Comment on "Stimulated emission from trap electronic states in oxide of nanocrystal Si" [Appl. Phys. Lett. 92, 221910 (2008)]

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In a recent Letter, Huang *et al.*¹ reported on stimulated emission from oxide states in laser-ablated, oxidized, and annealed silicon. The authors claim that (exact terms) "this stimulated emission comes from the nanostructures on porous silicon ... controlling the time of annealing can produce a good coherent emission." This statement is based solely on the observation of a doublet of narrow lines at 694 and 692 nm in photoluminescence spectra at room temperature. In spite of their claim, the authors give no further evidence of stimulated emission or coherence properties of the observed emission.

First, the authors ignore totally recent experimental works by other authors reporting on stimulated (or amplified spontaneous) emission in silicon nanostructures (for a review, see e.g., Ref. 2), which differ considerably from the results displayed in Ref. 3. Further, they do not explain properly how stimulated emission could arise from a photoexcited spot of a very limited size (1 μ m spot in a Renishaw micro-Raman system). Most importantly, the narrow appearance of the emission lines itself cannot be taken as an evidence of the stimulated emission. Other possibilities must be excluded, namely, the presence of optically active impurities. One of the most important impurities is Cr³⁺ ion that gives the deep red color to corundum (sapphire) Al₂O₃, known as ruby crystal. This material was used by Maiman⁴ to demonstrate the first laser.

In Fig. 1 we demonstrate that the ruby photoluminescent (PL) emission spectrum exactly matches the spectrum of hypothetical stimulated emission of defect states in Fig. 1(b) of the commented paper. Our PL measurement was done on ruby samples (0.01% of Cr₂O₃ in Al₂O₃, Crytur Ltd., Czech Republic) at room temperature, excited with the 514 nm line of an Ar-ion laser. Photoluminescence was dispersed by a double-grating monochromator (HRD-1, Jobin Yvon) and detected by a RCA 31034 photomultiplier connected to a lock-in amplifier. The spectrum shows clearly the well-known *R* lines (${}^{2}E \rightarrow {}^{4}A_{2}$ transitions) of ruby as well as a weak emission at slightly longer wavelength—perfectly matching results with Huang *et al.*²

Concerning the model proposed by Huang *et al.* we note that there are various optically active defect centers in SiO₂ studied in literature (see, e.g., the review⁵) but none of them, to our knowledge, is able to produce a narrow emission spectrum around 694 nm, especially at room temperature and in amorphous SiO₂. Besides, the density of states of the model defects calculated by Huang *et al.*² shows very wide bands



FIG. 1. Room temperature (spontaneous) PL spectra of the ruby crystal excited at 514 nm. The inset shows a detail of the R-line doublet.

[note: the axis in Figs. 2(b), 2(d), and 3(b) have no label, but the scale is probably energy in eV] and the authors give no explanation how it is related to the observed spectrum.

In conclusion, we have demonstrated that the narrow photoluminescence spectrum observed by Huang *et al.* can be simply interpreted as the rubylike emission of Cr^{3+} ions that contaminated the studied sample. In order to prove their interpretation as "coherent stimulated emission" authors must show some of the typical features of stimulated emission, for example, intensity dependence of PL with a super-linear increase in emission intensity for pump power exceeding a threshold level, narrowing of the PL spectra for pumping above threshold, or increased directionality of stimulated emission. In our opinion, the observations reported in Ref. 2 by no means provide sufficient grounds to be interpreted as evidence of stimulated emission in silicon nanocrystals.

¹W. Q. Huang, F. Jin, H. X. Wang, L. Xu, K. Y. Wu, S. R. Liu, and C. J. Qin, Appl. Phys. Lett. **92**, 221910 (2008).

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