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O. Jambois, H. Rinnert, X. Devaux, M. Vergnat. Photoluminescence and electroluminescence of size-controlled silicon nanocrystallites embedded in SiO₂ thin films. *Journal of Applied Physics*, 2005, 98 (4), pp.046105. 10.1063/1.2034087 . hal-02164227

HAL Id: hal-02164227

<https://hal.science/hal-02164227>

Submitted on 24 Jun 2019

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Photoluminescence and electroluminescence of size-controlled silicon nanocrystallites embedded in SiO₂ thin films

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(Received 6 July 2005; accepted 20 July 2005; published online 23 August 2005)

Silicon nanocrystallites (nc-Si) were obtained by thermal annealing treatments of SiO/SiO₂ multilayers, prepared by evaporation. The nc-Si size was controlled by the SiO thickness. In this study the SiO₂ thickness was maintained at 5 nm and the SiO thickness was varied from 2 to 6 nm. The film's microstructure was studied by transmission electron microscopy. A strong photoluminescence was obtained in the visible range which corresponds to the radiative recombination of electron-hole pairs in the nc-Si. The electroluminescence signal is weaker and broader than the photoluminescence one. A model taking into account SiO₂ defects and nc-Si is proposed to explain the electroluminescence results. © 2005 American Institute of Physics. [DOI: 10.1063/1.2034087]

The very interesting properties of silicon nanostructures have involved an intense research activity in recent years. Indeed the confinement of carriers in silicon structures leads to a strong enhancement of the radiative transition yield and to the increase of the emitted photon energy. If the photoluminescence (PL) can be obtained with a strong intensity from samples containing silicon nanocrystallites (nc-Si), the electroluminescence (EL) intensity generally remains too weak to allow the fabrication of light-emitter devices. Several EL mechanisms such as direct recombination in nc-Si, impact ionization processes, or blackbody emission are reported in the literature, but the exact EL mechanism is still not fully understood. Several preparation techniques such as implantation of silicon in silicon dioxide, chemical vapor deposition (CVD), or evaporation were used to create new materials containing nc-Si confined in an insulating matrix. The obtained layers emit an intense luminescence in the visible range when submitted to optical pumping. In previous studies¹ we obtained a PL emission from nc-Si prepared by the thermal dissociation of silicon suboxides. The PL spectra are broad because of the large size distribution of the silicon clusters. The control of the size of the nc-Si can be achieved by the preparation of multilayer structures. The advantage of such structures is to control with a good precision the thickness of the active layer that will produce the nc-Si. The PL in such systems have already been studied in Si/SiO₂ or SiO/SiO₂ multilayers.²⁻⁵ The SiO/SiO₂ configuration is particularly interesting because the silicon clusters are strongly confined by the surrounding SiO₂ matrix. However, no EL was reported on such a system. In this paper we study the PL and the EL from thermally demixed SiO/SiO₂ multilayers prepared with a very simple method using the direct evaporation of a SiO powder and of fused silica glass. It is shown that it is possible to obtain high-quality silicon oxide thin

films containing nc-Si with a good control of the size dispersion, as demonstrated by the PL properties and the structural study. The evolution of the PL energy with the nc-Si size strongly suggests that the PL originates from the radiative recombination of the photogenerated carriers in the nc-Si. The EL signal is weaker and broader than the PL one. A model taking into account SiO₂ defects and nc-Si is proposed to explain the EL results.

The SiO/SiO₂ multilayers were prepared by successive thermal evaporation of a SiO powder and evaporation of fused silica glass performed by an electron-beam gun. The deposition rate is controlled by a quartz microbalance system and is equal to 0.1 nm/s. The thickness of the active layer was varied from 2 to 6 nm, whereas the SiO₂ barrier thickness was maintained equal to 5 nm. The silicon substrates were maintained at 100 °C. For each sample, the total film thickness was 200 nm. The samples were then annealed under vacuum with a pressure equal to 10⁻⁶ Torr. The furnace is a molybdenum cavity heated by electron bombardment. The results presented in this paper correspond to samples heated at a temperature equal to 1000 °C. For the EL experiments, *p*-type silicon substrates were used and gold was chosen for the top electrode. The deposited electrode was circular with a diameter equal to 2 mm with a thickness equal to 15 nm. Microstructural observations were performed by transmission electron microscopy (TEM) at 200 kV with a Philips CM200. TEM analyses were carried out on cross-sectioned and on rear-thinned samples, both by the tripod method, without ion milling. Optical emission was analyzed by a monochromator equipped with a 150-grooves/mm grating and by a charge-coupled device (CCD) detector cooled at 140 K. The response of the detection system was precisely calibrated with a tungsten wire calibration source. For the PL experiments the excitation was obtained by a 200-W mercury arc lamp source.

Annealing the film at 1000 °C leads to the formation of three-dimensionally confined nc-Si, coming from the disso-

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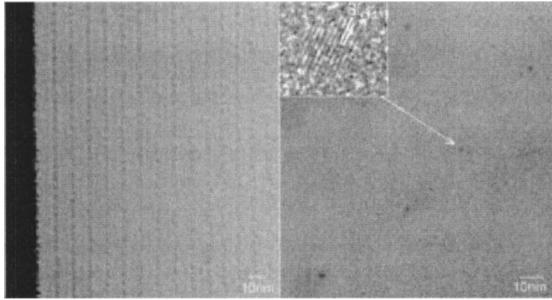


FIG. 1. Cross-section view (left) and plan view (right) of a multilayer. Inset HR-TEM micrograph shows Si(111) planes of a Si nanocrystal.

ciation of SiO into Si and SiO₂, their size being limited by the silicon oxide layer thickness. Typical TEM micrographs of the multilayer are shown in Fig. 1. The left part of Fig. 1 shows a cross-section view of a multilayer with a SiO thickness equal to 3 nm. The black lines are the Si nanoclusters containing layers and the white bands are the SiO₂ layers. To the right, a plan view of the same sample shows the Si nanoparticles. The crystalline character of the Si nanoclusters can be observed, both on the dark-field views and on the high-resolution (HR) TEM images [here on the inset, Si(111) planes]. For the sample with a SiO layer thickness equal to 3 nm, the size distribution measured on bright-field TEM images gives a mean diameter of 3.2 ± 0.7 nm. For each prepared sample, the mean size of the nc-Si is limited by the SiO₂ layer and controlled by the SiO layer thickness. The good stability of the SiO₂ layer and the separation phase of SiO in Si and SiO₂ allows us to control the mean size of the nc-Si. Moreover, the size distribution is narrow and can be fitted by a log-normal curve as shown in Fig. 2. For SiO layers thicker than 5 nm, the size is limited by the barriers but the size distribution becomes larger.

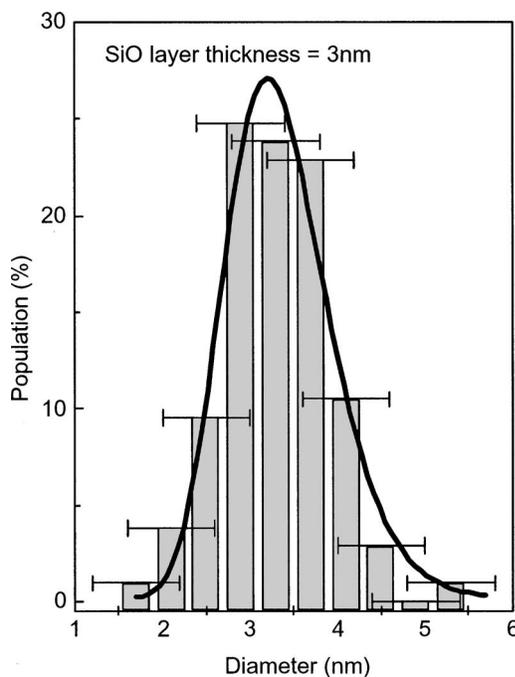


FIG. 2. Size distribution of nc-Si in the sample with a SiO thickness equal to 3 nm. The curve is a log-normal fit of the distribution.

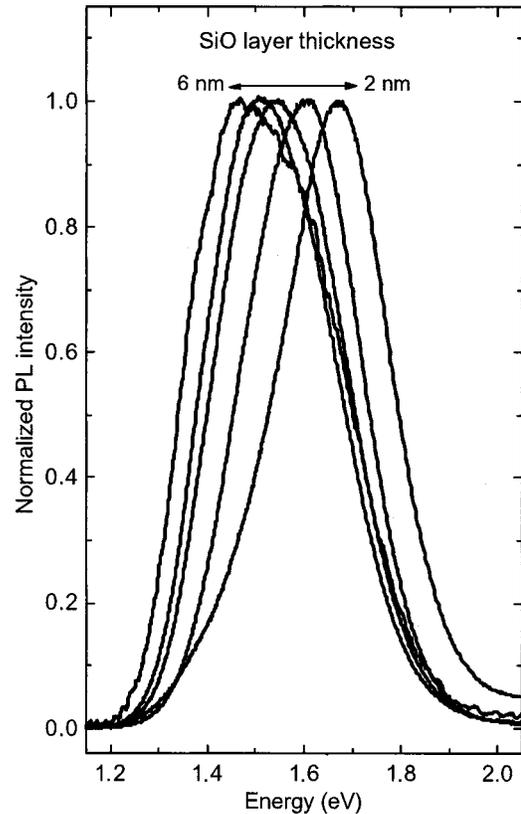


FIG. 3. Normalized photoluminescence spectra for the annealed samples with different SiO thicknesses.

The room-temperature photoluminescence results are presented in Fig. 3 for the annealed samples and for the different SiO layer thicknesses. The PL energy shifts from 1.68 to 1.45 eV as the SiO layer thickness increases from 2 to 6 nm. The PL energy is a decreasing function of the SiO layer thickness, i.e., of the nanocrystal size. This evolution is in qualitative good agreement with the quantum confinement theory. For the samples with thick SiO layers, the energy values are in good agreement with published theoretical values.⁶ For thinner SiO layers, the energy values are lower than the predicted values. This difference can be attributed to the fact that the potential well formed by the experimental system nc-Si/SiO₂ is probably not as sharp as the one used for theoretical calculations. Another explanation could be the hopping phenomenon that enhances the PL from the largest clusters of the size distribution. Moreover, it is interesting to note that we obtain a narrow full width at half maximum (FWHM) of the PL peaks. In particular, for the sample with a SiO layer equal to 2 nm, the PL peak can perfectly be fitted by a single Gaussian with a FWHM equal to 210 meV. This result is correlated to the narrow size distribution that can be obtained by this preparation method.

Electroluminescence experiments were performed at 80 K and the EL emission was obtained in the visible range for all the samples. The EL can be detected for a bias voltage as low as 2 V. The EL intensity is an increasing function of the bias voltage in the range 2–4 V. For higher bias voltages the EL decreases and is not reproducible anymore. The breakdown of the junction appears around 10 V. This behavior was observed for all the samples and the characteristic

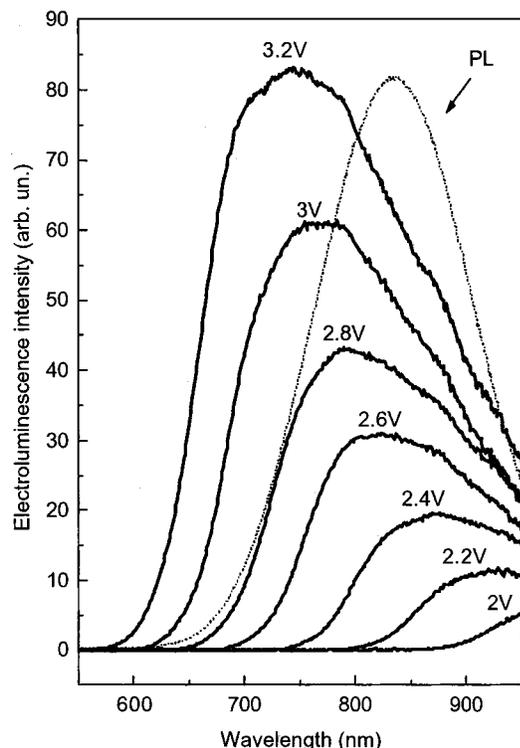


FIG. 4. Electroluminescence spectra for the sample containing nc-Si with a mean size equal to 2.8 nm as a function of the bias voltage. The PL spectrum of the sample is represented in dotted line.

evolution of the EL with the bias voltage is represented in Fig. 4. For low voltages, the EL appears with a maximum of the peak around 950 nm. The increase of the bias voltage leads to an increase of the intensity and a blueshift from 950 to 740 nm. A PL spectrum from the same sample was also added on the graph. The electroluminescence spectra are broad and different from photoluminescence. This strongly suggests that several luminescence origins are implicated. It must be noted that as-deposited multilayers also exhibit an EL peak with a maximum located at 740 nm, but with an intensity of 1000 times weaker. This peak does not shift with electric field. Since no nc-Si are present in as-deposited samples, the EL is attributed to defects in the matrix. Bae *et al.*⁷ observed an EL signal from SiO₂ films implanted with Si with a maximum at 750 nm and a shoulder at 920 nm. They attributed the EL to the neutral oxygen vacancies with the creation of a luminescent intermediate state in the gap caused by the electric field. When the nc-Si are present in the sample, the intensity of this peak is considerably increased.

The possible explanation is the better carrier injection allowed by nc-Si, as suggested in different works.^{8,9} However, the existence of defects in the SiO₂ matrix cannot explain the observed blueshift with the bias voltage. We believe that this blueshift could be the signature of an EL signal in the nc-Si. Indeed, an increase of the electric field can lead to an injection of carriers in smaller clusters, which creates a more energetic luminescence, as already observed by Valenta *et al.*¹⁰ For the low biases, only the bigger nc-Si are excited. For increasing electric fields, smaller nc-Si are excited and the spectrum blueshifts. When the voltage is sufficiently high to excite the SiO₂ defects, the peak at 740 nm arises, more intense than the nc-Si one. The existence of the too-high signal at 740 nm renders difficult the observation of a possible dependence of the EL with the nc-Si size.

In summary, silicon oxide samples containing size-controlled nc-Si were prepared with a narrow size distribution. The samples were highly luminescent in the visible range under optical pumping. The evolution of PL energy with the nc-Si size strongly suggests that the PL originates from the recombination of excitons in the nc-Si. The EL was also obtained for each sample at low bias voltage, and can be explained taking into account of an emission from SiO₂ defects and from nc-Si. The intensity of the EL must be improved to consider the fabrication of Si-based-electroluminescent devices. The reduction of the silicon oxide defects could be a promising way to improve the EL in such samples.

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