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Black-body emission from nanostructured materials

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Abstract

Photoluminescence (PL) experiments on materials of low thermal conductance can cause black-body emission from the sample even at low intensities of laser excitation. This thermal emission may be misinterpreted in terms of quantum emission. Although the quantum origin of most radiative emissions in nanostructured materials such as porous silicon is well established, we show in this paper that SiC nanoparticles and mechanically milled Si do exhibit thermal emission at typical excitation intensities for PL measurements provided the samples are under vacuum. An Si membrane was also investigated and the fact that it did not emit black-body radiation is explained with a simple analysis of the heating in materials of reduced dimensionality.

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1. Introduction

Quantum confinement of carriers in nanostructured materials leads to a high quantum efficiency of the radiative recombinations as well as to an increase of the optical band gap. In the case of silicon, this effect opens the possibility of light-emitting devices in the visible region [1]. With this aim, a variety of structures have been tested: porous silicon [2], silicon precipitates in SiO_2 matrices [3], powders [4] and nanocrystalline layers. In some cases, the PL of these structures is analysed in conditions of low thermal conductance, so that an important local heating due to the laser beam can be expected.

In a recent work [4] we have demonstrated that the intense radiative emission of silicon nanoparticles grown by plasma enhanced chemical vapour deposition (PECVD) was not luminescence but black-body emission. However, if one interprets it as being PL it appears extraordinary. Namely: (a) the dependence with laser power is supralinear and (b) it is quenched as the gas pressure increases. Apart from our own work, we have found in the literature several papers where the authors are faced, presumably, with the same effect. Savin et al. [5] report a supralinear dependence of the radiation emitted by laser-ablated porous silicon, and

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Shen et al. [6] find a pressure quenching of the radiative emission from mechanically milled Si and SiO_2 powders.

The present paper reports on a work undertaken with the aim to show that in the usual conditions of PL experiments, materials and structures with reduced thermal conductance can emit measurable black-body radiation.

2. Experiment and results

Samples were placed inside a chamber where the pressure could be controlled from 0.1 Pa to atmospheric pressure. The excitation source was an Ar laser working at multiline mode. Under the usual conditions, the laser on the sample surface reached a maximum power of about 500 mW. The emitted radiation was analysed with a 0.5 m monochromator and detected with a GaAs photomultiplier whose cut-off wavelength in the infrared was 1 μm. The spectra were corrected by the response of the system.

2.1. Black-body emission from mechanically milled Si

A piece of monocrystalline Si was manually milled to powder of particles smaller than 0.1 mm. Under vacuum the powder emitted an intense radiation that disappeared at atmospheric pressure. Its spectral shape is shown in Fig. 1. It consists of an unstructured band that increases monotonically up to the detector limit in the near infrared. The inset of Fig. 1 shows the supralinear dependence of the emitted intensity with laser power. To demonstrate that it is indeed black-body emission, we follow the analysis developed in our previous work [4] devoted to Si nanoparticles grown by PECVD.

First of all, the quenching of the radiative emission with the gas pressure is easy to understand as the gas molecules offer an alternative path to dissipate the energy supplied by the laser. In other words, the heat conduction through the gas diminishes the particle temperature and, consequently, the thermal radiation. In the case of Si nanoparticles we observed an exponential dependence with the gas pressure which is also found in

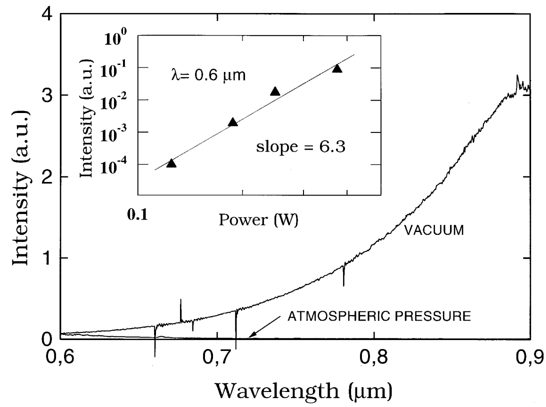

Fig. 1. Radiation emitted by mechanically milled Si when heated by a laser beam. The inset illustrates the high supralinear behaviour.

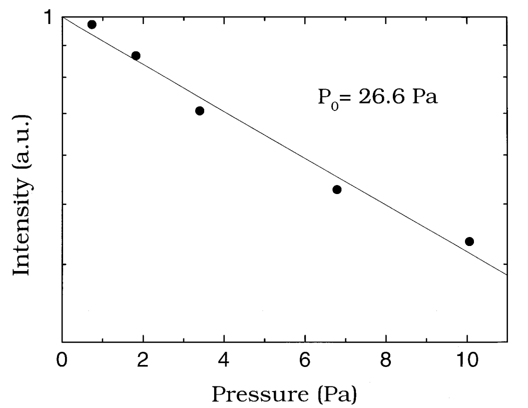

Fig. 2. Quenching of the thermal radiation emitted by mechanically milled Si when the gas pressure is increased. The behaviour can be fitted to an exponential dependence, $I_e = I_0 \exp(-P/P_0)$ (note that intensity values are plotted in logarithmic scale).

mechanically-milled Si (Fig. 2). In Fig. 3 we can see that the emitted intensity, I_e, in logarithmic scale is proportional to the fourth root of the excitation power, P. This relationship follows directly from the Planck distribution

$$I_e \propto \frac{1}{1+\exp(hc/\lambda kT)} \approx e^{-hc/\lambda kT} \tag{1}$$

(h and k are the Planck and Boltzmann constants, respectively, and c is the speed of light) if we consider that, in the absence of dissipation mechanisms

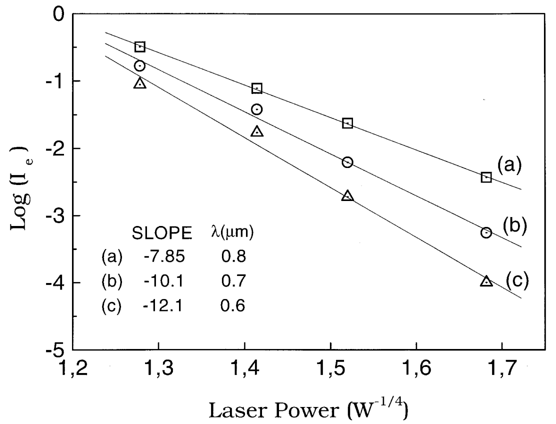

Fig. 3. Intensity emitted by milled Si plotted according to the dependence expected for a black-body thermal emission.

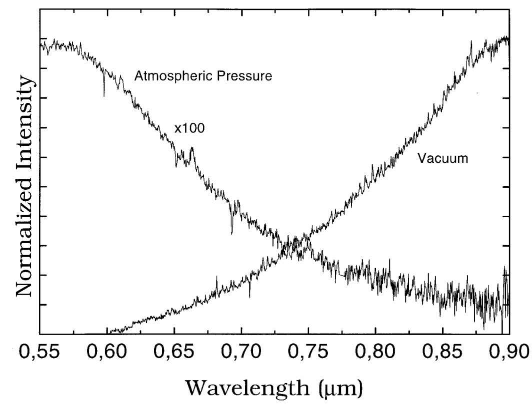

Fig. 4. Radiative emission of SiC nanoparticles. The luminescence band detected at atmospheric pressure is hidden by the more intense thermal radiation that is observed under vacuum.

other than thermal radiation, the temperature, T, according to the Stephan–Boltzmann law will be proportional to $P^{1/4}$. Furthermore, the expected proportionality of the slope with λ^{-1} (Eq. (1)) is followed within the experimental accuracy.

Finally, the temperature of the particles can be calculated from the slope of Fig. 3 [4]:

$$T = -\frac{1}{\text{slope}}\frac{\lambda k}{hc}P^{1/4}. \tag{2}$$

This formula gives a temperature that increases from 830 to 1090 K as the power varies from 125 to 375 mW.

2.2. Radiative emission from SiC nanoparticles

SiC nanoparticles were obtained in an RF reactor from methane and silane precursor gases. These particles are spherical with diameters below 200 nm. They are amorphous and highly hydrogenated [7].

In this case, the radiative emission had two distinct components. As shown in Fig. 4, in vacuum a continuous emission band appeared which was similar to that observed in milled Si. It disappeared as the pressure increased and showed the typical supralinear dependence with laser power. So, its origin is simply the thermal radiation of the particles. At atmospheric pressure, a band located at the visible spectral region remained. Its intensity did not depend on gas pressure and was hidden at vacuum by the much more intense blackbody radiation. Its dependence with laser power was linear. We conclude that it corresponds to luminescence that arises probably from recombination of carriers located at the band tails of the conduction and valence bands. This conclusion is supported by the large width of the band and its energy similar to the band gap of cubic SiC [8].

2.3. Experiments with other structures

We have tried to reproduce the experiments described in Ref. [5], where the supralinear dependence found in laser ablated porous silicon is a clear indication of its thermal origin. The result was negative: no radiative emission has been observed. Anyway, the structure of our samples could be very different from that of Ref. [5]. We do not know the experimental conditions in that work (possibly a very high laser power).

Finally, an Si membrane has been investigated. It was obtained by chemical etching a square of $1\times 1\ \text{cm}^2$ on a thick wafer until a thickness of 18 μm was reached. Although the laser was focused at its maximum power (375 mW), no radiation could be detected. The heating in this simple geometry can be easily calculated. The analysis given in the next section indicates that in order to observe thermal radiation from such a membrane a smaller thickness is needed.

3. Discussion: laser heating of reduced-dimensionality structures

The aim of this section is to establish simple criteria in order to evaluate in which of the cases the heating due to the laser beam excitation in PL experiments is high enough to observe black-body radiation.

A detailed analysis has been already done in the case of particles [4]. The thermal conductance between them is virtually zero implying that this is the case in which the highest heating can be expected. The thermal emission from particles [4] and that from the materials presented in this paper were not measurable at atmospheric pressure. Then, we can be sure that this will be also the case for structures of higher thermal conductance. So, black-body emission should be only expected at vacuum.

Consider now a circular plate or membrane of radius r_M and thickness Δx that is heated at its centre by a laser beam with section of radius R in contact with a heat sink at its contour. Neglecting the axial variations, the radial temperature distribution can be calculated by simple integration of the equation of heat conduction. The temperature at the centre turns to be

$$T(0) = T_\infty - \frac{Q_{abs}P}{4\pi\Delta x k}\left(1 + 2\mathrm{Ln}\frac{r_M}{R}\right), \qquad (3)$$

where T_∞ is the temperature of the heat sink, Q_{abs} the fraction of the laser power that is absorbed and κ the heat conductivity. If we apply Eq. (3) to our membrane of silicon ($\kappa \approx 0.6$ W/cm K, $r_M \approx 0.5$ cm, $\Delta x = 15$ μm, $P \approx 375$ mW and $Q_{abs} \approx 0.6$) it results in a heating 140 K above room temperature. According to the experiments with Si nanoparticles, this temperature is slightly too low to emit a measurable thermal radiation (see Fig. 7 in Ref. [4]). However, a reduction in thermal conductivity or thickness can strongly increase the heating. Such conditions can be encountered in experiments with self-standing porous silicon, where in the absence of substrate, the thickness will be below 1 μm and the effective thermal conductivity in the plane will be highly reduced due to porosity.

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