

# Hot photoluminescence or Raman scattering?

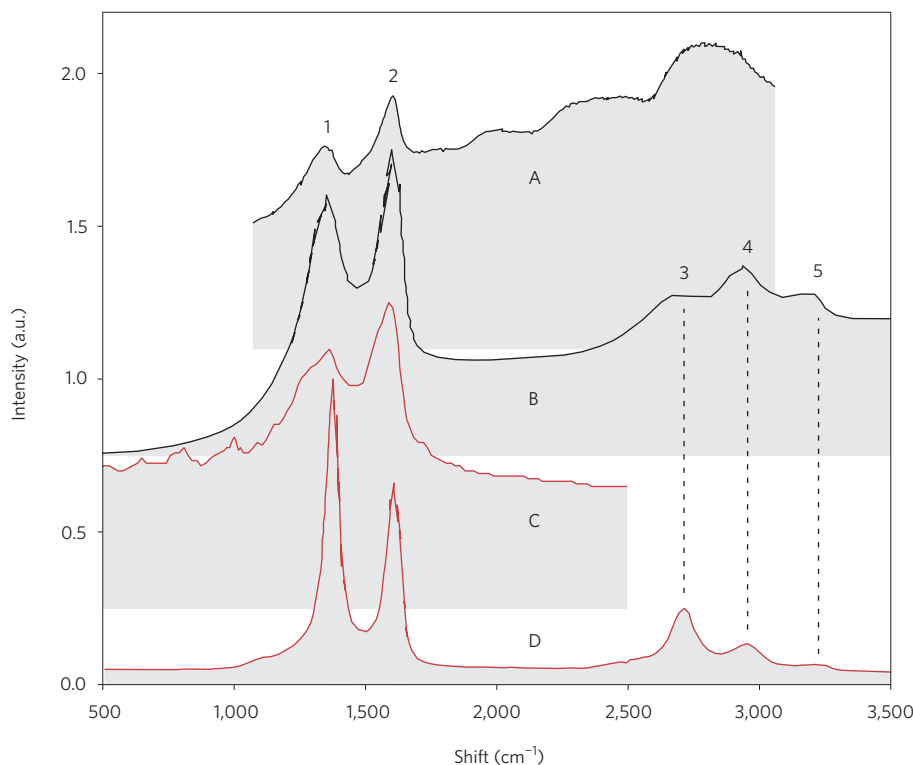
**To the Editor** — In a recent Letter in *Nature Photonics*, Cho *et al.*<sup>1</sup> claim to observe hot photoluminescence from silicon nanowires coated with silver. We believe, however, that their measured spectra are instead probably due to surface enhanced Raman scattering (SERS) from carbon contamination.

Several aspects of the measurements made by Cho *et al.*<sup>1</sup> are similar to SERS measurements. The external efficiency of their device was very low (the collected power was  $\sim 0.8$  nW for an incident power of 5 mW, giving an external efficiency of  $\sim 10^{-7}$ ); the device geometry was very similar to that of known SERS-active devices<sup>2</sup>; and grain boundaries in the

silver layer or sharp metal points formed at the contact line between the nanowire and the substrate could provide the field enhancement structures necessary for SERS. Most importantly, on changing the wavelength of the excitation laser, they found that the most pronounced spectral features (peaks 1 and 2 in Fig. 3a in ref. 1) shift in wavelength to maintain constant energy spacing relative to the excitation laser (with excitation energies of 2.708 eV and 2.331 eV, respectively). Spectral features that shift in this way are a hallmark of Raman scattering. In the theory proposed by Cho *et al.*<sup>1</sup>, these features result from peaks in the phonon density of states of Si that lead to enhanced

electron–phonon scattering and hot luminescence. However, this theory links specific wavevectors in the electronic and phononic band structure of Si that correspond to definite energies, irrespective of the energy of the excitation laser (thereby yielding the proposed hot luminescence bands at 2.51 eV, 2.34 eV and 2.18 eV; see Supplementary Fig. S10 in ref. 1). It is therefore unclear from their model how these features could shift with the energy of the excitation laser. In addition, the energies of two of these bands exceed the excitation energy used in some cases (2.331 eV; see Supplementary Fig. S9 in ref. 1).

A more parsimonious explanation is that the data of Cho *et al.*<sup>1</sup> result from SERS of amorphous carbon contamination. The agreement between their data (plotted in units of relative wavenumbers) and the Raman spectrum of amorphous carbon<sup>3–7</sup> is excellent (Fig. 1). Carbon contamination has been a long-standing (decades) problem for SERS measurements<sup>4,6,7</sup> and, as noted by A. Otto, “apparently much less than a monolayer of amorphous carbon on silver yields a strong Raman signal”<sup>7</sup>. However, Cho *et al.*<sup>1</sup> described no special precautions to avoid carbon contamination. In addition, the polarization dependence they observed is in agreement with what would be expected from SERS<sup>2</sup>. All of these factors combine to suggest that the spectra observed by Cho *et al.*<sup>1</sup> is due to SERS from carbon contamination. □



**Figure 1** | Comparison of spectra. A is a spectrum taken from Supplementary Fig. S9 in Cho *et al.*<sup>1</sup> for an excitation laser wavelength of 532 nm; B is taken from Fig. 2a in Cho *et al.*<sup>1</sup> with 457.9 nm excitation; C is the surface enhanced Raman scattering spectra of amorphous carbon contamination (taken from Fig. 1a in ref. 4, © 1978 Elsevier; 488 nm excitation); and D is a conventional Raman spectrum of ‘glassy’ carbon (taken from Fig. 1 in ref. 5, © 1979 APS; 488 nm excitation). Peaks 1–5 are labelled according to Fig. 3a in ref. 1. Traces were digitally extracted from published data and are shifted vertically for clarity. The y axis has arbitrary units (a.u.).

## References

1. Cho, C.-H., Aspetti, C. O., Park, J. & Agarwal, R. *Nature Photon.* **7**, 285–289 (2013).
2. Yoon, I. *et al.* *J. Am. Chem. Soc.* **131**, 758–762 (2009).
3. Tuinstra, F. & Koenig, J. L. *J. Chem. Phys.* **53**, 1126–1130 (1970).
4. Otto, A. *Surf. Sci.* **75**, L392–L396 (1978).
5. Nemanich, R. J. & Solin, S. A. *Phys. Rev. B* **20**, 392–401 (1979).
6. Tsang, J. C., Demuth, J. E., Sanda, P. N. & Kirtley, J. R. *Chem. Phys. Lett.* **76**, 54–57 (1980).
7. Otto, A. *J. Raman Spectrosc.* **33**, 593–598 (2002).

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