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Enhancement of the luminescence by the controlled growth of silicon nanocrystals in SRO/SiO_2 superlattices

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ABSTRACT

This work reports the study of highly-luminescent silicon nanocrystals (Si—NCs) in silicon rich oxide (SRO)/SiO_2 multilayers (MLs). Parameters such as silicon excess (Si-excess) and SRO-thickness were modified to evaluate the structure and composition and their effect on the photoluminescence (PL) response of the different superlattices. SRO monolayers with the same silicon excess were also deposited for comparison. Both, monolayers and MLs, emit a broad emission band in the red-orange region (1.45—2.1 eV). The PL of SRO monolayers strongly increases as Si-excess decreases from 10.2 to 5.2 at.%. Nevertheless, SRO/SiO_2 MLs allow up to 14-fold PL enhancement as compared to SRO monolayers. A silicon diffusion from SRO nano-layers towards the SiO_2 ones reduces the Si content within the SRO allowing the Si—NC size reduction (thus increasing the Si—NC density) as compared to SRO monolayers. Therefore, the high luminescence is correlated with the Si—NCs formation with a mean size below 3 nm where the surface defects (Si═O bonds) are strongly active.

1. Introduction

Nanostructured materials such as silicon nanocrystals (Si—NCs) embedded in a non-stoichiometric dielectric matrix (SiO_x), also known as silicon rich oxide (SRO), have been widely investigated in the last decades with the aim of providing complementary metal-oxide-semiconductor (CMOS)-compatible Si-based light sources [1—3]. Unfortunately, the electro-optical efficiency in electroluminescent devices is still low, mainly due to the following reasons: a) Since the band-gap value of dielectric material (SiO_x) is high (4—9 eV), high voltage levels are required to promote the flow of carriers [4,5], b) Poor quality of the Si—NCs:SiO_x composite yields parasitic current paths, while low density of nanocrystals due to low Si-excess makes direct charge injection into the nanocrystals difficult [4], and c) the control of the emission energy in SRO monolayers is complicated because of the low control on the size distribution and density of Si—NCs, which produce a broad band emission [6,7].

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Some alternatives have been proposed to improve the electro-optical efficiency in the SRO films such as SRO/SiO_2 multilayered (ML) structures [8–10] and Si-rich SiN_x/SRO MLs in distributed Bragg reflector (DBR)-based architectures [11,12]. In such structures, the SRO-thickness, Si-excess and annealing temperature are parameters that promote the formation of Si–NCs and radiative defects, affecting the optical and electrical properties of the ML. Some techniques with high degree of accuracy in thickness and homogeneity films have emerged for the design of these SRO/SiO_2 ML structures. Among them: low pressure chemical vapor deposition (LPCVD), plasma-enhanced chemical vapor deposition (PECVD) and sputtering are the most common techniques [8–13].

In this work, 10 SRO/SiO_2 bilayers were deposited by the co-sputtering method. The atomic concentration ratio *x(O/Si)* (and Si-excess) of SRO layers were $x = 1.65$ (5.2 at.%), $x = 1.3$(10.2 at.%) and $x = 1.1$(14.3 at.%). The SRO-thickness was also modified from 2.5, 5 and 7.5 nm for each atomic concentration and keeping constant the SiO_2 layer thickness at about 6 nm. SRO monolayers with the same Si excess were also deposited for comparison.

Both, SRO monolayers and SRO/SiO_2 MLs show a broad emission band in the orange-red region (1.45–2.3 eV). Nevertheless, the SRO/SiO_2 MLs emit a stronger PL intensity when compared with SRO monolayers. The most intense PL emission is observed when the SRO-thickness is 5 nm, and with the highest Si-excess (14.3 at.%), which is important for the design of electroluminescent devices with low threshold voltage. To the best of our knowledge, there are few reports where an improved emission was obtained for a high Si-excess. Although multilayer structures with good control in crystal size have been reported [14], a comprehensive study of SRO/SiO_2 MLs as a function of Si-excess (5.2–14.3 at.%) and modulating the SRO-thickness layer (2.5–7.5 nm) have not been discussed in detail.

2. Experimental details

SRO monolayers and SRO/SiO_2 MLs were deposited on p-type (100) Si wafers with resistivity of 2–5 Ω-cm by using a Torr International magnetron sputtering system (13.56 MHz). Before deposition, Si substrates were cleaned in ultrasonic bath with acetone, ethanol, and deionized water successively. Si wafers were immersed in a 10% hydrofluoric acid (HF) aqueous solution for 2 min to remove the native oxide. After being dried with nitrogen, the substrates were immediately loaded into the chamber of the sputtering system. Once a base pressure of ~1×10^{-6} Torr is achieved, Ar flow of 60 sccm is introduced into the chamber at a working pressure of 2.4 *mTorr*.

The SRO monolayers were deposited by the simultaneous co-sputtering of Si and fused quartz (SiO_2) targets. The Si content in the SRO layers was modified by a variation of RF-power applied to Si (Psi) target at 50, 60 and 70 W, keeping constant the RF-power applied to SiO_2 ($PSiO_2$) target at 100 W. Table 1 shows the thicknesses and Si-excess of SRO monolayers.

For SRO/SiO_2 MLs, SRO layers with the same atomic concentration that monolayers were used. First, a SiO_2 layer was deposited onto the silicon substrate followed by a SRO film to obtain a SRO/SiO_2 bi-layer. 10 periods of SRO/SiO_2 bi-layers were deposited with an additional (upper) SiO_2 film (10 nm) to avoid oxidization during high temperature annealing. Each SiO_2 layer was about 6 nm in thick while the SRO layer thickness was modified from 2.5, 5 and 7.5 nm (see Table 2). All films were deposited at 100 °C. After deposition, samples were thermally annealed in a conventional tube furnace at 1100 °C in N_2 environment for 2 h.

Thickness of the films was measured by reflectance using a Filmetrics F20UV equipment. The chemical compositions and Si-excess in the SRO layers were analyzed by a Thermo Scientific X-ray photoelectron spectroscopy (XPS) Escalab 250Xi equipment. The Si oxide phase was studied by Fourier transform infra-red (FTIR) spectroscopy using a Bruker Vector 22 spectrometer in the range 400–4000 cm^{-1}. The PL emission spectra were measured with a Horiba Fluoromax 3 system. The samples were excited using a 300 (4.13 eV) nm radiation and the PL emission signal was collected from 400 to 900 nm (1.37–3.1 eV) with a resolution of 1 nm. Finally, cross-view high resolution transmission electron microscopy (HRTEM) images were obtained to study the structural properties of the SRO layers and SRO/SiO_2 MLs using an electron microscopy JEOL JEM 2200.

3. Results and discussions

The Si-excess, as analyzed by XPS in depth profile, within SRO monolayers is about 5.2, 10.2 and 14.3 at.% for Rp ($PSiO_2$/PSi) = 2, 1.66 and 1.4, respectively. These values are very similar to those one obtained in a previous work, indicating the process is repetitive [15].

Table 1
Thickness and Si-excess obtained for SRO monolayers.

Sample	Sample Topology	Si-excess (at.%)	Thickness (nm)	
			As-deposited	Annealed
A	SRO-Monolayer	5.2 ± 0.2	108 ± 1.6	90 ± 0.6
B	SRO-Monolayer	10.2 ± 0.3	82 ± 1.0	70 ± 0.8
C	SRO-Monolayer	14.3 ± 0.1	90 ± 1.2	76 ± 1.1

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