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Erbium-doped silicon nanocrystals in silicon/silicon nitride superlattice structures: Light emission and energy transfer

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1. Introduction

Silicon nanocrystals (Si-nc) embedded in silicon nitride matrices [1] provide an alternative approach, with respect to silicon oxide-based structures, for the fabrication of inexpensive light-emitting devices compatible with mainstream silicon technology. Light-emitting Si-nc dispersed in amorphous silicon nitride provides significant advantages with respect to the more characterized oxide-based Si-nc systems. In particular, due to the low diffusivity of Si atoms in silicon nitride matrices, thermally induced phase separation in silicon-rich nitride results in a higher density of smaller Si clusters, which are prevalently amorphous. This fact deeply affects the optical emission properties of Si clusters in silicon nitride systems. In fact, the influence of surface states becomes predominant for small Si amorphous clusters below 3 nm in diameter [2], and the probability of radiative recombinations is enhanced due to nitrogen-related optical transitions localized at the surface of the Si clusters [3,4]. These surface transitions can give rise to intense near-infrared light emission with nanosecond-fast dynamics, small temperature quenching and efficient energy transfer to erbium (Er) ions [3–5]. In particular, efficient energy transfer to Er ions is a crucial element to engineer compact amplifiers with lower pumping threshold compared to traditional Er-doped glass matrices. Recently, strong Er emission sensitization has been demonstrated in Er-doped SRN/Si superlattice structures, which show nanose-

ABSTRACT

In this paper, we discuss optical emission, energy transfer and electroluminescence from a superlattice structure containing small (\sim 2 nm diameter) amorphous silicon (Si) clusters coupled to erbium (Er) ions. The superlattice structure is fabricated by direct co-sputtering of thin (\sim 3–5 nm) Er-doped siliconrich nitride/Si (Er:SRN/Si) layers subsequently annealed at different temperatures in order to induce the nucleation of Si clusters and to activate Er emission. In this paper, we discuss efficient Er emission and sensitization with nanosecond-fast non-radiative transfer time and we report on low turn-on voltage (\sim 7 V) electroluminescence from simple electrical device structures. Our results demonstrate that small Si clusters embedded in silicon nitride-based superlattice structures provide a viable approach for the fabrication of Si-compatible optical devices.

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cond-fast transfer to Er, additionally controllable by the layers' thicknesses [5]. Furthermore, it is important to mention that lightemitting silicon-rich nitride systems have typically a large effective refractive index (about 2.3), which provides the additional opportunity to strongly confine optical modes. Si clusters embedded in high-index silicon nitride films have recently led us to the demonstration of high-quality Er-doped photonic crystal structures [6]. Finally, silicon nitride-based structures offer another important advantage over oxide-based active materials: a considerable reduction in the electron/hole injection barriers at the Si/silicon nitride interfaces, potentially resulting in the fabrication of low-voltage electroluminescent devices with improved electrical stability. In this paper, we will focus on discussing the fabrication and the optical properties of a novel type of silicon nitride structure, based on the alternation of nanometer-size Er-doped silicon nitride and Si layers forming a superlattice structure. In particular, we demonstrate Er emission sensitization with nanosecond transfer dynamics and we discuss the electroluminescence (EL) properties of simple test structures. Our preliminary results demonstrate that intense room temperature EL, overlapping with the photoluminescence (PL) spectra, can be achieved at small operating voltages (7V) in SRN/Si superlattice structures.

2. Samples fabrication and experimental details

Er-doped SRN/Si superlattice (Er:SRN/Si) structures with 400 nm total thickness were fabricated on Si substrates by radio frequency (RF) magnetron co-sputtering using Si, Si_3N_4 and



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metallic Er targets and annealed using a rapid thermal annealing (RTA) furnace in N₂/H₂ forming gas (5% hydrogen) for 10 min at temperatures ranging between 500 and 1000 °C. The sputtering was performed in a Denton Discovery 18 confocal-targets sputtering system. During sputtering, the silicon nitride cathode power was kept constant at 350 W, while 35 W on the Si cathode was used to create a Si-rich film. Identical samples without Er ions were also fabricated in order to investigate the intrinsic Si-nc emission properties and to investigate the Si-nc EL properties. The atomic concentrations of Si, N and Er in the deposited films were measured, within 0.5% accuracy, using energy dispersive X-ray analysis (EDX, Oxford ISIS). Time-resolved PL experiments have been performed using a frequency-doubled Ti:Sa laser (Mai Tai HP, Spectra Physics) with 100 fs pulses at 430 nm. The emitted light was dispersed through a double grating spectrometer (Acton Spectra Pro. 2300i) and detected using a single-photon counting streak camera with 10 ps time-resolution (Hamamatsu, C4770). Steady-state room temperature PL was excited using the 457 nm line of an Ar pump laser (Spectra Physics, 177-602) and detected using either a photomultiplier tube (Oriel 77348) for the visible range or an InGaAs detector (Oriel 70368) for the 1540 nm Er emission. All PL spectra have been accurately corrected by the spectral response of the PL set-up.

Fig. 1 shows a transmission electron microscopy (TEM) brightfield image of a superlattice sample annealed at 700 °C for 10 min, containing 47% Si as directly measured by EDX. The image is representative of a light-emitting SRN/Si superlattice structure in cross-section, taken using a JEOL 2010 TEM operated at 200 kV. The average Si and SRN layer thicknesses were measured to be 3.4 and 4.2 nm, respectively. The inset shows a high-resolution micrograph taken on the same sample. Si quantum dots can be seen (dark spots) embedded in the SRN layers. The Si quantum dots appear to be amorphous with an average diameter of ~2.5 nm. These amorphous Si clusters samples lead to intense light emission in the 750–800 nm range at room temperature (Fig. 2a), show non-exponential PL decay with nanosecond dynamics (Fig. 2c, black curve) and strongly sensitize Er emission (Fig. 2a and b).



Fig. 1. Bright-field TEM cross-section micrograph of a representative SRN/Si superlattice structure fabricated by direct co-sputtering. Inset: high-resolution TEM cross section of a portion of the same SRN/Si superlattice structure.



Fig. 2. (a) PL spectra under 457 nm steady-state excitation for Er:SRN/Si superlattice structures annealed at different temperatures (as shown in the figure). All the samples contain 47% and are annealed for 10 min in an RTA furnace in N₂/H₂ atmosphere. (b) Reciprocal PL risetime at 1540 nm under 457 nm excitation with different photon flux. (c) PL decay curves measured at 800 nm under identical pumping conditions (3.7 μ J/cm²) for a superlattice sample without Er (black) and with Er (light grey). The pump wavelength used was 430 nm.

3. Energy transfer to Er ions

Rare-earth doping of Si nanostructures is motivated by the recent discovery of efficient resonant energy transfer between Sinc embedded in SiO₂ and Er ions [7]. Several studies have focused on the understanding and the optimization of Er energy transfer from SRO systems. However, little is currently known on Er energy transfer from silicon nitride-based materials. In this section, we discuss our results on Er emission sensitization from amorphous Si clusters embedded in silicon nitride superlattice structures. Fig. 2a shows the Si clusters' near-infrared emission spectra as well as the Er emission for superlattice samples annealed at different temperatures (indicated in the figure). The emission spectra were excited with 457 nm radiation, which is nonresonant for Er absorption. Therefore, Fig. 1 provides direct evidence of Er emission sensitization from Si clusters dispersed in silicon nitride. As shown in Fig. 1, Er sensitization can occur at different annealing temperatures, but samples annealed in the range 700–800 °C are found to maximize the Er signal. At these annealing temperatures, the near-infrared emission from Er-doped Si clusters is strongly reduced due to energy transfer (Fig. 2a).

The strength of Er sensitization can be quantified by measuring, in the weak pumping regime, the Er effective excitation crosssection. This is obtained by measuring the dependence of the Er PL risetime versus the pumping photon flux (Fig. 2b). The linear fit to the experimental data yields a cross-section value of $\sigma_{\rm exc} =$ $(4\pm1)\times10^{-16}$ cm², which is comparable with the cross-section values reported in the literature for Er:SiO_x systems [8]. However, due to the nanosecond-fast recombination rate characteristic of the Si clusters embedded in the superlattice structure (Fig. 2c), the experimental observation of comparable Er effective excitation cross sections for both SRN/Si and SiO_x-based structures implies directly that the coupling rate to Er is larger for the former system [5]. In fact, Er sensitization from nitride-based Si clusters is observable despite their nanosecond-fast de-excitation dynamics, and it is as effective as for SiO_x systems which typically possess a much slower relaxation time (in the microsecond to millisecond range) for comparable cluster densities ($\sim 10^{17} \text{ cm}^{-3}$). In the absence of a microscopic theory that accounts for the enhanced transfer rates in nitride-based Si clusters, we can only speculate that the strong exciton localization at the surface of the clusters should play an important role, since it has recently been shown that Er ions are preferentially located in close proximity to the Si clusters' surfaces [9].

In order to better understand the mechanism of energy transfer in SRN/Si systems we need to carefully investigate the de-excitation dynamics of Si clusters coupled to Er ions. For this reason, we have directly measured the effect of Er incorporation on the PL decay dynamics of Si clusters by comparing the PL peak emission at 800 nm for the Er-doped superlattice structure and a reference sample without Er, prepared under identical conditions. EDX analysis shows that no significant perturbation of the Si/SRN stoichiometry is induced by the small fraction (<1%) of Er ions incorporated in our samples. Therefore, under these conditions (small donor matrix perturbation due to the incorporation of the Er acceptor), if a shortening of the lifetime is observed upon Er incorporation, it can be directly related to the efficiency of the energy transfer process in the system [4,10]. The time-resolved data, obtained under femtosecond excitation at 430 nm, are shown in Fig. 2c. As expected for a non-resonant energy transfer process, our data demonstrate that Er incorporation significantly affects the de-excitation dynamics of the donor (Si clusters) systems over nanosecond time-scales. By the shortening of the Si clusters PL lifetime due to energy transfer we can estimate the maximum transfer rate of the system as [10] $w_{\rm tr} = 1/\tau_1 - 1/\tau_2$, compatible with \sim 3 ns transfer time and a maximum transfer efficiency [10] of $\eta_{tr} = 1 - \tau_1 / \tau_2 \approx 50\%$.

4. EL from superlattice structures

In addition to the observation of intense room temperature light emission and the strong Er sensitization discussed previously, a particularly attractive feature of the SRN/Si superlattice system is the possibility to achieve efficient and stable electrical injection under low biasing voltages. In order to investigate EL in these systems we fabricated simple test electrical structures on pand n-type Si substrates. We lithographically defined circular contact areas with 1 mm² area and sputtered transparent ITO top contacts with \sim 80% transmission at 800 nm. Aluminum thin films were evaporated on the back surface of the devices and used as cathode contacts. The total thickness of the active region of the devices (the superlattice structure) was 400 nm. A schematic of the device structure is sketched in Fig. 3. Fig. 3 shows the EL spectra of the devices measured at different bias voltages. For comparison, a representative PL spectrum is also shown (Fig. 3, dashed-dot line), and spectrally overlaps the EL spectra. This fact indicates that the EL and PL mechanisms are the same, and correspond to radiative de-excitation of Si clusters. The integrated EL versus the injected current density is displayed in the inset of



Fig. 3. Room temperature EL spectra of SRN/Si superlattice under different bias voltages (indicated in the figure). A typical PL spectrum of the same material is also shown (dash-dot line). Inset: integrated EL for different injection current densities.

Fig. 3, which shows a turn-on voltage at \sim 7 V. A systematic study of the electrical injection mechanism in SRN/Si superlattice structures is currently in progress. Based on our preliminary data, we believe that, within the injection conditions required to induce EL, the electrical transport properties of our thin-film SRN/Si superlattice structures are driven by the space charge limited conduction (SCLC) mechanism [11].

Our results demonstrate that SRN/Si superlattice structures have a large potential for stable, low-voltage operation of EL light sources based on Si technology.

5. Conclusions

In this paper, we discussed light emission, Er sensitization and EL from amorphous Si nanoclusters embedded in silicon nitride/Si superlattice structures fabricated by direct co-sputtering. We have demonstrated 50% efficient Er sensitization with nanosecond transfer times in silicon nitride/Si superlattice systems and reported on room temperature EL with \sim 7V turn-on voltage, spectrally overlapping the PL spectra.

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