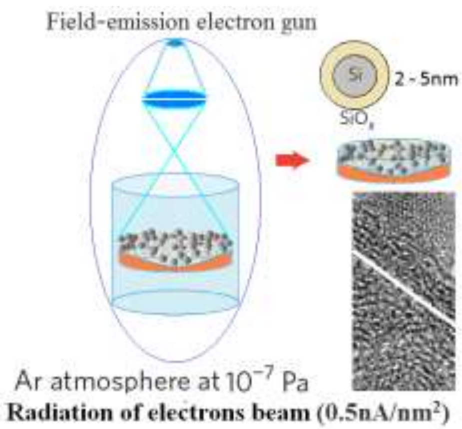

Fig.1 Fabrication system with electron beam irradiation device, in which the right bottom top inset shows TEM image of edge area of electron beam spot on amorphous Si film, and The left top inset shows the area exposed under electron beam spot whose diameter is about 300nm

Some silicon wafers of P-type (100) oriented substrate with 1-10 Ωcm were taken on the sample stage in the combination fabrication system with pulsed laser etching (PLE) and PLD devices. A pulsed Nd:YAG laser (wavelength: 1064nm, pulse length: 60ns FWHM, repetition rate: 1000) was used to etch the Purcell micro-cavity on Si sample in PLE process. In the cavity, a third harmonic of pulsed Nd:YAG laser at 355nm was used to deposit amorphous silicon film in PLD process. Then, the amorphous silicon film was exposed under electron beam with 0.5nA/nm^2 for 5~30min in Tecnai G2 F20 system in Fig.1, in which electron beam from the field - emission electron gun, accelerated by 200KV, has higher energy and better coherent. The right bottom inset in Fig.1 shows TEM image of edge area of electron beam spot, which indicates the irradiation area of electron beam in silicon crystallization (top region in spot). The left top inset in Fig.1 shows the area exposed under electron beam spot whose diameter is about 300nm. Having been irradiated under electron beam for 15min, silicon quantum dots (Si QDs) structures are built and embedded in SiO_x (with $x < 2$) or Si_yN_x (with $x < 4$ and $y > 3$) amorphous film related to oxygen or nitrogen environment respectively, in which the density of Si QDs is about $8x10^{18}cm^{-3}$.

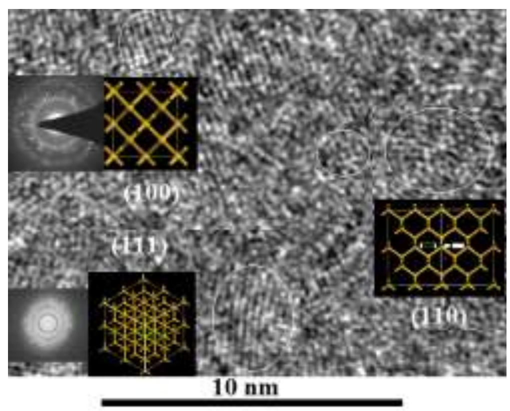

Fig.2 TEM images of Si QDs, in which the top insets show nanocrystal structures of QDs in various orientations, their simulation structures and their diffraction patterns (FFT images)

In Fig,2, it was observed that the nanocrystal structures of quantum dots form in the orientation of (100), (110) or (111) with the electron irradiation for 10~20min, in which the insets show the electronic diffraction image in selection region and the fast Fourier transform (FFT) image on the polycrystalline.

It is very interesting that gradually growing process of QDs structure was observed under electron beam with increase of exposure time. For example, the QDs structure has been observed after irradiation for 10min (TEM image in Fig.3(a)) on amorphous Si film prepared in nitrogen gas, and the larger bulks crystals gradually grow in various orientations with increasing the exposure time under electron beam as shown in Fig.3(b). It is discovered that the QDs size distribution is narrower (diameter is about 3-4nm) for electronic irradiation time of 10-15min.

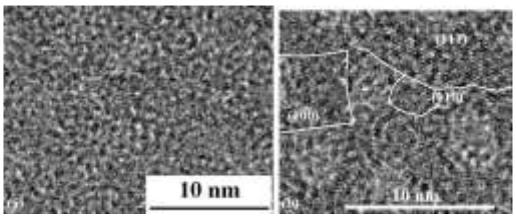

Fig.3(a)TEM images of Si QDs prepared by irradiation of electron beam for 10min on amorphous Si film prepared in nitrogen gas, (b) TEM image of larger bulks Si crystals, which gradually grow in various orientations with increasing the exposure time under electron beam

In Fig.4(a), Si − Yb QDs structures are built in the (111) orientation after irradiation under electron beam for 15min on the Si − Yb amorphous film prepared by PLD process, the bottom inset shows the FFT image of QDs structure and the top inset shows the simulation of Si − Yb QDs structure and its density of states in which the localized states form in band gap. Figure 4(b) shows the Si – Yb crystals with larger bulks in various orientations with longer exposure time (over 30min) under electron beam, in which a lot of defects occur in interface of polycrystalline.

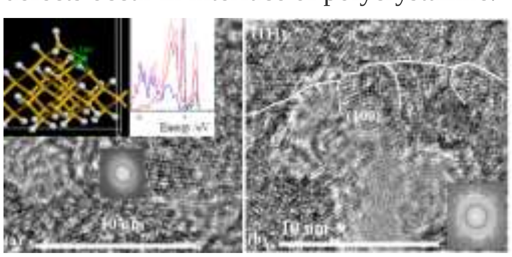

Fig.4

(a) TEM image of Si - Yb QDs structures are built in the (111) orientation after irradiation under electron beam for 15min on the Si - Yb amorphous film prepared by PLD process, in which the bottom inset shows the FFT image of QDs structure and the top inset shows the simulation of Si - Yb QDs structure and its density of states

(b) TEM image of Si – Yb crystals with larger bulks in various orientations with longer exposure time (over 30min) under electron beam, in which a lot of defects occur in interface of polycrystalline.

We have chosen some model in order to simulate the experiment process. The electronic behavior is investigated in the work by an abinitio non-relativistic quantum mechanical analysis. The DFT calculation were carried out by using the local density approximation (LDA) and non-local gradient-corrected exchange-correlation functional (GGA) for the self-consistent total energy calculation. It is considered that both LDA and GGA underestimate the band gap for semiconductor and insulator.

In the crystallizing process under irradiation of electron beam, it was observed that condensed speed is different to form different structures of silicon nanocrystal with different impurity atoms on silicon film, for examples oxygen or Er atoms make a stronger condensed trend than doing of nitrogen or Yb atoms in impurity.

On the silicon nanocrystal sample prepared by using irradiation of electron beam, photoluminescence (PL) spectra were investigated in oxygen impurity atoms. Figure 5(a) shows TEM image of silicon QDs embedded in SiO_x prepared by using irradiation of electron beam for 15min, whose sharper PL peak at 604nm is observed as shown in Fig.5(b). Here, the PL peak at 604nm with a very narrow linewidth belongs to a kind of localized states emission originating from Si – O bonds on silicon QDs.

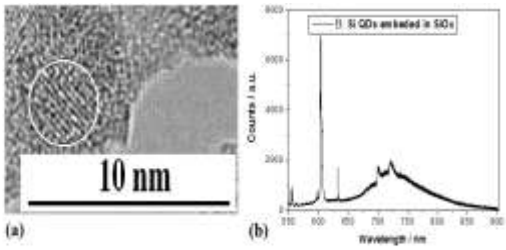

Fig.5 TEM image of Si QDs embedded in SiO_x and their PL spectra, (a)TEM image of silicon QDs embedded in SiO_x prepared by using irradiation of electron beam for 15min, (b)PL peaks on the Si QDs oxidized sample prepared with irradiation of electron beam for 15min

In conclusion, various silicon nanocrystals are fabricated by using irradiation of electron beam on Si amorphous film prepared by PLD process, in which Si QDs near 3nm diameter could be obtained by controlling exposure time of electron beam. It is interesting that the irradiation of electron beam promotes the growth of nanosilicon. Through electron beam exposure for 15min on amorphous Si film doped with oxygen impurity atoms by PLD process, enhanced PL emission peaks are observed in visible light. In the process, the physical phenomena and effects are very interesting, and a new way will be developed for fabrication of silicon nanostructures, which would have good application in emission materials and LED devices.

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