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EVIDENCE OF ENERGY ENHANCEMENT IN PHOTOLUMINESCENCE EMISSION FROM GE NANOCRYSTALS

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ABSTRACT. We report on the large photoluminescence emission (PL) obtained in germanium nanocrystals of about 100 nm, in porous deposition. Investigating Raman and PL spectra in such closely spaced agglomerates, we discovered that photoluminescence emission can be obtained with energy yield enhancement with respect to the laser beam used for the Raman detection (He-Ne laser, $\lambda = 632.8$ nm). We demonstrate that such crystalline germanium nanoparticles can undergo a local high temperature increase with consequent stimulation of photoluminescence in the visible range. With respect to the bulk crystal, we found: i) a high gain of Raman yield larger than a factor 10; ii) photoluminescence emission increased up to a factor 100 between 750 K and 520 K; iii) radiation emission with energy yield enhancement with respect to the red laser light. A simple explanation is discussed in the light of the Ge specific energy bands both of electrons and phonons. This result is of particular importance for applications in optoelectronic devices.

> *"Quocirca et absentes adsunt ....et mortui vivunt;*
> *tantus eos honos, memoria, desiderium prosequitur amicorum."*
> *Cicero, De amicitia, 23.*

1. Introduction

The photoluminescence emission of semiconductor nanostructures are today widely studied for their technological applications in optoelectronics. Several review articles describe the present state of this research, not only for silicon quantum dots (Belyakov *et al.* 2008; Hernández *et al.* 2008; Timmerman *et al.* 2011; Barbagiovanni *et al.* 2014) but also for other semiconductors such as Ge or SiGe in nanostructural configuration (Riabinina *et al.* 2006; Lieten *et al.* 2012; Barbagiovanni *et al.* 2014). At present the efforts dedicated to the preparation and characterization of semiconductor nanostructures require high resolution technology.

However, often the size reduction, although quite expensive for the enormous costs necessary for the corresponding realization, is not mandatory (Faraci *et al.* 2013b; Mannino

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This paper is dedicated to the memory of Prof. Gaetano Giaquinta (1945–2016)

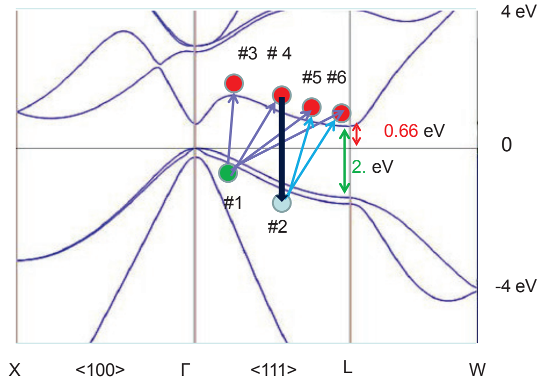

FIGURE 1. (Color online) Electron energy bands for bulk germanium along different wave vector directions. Clearly sketched, typical direct (# 1 - # 3) and indirect (# 1 - # 4,5,6) possible electron transitions from valence to conduction band, allowed by the laser energy (1.95 eV), with the eventual contribution of a phonon at temperature larger than 300 K. Direct emission, with energy amplification, larger than the laser radiation, is sketched, by a black arrow, from #4 electron state to # 2 hole state.

et al. 2015). In fact, some important properties of the semiconductor can be developed also in a range, such as the submicrometer size, very simply affordable. In addition, this size range has also the advantage of excluding possible quantum confinement contributions (Faraci *et al.* 2009, 2013a), which could be superimposed to or mixed with the specific physics effect investigated. A valuable spectroscopic tool in the optical field is represented by the first order Raman effect, since it can provide non destructive information on the acoustical and/or optical branch phonons at $q \approx 0$ (Faraci *et al.* 2006; Gibilisco *et al.* 2010). Actually, the phonon distribution as a function of the temperature dramatically influences the electron indirect transitions in a semiconductor. In fact, electron-hole excitations, phonon-assisted, can decay with photoluminescence emission in the visible and/or infrared range, according to the electron energy dispersion curves. However, we argue that Ge along the $\langle 111 \rangle$ direction has a conduction band curve separated by about 2 eV from the correspondent valence band (see Fig.1). This value can be tuned with the He-Ne laser energy at 632.8 nm (1.95 eV), in such a way to obtain indirect or direct electron transitions particularly strong at high temperature. This in turn can produce the following important consequences:

i) a higher Raman yield with respect to the bulk crystal;
ii) a strong PL decay in a range of wavelength higher than 633 nm;
iii) a strong photoemission yield enhanced even at energy higher than 2 eV.

2. Results and discussion

Here, we report, for the first time, on these effects obtained from germanium nanocrystals about 100 nm in size, deposited in porous configurations. Recently (Faraci *et al.* 2013b), microRaman spectra observed in faceted grains of silicon nanostructures, formed by octahedral nanocrystals, gave high local temperature increase under the laser beam. We have been able to obtain this effect also in Ge nanograins agglomerates (GeNA) of irregular form and shape, and thanks to the particular Ge energy bands, it was possible to stimulate not only a high photoluminescence emission in the visible range but also an energy augmented yield around the laser frequency used for the Raman detection. We used germanium since the energy gap between the valence and conduction band along the $\langle 111 \rangle$ direction is very close to the He-Ne laser energy (1.95 eV); furthermore, the TO phonon of germanium has an energy of 37 meV implying Stokes and anti-Stokes energy values respectively 1.915 and 1.99 eV. A thermal contribution can also be considered in the order of 50 meV at 600 K.

Ge crystalline samples as powder nanoparticles were purchased by American Elements Inc., with a maximum size of 1 μm. After reduction to about 100 nm nanoparticles, by means of micro-machining, a closely spaced deposition of such particles on a quartz substrate was performed.

Micro Raman spectroscopy was used for detecting the transversal optical (TO) vibrational peak situated for bulk Ge at 300 cm^{-1}, at room temperature (300 K). Raman spectra were taken in backscattering geometry with a HORIBA Jobin-Yvon system, equipped with Olympus BX41 microscope. He-Ne laser radiation at a wavelength of 632.8 nm is focused to a spot size of the order of 1 μm by a 100x objective. The laser power on the sample was about 6 mW, and a 550 mm focal length spectrometer with 1800 lines/mm grating was used. The apparatus is equipped with an optical microscope allowing to check the microspot under investigation.

A typical image of our samples is reported in Fig. 2, with typical size about 100 ±50 nm.

The Raman spectra relative to each sample can be distinguished according to the TO peak position, linewidth, and Raman intensity. As pointed out above, also the local temperature can be monitored by measuring the ratio between Stokes/a-Stokes peak area, taking into account the Raman cross section (Yu and Cardona 1995):

$$\frac{Y_S}{Y_{aS}} = \frac{(\omega_0 - \omega_p)^4}{(\omega_0 + \omega_p)^4} \exp[(\hbar\omega_p)/kT], \tag{1}$$

where Y indicates the yield, ω_0 the laser frequency, ω_p the phonon frequency, k the Boltzmann constant and T the temperature.

This permitted the measurement of the local temperature for each observed configuration of nanocrystal deposition. Some closely spaced nanograins in porous configuration, (i.e., a few nanograins per square micrometer) determined the correspondent temperature, according to a reduced thermal exchange between the particles (Gibilisco *et al.* 2010; Faraci *et al.* 2013b).

In Fig. 3 we compare typical Raman spectra of some GeNA samples with respect to Raman spectra of a bulk germanium wafer. Clearly visible the Raman peak shift and broadening for higher local temperature, related to a relative modification of the ratio Stokes/anti-Stokes Raman peaks. In Fig. 4, the Raman shift and broadening for our Ge nano

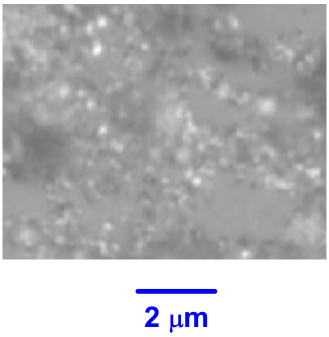

FIGURE 2. (Color online) Typical optical microscopy of our germanium grains with size 100 ±50 nm.

agglomerates is reported as a function of the temperature reached by the spot illuminated by the laser beam. Note that the penetration depth of red radiation in Ge is about 50 nm (Aspnes and Studna 1983).

The Raman apparatus can also be used for photoluminescence (PL) detection over the entire visible and near infrared range. This was accomplished with the same resolution (1800 lines/mm grating), detecting the PL spectra as a function of the wavelength on the same spot observed for the Raman spectra.

In Fig. 5 we display the PL spectra obtained at several temperatures, for GeNA compared to bulk Ge. As clearly visible, bulk Ge does not show any increase of temperature and, as a consequence, no PL is observed. In contrast, for GeNA at higher temperature, a wide radiation emission is detected. Of course, both the Raman peaks are present, together with a diffused PL ranging from 500 up to 900 nm. If we consider that the laser photon has a wavelength of 632.8 nm (1.95 eV), and the eventual contribution of phonons is quite limited in energy, we conclude that the yield along the entire tail of the spectrum between 2.5 and 2. eV is strongly enhanced.

Furthermore, comparing the curves at higher temperature with that of bulk germanium, contributions in the green visible range (around 2.4 eV, i.e., 515 nm) up to the IR range (around 1.4 eV, i.e., 900 nm) appear with a maximum intensity around 700 nm. Considering that the eventual contribution of two acoustical or optical phonons (so-called overtones) are present as satellites of the Raman peaks, it is evident that the increase of energy in the decay spectrum should be ascribed to a specific mechanism in the semiconductor. We propose a simple explanation, looking at the electron energy bands of Ge displayed in Fig. 1.

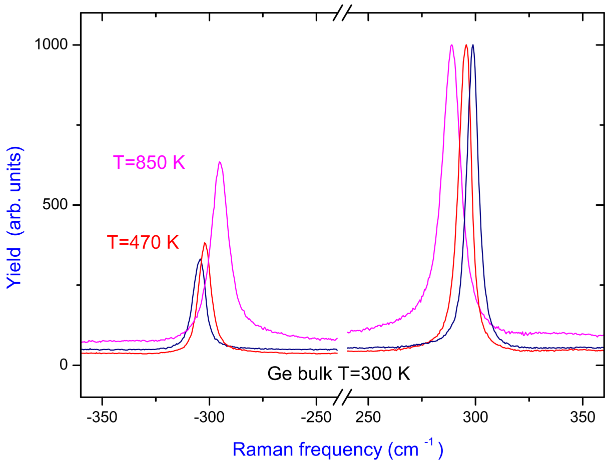

FIGURE 3. (Color online) Stokes and anti-Stokes Raman spectra for a bulk Ge wafer ($T = 300$ K), and for GeNA at two different temperatures. The Stokes peaks are normalized to the same height, whereas the anti-Stokes curves maintain their correspondent value as determined by their temperature.

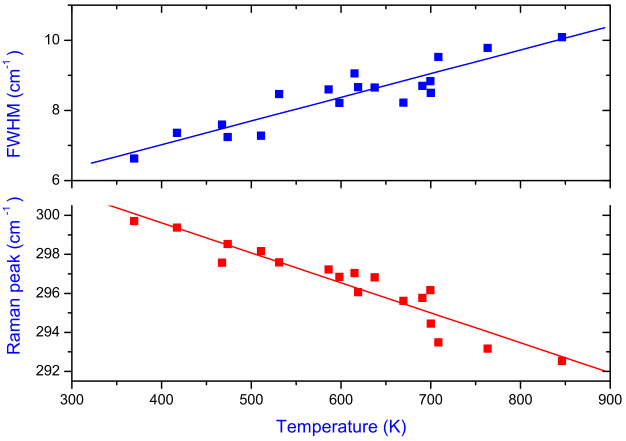

FIGURE 4. (Color online) Plot of the Raman peak shift and FWHM of the Ge nano agglomerates as a function of the temperature. The line is a linear fit of the data.

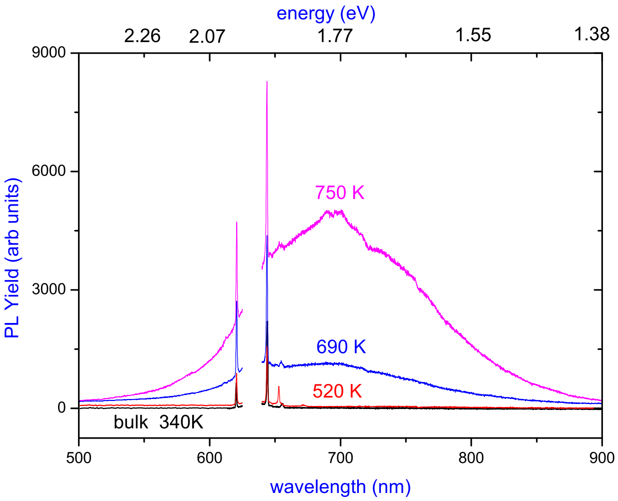

FIGURE 5. (Color online) Spectra showing anti-Stokes, Stokes, and PL emission in a wide range of wavelength, for GeNA compared to Ge bulk. Clearly visible for the GeNA, the Raman peak shift, and the large photoluminescence enhancement for higher temperature and the relative energy amplification at energy larger than the laser value. The small peaks near the Raman features are the overtones due to superposition of two acoustical or optical phonons.

Electrons along the branch $\langle 111 \rangle$ can be easily excited by the laser light tuned at 1.95 eV, matching the gap, along $\Gamma - L$. Both direct or indirect transitions are possible as indicated in the figure. Of course, the indirect excitations require the appropriate cooperation of a phonon. The excitations imply a depletion of states in the valence band with excited electrons in the conduction band. The electron-hole couples, i.e., the excitons, can now decay preferentially in direct transitions not involving a phonon. When this happen a higher energy of emitted photon can be detected with respect to the excitation energy. But also phonon assisted indirect decays can be stimulated with some energy enhancement, whereas lower energy decays are distributed along the entire Brillouin zone, from the center up to the zone border.

As can be observed in Fig. 5, also a strong Raman yield increase can be clearly detected, larger than a factor 10, between a Raman spectrum at higher temperature with respect to the bulk yield at room temperature. As far as concerns the PL yield, the cross section gain, e.g., between 690 K and 750 K (see Fig. 5) is larger than a factor 10, whereas between 750 K and 520 K is larger than a factor 100. Of course a detailed comparison can be performed using the entire area of the spectrum, and/or partial zones of each curve. These effects although already detected for silicon octahedral nanocrystals (Faraci *et al.* 2013b; Mannino *et al.* 2015; Jong *et al.* 2016), are here reported for Ge nanocrystals of irregular morphology, and the explanation can be briefly resumed. The Raman yield amplification is simply due to a reduced reflectivity of nanocrystals acting as traps for the radiation, undergoing multiple scattering effects between the particles. The reason can be attributed to the Ge optical parameters, having a refractive index of 5.48 at 633 nm, with an extinction coefficient of 0.784. This means a great capability of trapping the red light inside the nanocrystal acting as a reflector-amplifier. Compare with the correspondent silicon values, respectively 3.88 and 0.016. In contrast, the PL amplification should be attributed to the larger temperature on the laser spot, whenever the limited thermal exchange causes a temperature increase depending on the rarefied spacing between the nanocrystals. In fact, the large spacing configuration between the particles, and the presence of a thin native oxide prevent the phonon propagation, and determine the local temperature increase.

The hypothesis could be raised whether a large thermal contribution is present, at temperature higher than 300 K, in the PL spectrum.

Of course, at higher temperature a black body thermal emission could be present according to the Planck's formula

$$I(\lambda,T) = \frac{2hc^2}{\lambda^5 \left(\exp\left(\frac{hc}{\lambda kT}\right) - 1\right)} \tag{2}$$

where h is the Planck's constant, k the Boltzmann parameter, λ the wavelength and T the temperature. However, the previous expression gives, in the temperature range of interest, several orders of magnitude of increase between, e.g, 520K and 750K. This is not reflected by the experimental Raman peak and PL radiative emission.

Of course thermal emitted radiation should be present at any temperature but the peak of the distribution for the temperatures of our interest is found not in the visible but in the FIR range according to the Wien's law (maximum at wavelength $\lambda_m = 0.3/T$ cm). We argue that this contribution is negligible, because, otherwise all the features in the spectra should increase uniformly. In contrast, looking at the values reported in Fig. 5, it is evident that the enhancement of the PL is much larger than the increase of the Raman peaks. Furthermore, the PL spectrum detected in the visible range has a maximum intensity at about 750 nm whereas the thermal radiative emission should increase monotonically in this range. Therefore a large thermal contribution is disproved.

The present results are of great importance in optoelectronics, demonstrating how to obtain radiation emission from Ge particles not in the size confinement range. In conclusion, we showed clear evidence of three enhancement mechanisms observed in germanium nanocrystals 100 nm sized. The first is the energy increase of the spectral yield, with respect to the laser energy, at high temperature. The second is the Raman yield amplification, due to the specific configuration of our samples. The third is the high PL emission as a function of the temperature.

In Memoriam

With Gaetano Giaquinta, two years younger than me, in 1960-61, I frequented the "Liceo classico Nicola Spedalieri" in Catania. Afterwards, we were students at the Institute of Physics of the University of Catania, where I obtained my "Laurea" in Physics in july 1965. About two years later, for his thesis Gaetano studied the superconducting behavior of unconventional junctions prepared by Antonio Mancini, his advisor, by means of a very *thin formvar layer between two Pb/Sn metallic films. Our first article on this argument was published in 1969 (G. Faraci, G. Giaquinta, N. A. Mancini, "Superconducting tunnel junction with a non-conventional insulator" Physics Letters A 30, 400, 1969). After the initial collaboration, related to some scientific research on superconductivity problems, our interests were diversified. However, we had parallel academic paths at the University of Catania: Lecturers, Assistant Professors (1974), Associate Professors (1983) and finally Full Professors. Both of us, in the eighties, were involved in some local fights, when for contrasts with the directors, our Institute of Physics was separating in two different institutions, one affiliated with the Faculty of Science and the other with the Faculty of Engineering, recently joined again in the Department of Physics and Astronomy.*

References

Aspnes, D. E. and Studna, A. A. (1983). "Dielectric functions and optical parameters of Si, Ge, GaP, GaAs, GaSb, InP, InAs, and InSb from 1.5 to 6.0 eV". *Physical Review B* **27**(2), 985–1009. DOI: 10.1103/physrevb.27.985.

Barbagiovanni, E. G., Lockwood, D. J., Simpson, P. J., and Goncharova, L. V. (2014). "Quantum confinement in Si and Ge nanostructures: Theory and experiment". *Applied Physics Reviews* **1**(1), 011302. DOI: 10.1063/1.4835095.

Belyakov, V. A., Burdov, V. A., Lockwood, R., and Meldrum, A. (2008). "Silicon Nanocrystals: Fundamental Theory and Implications for Stimulated Emission". *Advances in Optical Technologies* **2008**, 1–32. DOI: 10.1155/2008/279502.

Faraci, G., Gibilisco, S., and Pennisi, A. R. (2009). "Quantum confinement and thermal effects on the Raman spectra of Si nanocrystals". *Physical Review B* **80**(19). DOI: 10.1103/physrevb.80.193410.

Faraci, G., Gibilisco, S., Russo, P., Pennisi, A. R., and Rosa, S. L. (2006). "Modified Raman confinement model for Si nanocrystals". *Physical Review B* **73**(3). DOI: 10.1103/physrevb.73.033307.

Faraci, G., Mannino, G., Pennisi, A. R., Ruggeri, R., Sberna, P., and Privitera, V. (2013a). "Raman and photoluminescence spectroscopy of Si nanocrystals: Evidence of a form factor". *Journal of Applied Physics* **113**(6), 063518. DOI: 10.1063/1.4792063.

Faraci, G., Pennisi, A. R., Alberti, A., Ruggeri, R., and Mannino, G. (2013b). "Giant photoluminescence emission in crystalline faceted Si grains". *Scientific Reports* **3**(1). DOI: 10.1038/srep02674.

Gibilisco, S., Faraci, G., Pennisi, A., and Irrera, A. (2010). "Laser induced heating of Si nanocrystals". *Journal of Non-Crystalline Solids* **356**(37-40), 1948–1950. DOI: 10.1016/j.jnoncrysol.2010.05.035.

Hernández, S., Martínez, A., Pellegrino, P., Lebour, Y., Garrido, B., Jordana, E., and Fedeli, J. M. (2008). "Silicon nanocluster crystallization in SiOx films studied by Raman scattering". *Journal of Applied Physics* **104**(4), 044304. DOI: 10.1063/1.2968244.

Jong, E. M. L. D. de, Mannino, G., Alberti, A., Ruggeri, R., Italia, M., Zontone, F., Chushkin, Y., Pennisi, A. R., Gregorkiewicz, T., and Faraci, G. (2016). "Strong infrared photoluminescence in highly porous layers of large faceted Si crystalline nanoparticles". *Scientific Reports* **6**(1). DOI: 10.1038/srep25664.

Lieten, R. R., Bustillo, K., Smets, T., Simoen, E., Ager, J. W., Haller, E. E., and Locquet, J.-P. (2012). "Photoluminescence of bulk germanium". *Physical Review B* **86**(3). DOI: 10.1103/physrevb.86.035204.

Mannino, G., Alberti, A., Ruggeri, R., Libertino, S., Pennisi, A. R., and Faraci, G. (2015). "Octahedral faceted Si nanoparticles as optical traps with enormous yield amplification". *Scientific Reports* **5**(1). DOI: 10.1038/srep08354.

Riabinina, D., Durand, C., Chaker, M., Rowell, N., and Rosei, F. (2006). “A novel approach to the synthesis of photoluminescent germanium nanoparticles by reactive laser ablation”. *Nanotechnology* **17**(9), 2152–2155. DOI: 10.1088/0957-4484/17/9/012.

Timmerman, D., Valenta, J., Dohnalová, K., Boer, W. D. A. M. de, and Gregorkiewicz, T. (2011). “Step-like enhancement of luminescence quantum yield of silicon nanocrystals”. *Nature Nanotechnology* **6**(11), 710–713. DOI: 10.1038/nnano.2011.167.

Yu, P. Y. and Cardona, M. (1995). *Fundamentals of Semiconductors: Physics and Material Properties*. Springer.

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