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# On relation between the 1.5 μm Er-related emission and 9 μm vibrational modes of oxygen in silicon

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ABSTRACT

We demonstrate that excitation of $Er^{3+}$ ions embedded in crystalline silicon is effectively quenched when vibrational modes of interstitial oxygen are activated. In a two-color pump–probe experiment with a free-electron laser, we show that the 1.5 μm Er-related photoluminescence diminishes as the probing beam scans through the relevant 9 μm absorption band. Making use of time resolution of the experimental set-up, we investigate temporal aspects of this effect.

## 1. Introduction

Doping with Er continues to draw attention as a way to improve optical properties of crystalline Si (c-Si) [1]. This follows from the conceptual simplicity as well as from the fact that doping with Er, realized by implantation or during growth, is fully CMOS compatible. This very important condition is much more difficult to achieve by other routes towards enhancement of optical activity of Si, such as introduction of Si nanocrystals [2] or formation of Er silicides, among others. Until the present, large progress was made in both material development and in understanding of physical mechanisms governing excitation and de-excitation of $Er^{3+}$ ions embedded in c-Si matrix [3–9]. Also practical devices have been demonstrated [10]. Recently, we have reported on the preferential formation of a particular type of Er-related optical center [11,12]: its homogeneous and ultra-narrow linewidth renewed hopes for realization of optical gain in c-Si:Er.

Nevertheless, important problems remain, with the most prominent one being the poor thermal stability of Er emission: intensity of photo- and electroluminescence of c-Si:Er exhibits strong thermal quenching already above liquid–nitrogen temperature. Possible origin of this effect has been suggested in terms of:

(1) thermally activated, phonon-assisted excitation reversal—the so-called back-transfer process [13] whose efficiency is enhanced due to the long radiative lifetime of the excited state of $Er^{3+}$ ion,
(2) auger process of energy transfer to free carriers thermally liberated from shallow traps, and
(3) dissociation of bound exciton state mediating the excitation.

It is clear that the problem of thermal stability of Er emission has to be solved in order to enable efficient room-temperature photonics based on c-Si:Er. For that, comprehensive understanding of energy transfer processes is necessary.

It is well established that thermal stability (as well as the level of optical activity) of Er in c-Si can be considerably enhanced by co-doping with oxygen [3]. While detailed origin of this effect is not really clear, microscopic models of optically active Er-related centers in Si postulate multiple O atoms in the direct surrounding of $Er^{3+}$ ions. In particular, the model of the preferentially formed Er center presented in Ref. [14] featured 8 oxygen atoms in the usual puckered bond-centered sites surrounding an $Er^{3+}$ ion in a high-symmetry interstitial position. In that case, participation of O was concluded from SIMS measurements, which revealed high oxygen concentration in the Er-doped layer. We recall that in the past, also EXAFS experiments reported on average 6 oxygens per one $Er^{3+}$ ion [15] in Er-doped oxygen-rich c-Si.

## 2. Experimental results and discussion

In the current study, we investigated the behavior of the 1.5 μm Er-related emission band upon activation of vibrational modes of interstitial oxygen. The experiments have been performed at

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$T = 4$ K on a multinanolayer Si/Si:Er structure where the aforementioned preferential formation of a single Er-related optical center is realized—for details see Ref. [11]. The sample is excited by a band-to-band pump pulse from the Nd:YAG laser, and then, with a tunable delay, by a mid-infrared free-electron laser (FEL) pulse, whose wavelength is scanned in the region of the 9 μm vibrational band of oxygen [16]. The result of the two-color (2C) experiment is depicted in Fig. 1. In the vertical axis we plot the percentage of Er-related PL intensity left after the quenching provoked by the FEL pulse normalized to the PL intensity recorded without FEL excitation. We note that the spectral characteristics of the quenching effect reproduce very well the 9 μm absorption band related to local vibrational modes of Si–O–Si "molecule".

Fig. 2 illustrates temporal characteristics of this resonant quenching of Er PL induced by the activation of Si–O–Si vibrational mode.

Fig. 2a shows the magnitude of the effect, with FEL set to $\lambda = 8.84$ μm, as a function of delay time $\Delta t$ between the pump (Nd:YAG) and the probe (FEL) pulses. We note two important features of the quenching effect:

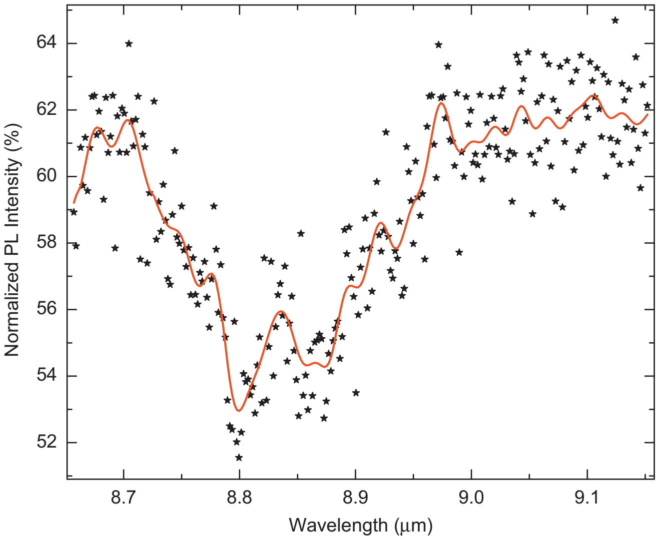

**Fig. 1.** Er PL intensity left after IR excitation, normalized to the intenisity recorded without IR excitation, in function of the IR excitation wavelength. In addition to the wavelength independent quenching (of approximately 37%) a clear resonant effect (quench value ~48%) can be distinguished. Its spectral characteristics are coincident with the well-known 9 μm vibrational band of interstitial oxygen.

- Firstly, the reduction of PL intensity commences simultaneously with the onset of the FEL pulse. The experimentally recorded decay time ($\tau_Q \approx 60$ μs) is clearly longer than the detector response time of $\tau_{PMT} \approx 30$ μs and therefore reflects the additional non-radiative decay of excited Er induced upon FEL illumination.
- Secondly, the quenching level is independent of the delay time, being determined exclusively by the number of IR photons in the FEL pulse. This confirms that FEL introduces a PL quenching process with the specific rate, and therefore the quench magnitude is directly proportional to number (concentration) of excited $Er^{3+}$ ions available at that particular moment.

It is interesting to note that the rate of decrease of luminescence after FEL excitation changes when different FEL wavelengths are applied. Fig. 2b shows three different PL transients for FEL at different wavelengths (all fired at $\Delta t = 100$ μs after the YAG excitation), namely 8.84, 7.5 and 7 μm. It is clear that two different components are present in the decay, a fast one changing with the FEL wavelength and a slow one, equal for all of them. The fast decay time is ~60 μs for 8.84 μm, i.e. for the maximum of the quenching effect depicted in Fig. 1 and increases to ~100 μs for FEL set to 7.5 and 7 μm. The increase of decay time for FEL wavelengths away from resonance is a further confirmation for the existence of the resonant quenching (activation of Si–O–Si vibrational mode) superimposed on nonresonant quenching, most probably due to lattice heating by two-phonon absorption.

A further difference of the quenching effect on FEL wavelength can be found in Fig. 3, which shows quenching of Er PL for the three chosen FEL wavelengths (8.84, 7.5 and 7 μm) for a large time difference between the pump and the probe pulses. We again conclude that the quench changes drastically when FEL wavelengths move away from resonance. When the FEL pulse is applied before the pump—negative delay times in Fig. 3—the quenching is due to the effective higher temperature of the matrix. The higher "on resonance" quench we associate then with the increase of absorption due to oxygen. At the same time, since the PL signal due to exciton recombination is independent of the FEL wavelength (not shown) we conclude that the enhanced photon absorption takes place in the Er-doped layer: in that way the "effective" matrix temperature experienced by $Er^{3+}$ ions, and affecting their emission, must be considerably higher than the

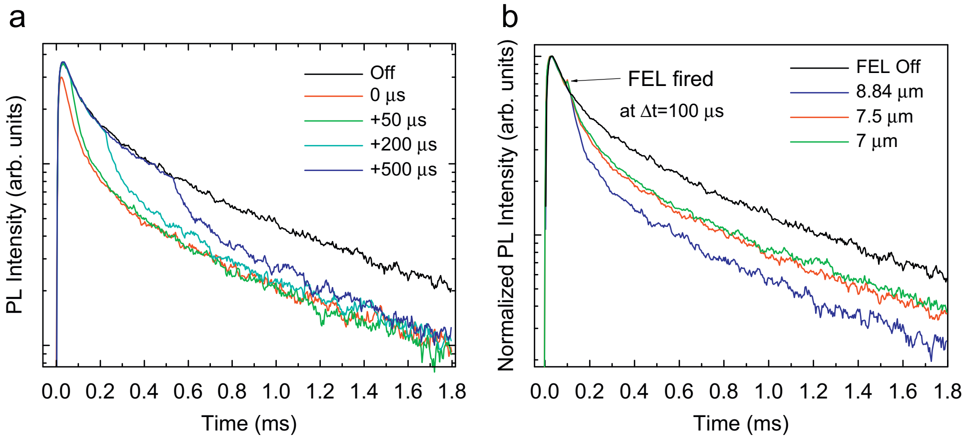

**Fig. 2.** (a) Er PL transient for different FEL–YAG delay times (FEL set to $\lambda = 8.84$ μm) and (b) normalized Er PL transients for FEL at three different wavelengths of 8.84, 7.5 and 7 μm, fired at $\Delta t = 100$ μs.

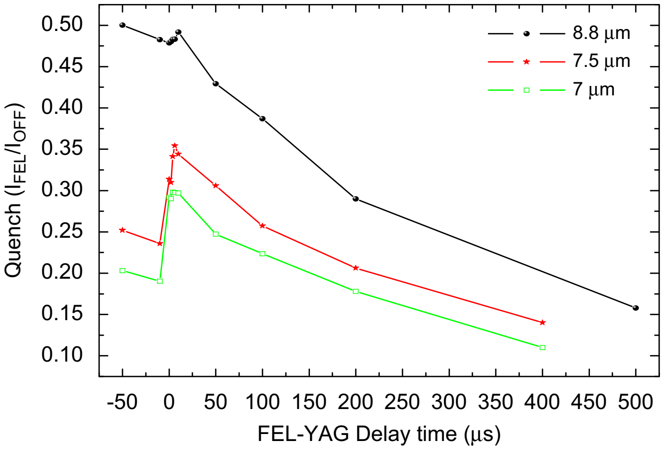

**Fig. 3.** Quenching of Er PL in function of the delay time between FEL and YAG pulses for three different FEL excitation wavelengths.

overall heating of the bulk of the sample, where exciton recombination takes place. As the negative delay time $\Delta t$ approaches coincidence of the two pulses, the quenching effect increases—reflecting a shorter cooling time between the pulses, and a higher matrix temperature in the moment of excitation. When the two pulses start to overlap—$\Delta t = 0$—an additional quenching appears which grows as the "effective" duration of the FEL pulse increases—$\Delta t \approx 0$–$10\,\mu$s. We suggest that in this case, the quenching effect arises due to direct perturbation of the Er excitation process by MIR radiation, independent of the matrix temperature effect. For still longer delays the quench decreases, in fact monotonically following the decay rate of Er PL. This indeed can be expected as the result of (local) matrix temperature increase by FEL. We note that, in contrast to the overall effect, the additional quenching appearing upon coincidence of pump and probe is clearly less pronounced when FEL is set in resonance with oxygen vibrational band. While this effect needs to be further investigated, a possible speculative explanation could be that in this case the intense FEL pulse leads to (partial) saturation of 9 µm vibrational modes of oxygen atoms in direct vicinity of $Er^{3+}$ ions, partially blocking in that way the back-transfer process [13] in which phonons of that wavelength (energy of ~150 meV) need to be dissipated. This attractive possibility will be investigated in the future by looking at the lifetime of oxygen vibrational modes in presence of Er dopants.

## 3. Conclusions

The current research establishes a direct link between intensity of emission of $Er^{3+}$ in Si and oxygen doping. Based on the combined results obtained in 2C spectroscopy and IR absorption, we conclude that the 150 meV activation energy commonly observed to govern thermal stability of Er emission, corresponds to the Si–O–Si vibrational mode whose activation increases the "effective" temperature of the excited $Er^{3+}$ ions promoting in this way non-radiative recombination by the back-transfer process.

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