Polarized Optical Gain and Polarization-Narrowing of Heavily Oxidized Porous Silicon

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We report on a polarization-sensitive optical gain in a blue-emitting Si/SiO_2 nanocrystalline system having a high degree of emission polarization memory. This system can show a positive optical gain or optical loss depending on the polarization state of the pump and emitted light. Under optical gain conditions, the degree of polarization of the amplified spontaneous emission increases with the pumping fluence. This effect has been attributed to an increase in the stimulated emission efficiency occurring for the linearly polarized emission component characterized by high photon occupation numbers (stimulating photon flux). This finding is independently supported by other experimental observations. The occurrence of polarization dependent stimulated emission strongly indicates the relevance of morphological effects in light emission from ultrasmall elongated silicon nanostructures.

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After the report of optical gain in ion implanted Si nanocrystals (Si-nc) [1], optical gain has been demonstrated for nanocrystalline Si/SiO_2 systems prepared by reactive Si deposition onto fused quartz [2], by plasma enhanced chemical vapor deposition [3], by magnetron sputtering [4], and by the sol-gel technique [5], as well as in colloidal films containing ultrasmall ($\simeq$1 nm) Si-nc [6]. The emerging interpretation is that Si-nc behave as four-level systems, where the stimulated emission originates from localized interface energy levels, originating from the relaxation of Si-nc under intense optical excitation [7,8]. These interface states can originate from Si═O [1–4,9] or Si-Si surface bonds [6]. On the other hand, in the four-level scheme, these states are not directly involved in the absorption process; thus one might at first expect little correlation—for example, in terms of polarization—between absorbed and emitted photons.

A progressive oxidation of Si-nc contained in porous silicon (PS) results in their size reduction and in the appearance of a blue photoluminescence (PL) band having nanosecond lifetime and $\simeq 1\%$ external quantum efficiency [10,11]. One feature of the blue band is the high level of linear polarization memory: when the Si-nc are excited by linearly polarized light, they preferentially emit with the same polarization. This result came as a surprise because absorption and emission channels should be quite different when taking into account that the photoexcited *e-h* pair loses an energy on the order of 1 eV in inelastic processes and, therefore, the observed polarization is not a coherent effect [12]. Therefore it was suggested that the luminescing sources responsible for the blue emission are Si chainlike structures behaving as dipole absorbers and radiators [13]. Indeed, a similar linear polarization memory effect has been observed for polysilane chains [14]. On the contrary, despite similar PL properties of point defects in fused quartz, these do not show any PL polarization memory. Anisotropic morphology also gives rise to anisotropy of the nanocrystal quantum-confined states, affecting the polarization of absorption and emission of such states [15,16].

The linear polarization memory effect is expressed quantitatively in terms of the degree of polarization (DOP) level, $\mathrm{DOP} = [(I_{\parallel} - I_{\perp})/(I_{\parallel} + I_{\perp})] \times 100\%$, where $I_{\parallel}$ ($I_{\perp}$) is the intensity of the PL polarized parallel (perpendicular) to the direction of the electric field of the exciting light. In the system of randomly oriented linear dipoles, linearly polarized light preferentially excite those of them whose axes have large projections on the direction of the electric field of the exciting photons. Therefore the excitation pattern in the plane of ideal dipoles is a $\cos^2\theta$ function, where θ is the angle between the polarization of the pump and the axis of the absorbing/emitting dipole. Because absorption and emission are mirrorlike processes, the resulting emission pattern has a $\cos^4\theta$ dependence for the dipoles contributing to $I_{\parallel}$ and a $\cos^2\theta \times \sin^2\theta$ dependence for those giving rise to $I_{\perp}$. The resulting PL from an ensemble of randomly oriented dipoles becomes predominantly polarized along the direction of linear polarization of the exciting light. Thus the polarization of exciting photon defines the polarization state of emitted one.

Stimulated emission requires high occupation numbers of the emitted photons and a large stimulated emission rate [17]. For oxidized PS both of these two conditions can be fulfilled by taking into account the nanosecond PL lifetime and the linear polarization memory effect, which assures that the occupation number of emitted photons having the same polarization as the pumping photons is high. Therefore, if stimulated emission takes place, there is an increased chance that the new photon will have the same polarization as the "input" photon. In this Letter we demonstrate net optical gain in oxidized porous silicon and that this gain can be achieved only for linearly polarized photons having large occupation numbers and only for propagation directions orthogonal to the electric field vector of the incident photons.

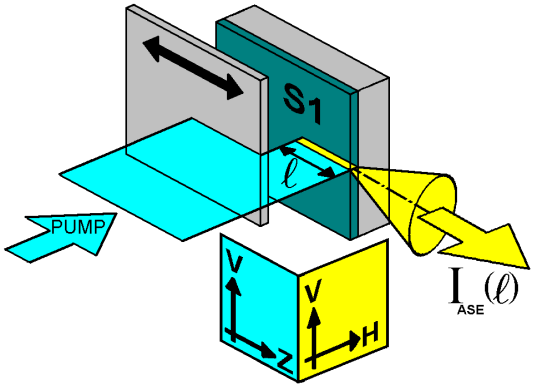

FIG. 1 (color online). Sketch of the VSL method with linearly polarized excitation (polarization labels are V and Z). Edge emission (I_{ASE}) is measured for two orthogonal polarization directions, labeled as V and H. The thick two-sided arrow indicates the directions of displacement of the movable slit which define the excited stripe of length ℓ. The sample is S1.

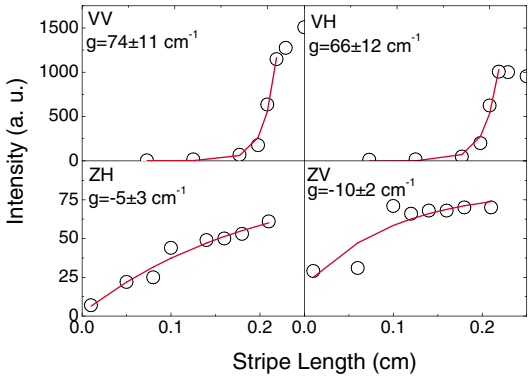

FIG. 2 (color online). PL peak emission intensity versus the illuminated stripe length for various polarization configurations. The numbers shown in the frames are the gain coefficient (g) deduced by the one-dimensional amplifier fit of the data. The observation wavelength was centered at 460 nm. The sample was S1. The excitation fluence was 111 mJ cm^{-2}. The first (second) letter of the label of each panel indicates the pumping (detection) polarization.

Our PS samples were fabricated by electrochemical anodization with an HF-based solution of (100)-oriented, B-doped Si wafers. The electrochemical etching was followed by thermal oxidation in air. The oxidation step transformed the PS sample into a porous quartz matrix containing ultrasmall Si fragments in the form of clusters or chains. We prepared two types of samples to perform different optical experiments. The first sample (S1) was a 5 μm-thick layer on crystalline Si substrate [18]. The second sample (S2) was a 100 μm-thick, freestanding sample. The anodization parameters were adjusted to achieve similar emission properties. The optical experiments have been performed with a time-resolved apparatus: pumping at wavelength $\lambda = 355$ nm was provided by the third harmonic emission of a Q-switched Nd-doped yttrium aluminum garnet laser (6 ns pulse duration, 10 Hz repetition rate, 95% Gaussian beam), whereas detection was performed with a streak-camera having 10 ps resolution.

The first evidence of gain and of its polarization dependence was obtained by using the variable stripe length (VSL) technique [19] with the setup described in [3] (Fig. 1).

The pumping beam was linearly polarized along either the V and Z axes (labeling conventions as in Fig. 1), and focused onto the S1 with a cylindrical lens to define an excited stripe whose length ℓ can be varied. Emission (I_{ASE}, where ASE stands for amplified spontaneous emission) is collected from the edge of the sample as a function of ℓ. For both polarizations of the pump, the linearly polarized PL components were separately analyzed (they are labeled as V and H). When the pumping beam is linearly polarized along the V direction, I_{ASE} grows exponentially with ℓ (Fig. 2), which shows that positive gain is present in the sample for these polarization conditions. When the pumping beam is linearly polarized along the Z direction, I_{ASE} shows a saturation behavior with ℓ due to the lack of positive optical gain (negative g value). This clearly shows that positive optical gain is present only when the pumping beam is linearly polarized along the V direction. Consistently, only for this pump beam polarization, the dependence of I_{ASE} versus the pumping fluence (ϕ_P) at a fixed long ℓ reveals a threshold behavior (second evidence of stimulated emission). Starting from $\phi_P \simeq 100$ mJ cm^{-2}, I_{ASE} increases superlinearly with ϕ_P (see Fig. 3).

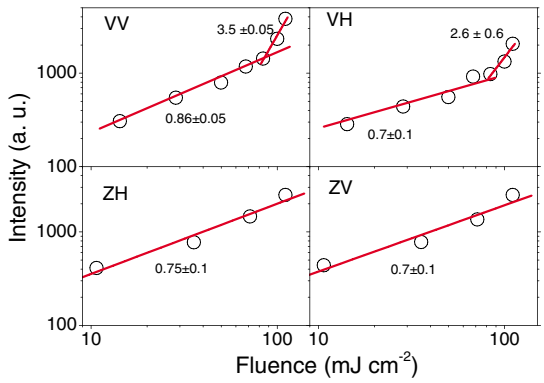

FIG. 3 (color online). Integrated edge emission intensity versus the incident fluence for various polarization configurations and for a long stripe length (2.5 mm). The numbers on the various curves are the exponents deduced by a power law fit of the data. The observation wavelength was centered at 450 nm for V excitation and at 460 nm for Z excitation (the observation bandwidth was 90 nm). The sample studied was S1. The first (second) letter of the label of each panel indicates the pumping (detection) polarization.

These two independent observations evidence stimulated emission from our sample and can be understood in the terms of randomly distributed light absorbing and emitting dipoles. For both V- and Z-polarizations, the pump beam excites most efficiently those dipoles aligned in the layer plane and having largest projections on to the electric field direction of the pumping light. Therefore, the dipole excitation pattern, as observed from the top of the layers, has a $\cos^2\theta$-like distribution. For V polarization, excited dipoles can reradiate photons equally in two directions: orthogonal to the electric field of the exciting light, i.e., along the layer (Z direction) and perpendicular to the layer (H direction). With VSL method, positive gain can be demonstrated if the intensity of the photoluminescence can buildup via stimulated emission along allowed Z propagation direction (along excitation stripe). As expected, the V-polarized component of the emission is the largest one, because dipoles aligned along this direction are preferentially excited. Since V-polarized photons have larger occupation numbers than H-polarized photons, the gain coefficient is larger and the exponent of the power law is higher, respectively (see Figs. 2 and 3). For the Z-polarized pump beam, only a small fraction of the excited dipoles can reradiate light in the Z direction of observation, emission intensity is weak and photon occupation numbers are small for V- and H-polarized PL components. Therefore no indications of gain were observed (Figs. 2 and 3).

The appearance of positive gain has a remarkable counterpart in the DOP (third evidence). For V-polarized pumping, the DOP increases with the pumping fluence (Fig. 4), which demonstrates that the linearly polarized component having larger occupation numbers ($I_{\parallel}$) grows faster with ϕ_P than with $I_{\perp}$. We note that the increase of DOP is observed also at $\phi_P \leq 100$ mJ/cm^2 where the gain coefficient is still negative; i.e., no population inversion has been achieved. Remarkably, the polarization-sensitive optical technique allows the observation of stimulated emission under these conditions. In the case of the Z-polarized pump, the polarization does not select a certain direction within the VH plane. Therefore, the DOP is equal to zero throughout the whole range of ϕ_P (Fig. 4). We believe that it is useful to envision the increase of DOP as a "polarization line narrowing," i.e., a narrowing of the emission over the polarization space (which has only two points, $\parallel$ and $\perp$), physically similar to the more familiar line narrowing over the continuum space of wavelengths. As such, this effect is a strong indication of stimulated emission and is robust to experimental artifacts. Readers experienced with the VSL technique know the care needed [20,21].

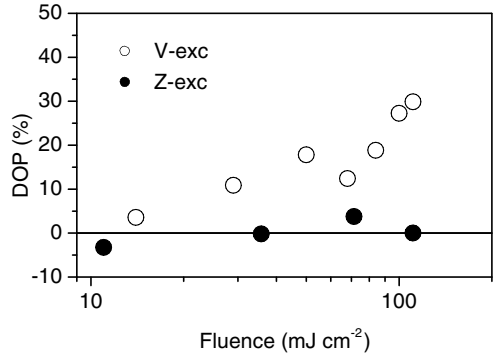

FIG. 4. The DOP of edge photoluminescence for a long (2.5 mm) stripe length, as a function of pumping fluence for vertically polarized (open circles, V-exc) and horizontally polarized (solid circles, Z-exc) excitation.

We have observed similar polarization line narrowing also in a reversed pumping and detection arrangement, as shown in the inset of Fig. 5. At low ϕ_P, the DOP for V polarization of the pump is about 15% due to the polarization memory of oxidized PS [10]. True backscattering PL experiments from the edge confirm the preferential orientation of the emitting dipole along the H axis. Consistent with the ϕ_P threshold of Fig. 3, starting from about 100 mJ cm^{-2}, the DOP increases with ϕ_P but, as expected, only when the sample is excited by the V-polarized pump. We interpret this result as a further independent demonstration of stimulated emission with propagation direction normal to the plane of the film (H propagation). Again, because the H-polarized pump does not select a certain direction within the VZ plane, DOP of PL emission is equal to zero for all pumping intensities used. This fact again confirms the possibility to tune stimulated emission by the polarization state of the pumping photons.

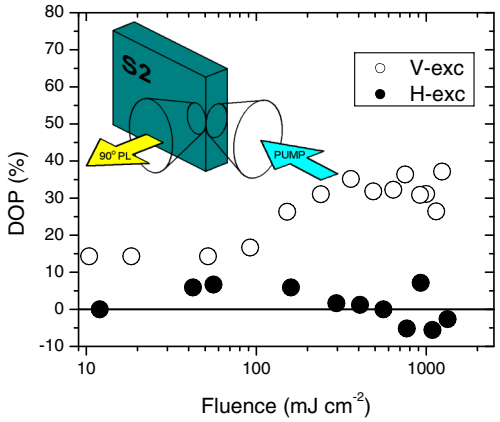

FIG. 5 (color online). The DOP of photoluminescence as a function of pumping fluence, under edge excitation and front collection. The excitation beam was linearly polarized (labels V and H follow the convention displayed in Fig. 1). The experimental setup is sketched in the top left corner, where focusing, collecting, and polarizing/analyzing optics are not shown for clarity. The PL signal was collected at 90° to the sample plane at the edge border. The sample was the free-standing sample S2.

To conclude, we demonstrated that local optical anisotropy of absorption/emission in heavily oxidized porous silicon allows one to realize polarization-sensitive stimulated emission and optical gain measurements. Under these conditions the polarization of emission and its propagation direction are shown to be crucial for net optical gain observation: by using polarized light we can increase the occupation number of a given photon mode and so define the polarization state of the stimulated emission process. It is necessary to mention that the measured high level of DOP implies a geminate character of recombination; i.e., absorbing and emitting states have a deeply correlated nature. On one side, this might requalify three-level schemes for the stimulated emission in ultrasmall heavily oxidized Si clusters. However, it is also compatible with four-level schemes. In the latter case, the physical origin of such correlation would reveal that the morphology of whole cluster is determinant for the optical transition, even though the involved states are introduced by localized surface bonds. In addition to the local optical anisotropy discussed in this Letter, another class of Si-nc systems which are formed in a superlattice structure could show polarization dependent gain due the form birefringence of the optical constant[22]. Finally, a polarization-resolved technique allows one to observe stimulated emission even if optical losses hinder the observation of net optical gain.

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