

*Letter to the Editor***Silicon as a candidate carrier for ERE****G. Ledoux¹, M. Ehbrecht², O. Guillois¹, F. Huisken², B. Kohn², M.A. Laguna³, I. Nenner¹, V. Paillard³, R. Papoular¹, D. Porterat¹, and C. Reynaud¹**¹ CEA/DSM/DRECAM/SPAM, CE Saclay, F-91191 Gif-sur-Yvette Cedex, France² Max-Planck-Institut für Strömungsforschung, Bunsenstrasse 10, D-37073 Göttingen, Germany³ Laboratoire de physique des solides, Université Paul Sabatier, 118 Route de Narbone, F-31602 Toulouse Cedex 4, France

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Abstract. Amorphous hydrogenated carbons and their alloys with silicon are discussed as candidate carriers of Extended Red Emission. In this respect, their photoluminescence spectra are too blue, weak and broad. By contrast, crystalline nanoparticles of pure silicon are shown to satisfy the constraints of available observations. Such dust can plausibly condense, even in carbon-rich circumstellar shells, in the form of polydispersed nuggets, either free or embedded in SiC, for instance.

Key words: interstellar medium: dust – reflection nebulae**1. Introduction**

Ever since Schmidt, Cohen and Margon (1980) noticed a broad, red emission feature superimposed upon the visible continuum of HD 44179 (in the Red Rectangle), a wealth of observational data has been accumulating on this so-called Extended Red Emission (ERE), especially on the hands of Witt and collaborators (Witt et al., 1984; see recent bibliography in Gordon et al., 1997), and Perrin and Sivan (1992, 1993, 1995).

Attention recently turned to the diffuse ISM, where ERE is also emitted in measurable amounts (Gordon et al., 1997; Szomoru and Guhathakurta, 1997). Altogether, these results effectively constrain putative models: a) if ERE is a type of photoluminescence (PL), it implies a distinctly high quantum yield ($\geq 1\%$ and possibly 10%), which is a very stringent constraint; b) ERE peaks between 600 and 800 nm, with a FWHM of 120–190 nm; c) no O-rich PN shows ERE, while most C-rich PNe do (Furton and Witt (1992)); d) ERE does not seem to require very specific irradiations or temperatures.

Based on early spectroscopy by Watanabe et al. (1982), various forms of amorphous hydrogenated carbons (a-C:H) were proposed as carriers of ERE: HAC (Duley, 1985; Witt and Schild, 1988), QCC (Sakata et al., 1992). However, the PL of a-C:H is very sensitive to preparation conditions and subsequent processing. According to Angus et al. (1986), PL can be observed at room temperature only for samples prepared by

low ion energy techniques, which result in soft, polymer-like materials. Even then, the absolute efficiency does not exceed 10^{-3} (Xu et al., 1993). Besides, in this case, the gap widens and the PL peak shifts shortward of 600nm. This anti-correlation between PL intensity and peak wavelength is clearly demonstrated by Fabisiak et al. (1991), using a range of substrate deposition temperatures, and by Bouree et al. (1996) and Rusli et al. (1996), using a range of ion energies. Subsequent annealing reduces the band gap, but the PL intensity also decreases. Furton and Witt (1993) tried to reverse this trend by exposure to H atoms, but seem to have arrived at the conclusion that this is not enough, and that addition of impurities should be considered, such as silicon (Witt et al., 1996), because of its much narrower band gap.

By contrast, a-Si_{1-x}:C_x:H has been shown to luminesce relatively strongly, peaking at a wavelength λ_{max} which increases monotonously with the concentration of Si (Siebert et al., 1987; Liedtke et al., 1989; Street, 1991; Tessler and Solomon, 1995). Unfortunately, it is found that the PL intensity exhibits a broad minimum as a function of x, around that value of x (slightly dependent upon preparation conditions), for which λ_{max} has the desired value, 700 nm. There, according to Tessler and Solomon, the efficiency is only about 0.3% at 77 K, and 0.03% at 300 K. Moreover, the spectral width of the PL peak exceeds 200 nm. Finally, such Si-rich alloys give rise to characteristic infrared features, the strongest of which appear at 2100 cm⁻¹, 630 cm⁻¹ and 900 cm⁻¹ (Tawada et al., 1982). These should be conspicuous in the sky if a-Si:C:H were abundant enough to provide the observed ERE, which does not seem to be the case.

This paper purports to show that nanometer-sized crystals of pure silicon are better candidates as regards PL efficiency, peak wavelength and bandwidth. We were prompted in this direction by the recent avalanche of data on the strong, room-temperature, red PL of porous Si (p-Si), described in Sect. 2. We were thus led to investigate in more detail nano crystallites of Si (Sect. 3), the controlled production and study of which have been pioneered by some of us (Ehbrecht et al., 1995, 1997). For this purpose, a dedicated laboratory facility was built which allows the measurement of the PL spectrum and efficiency as a function

of excitation energy, sample temperature and sample processing (heating, dosing with UV and atomic hydrogen, by analogy with IS environments). This is described in Sect. 4, together with the experimental procedure for the measurement of absolute PL efficiencies, and the main results of interest for astrophysics. Sect. 5 evaluates this material as a carrier of ERE

2. Porous silicon (p-Si)

Bulk crystalline Si (c-Si) is known to fluoresce very weakly. However, starting from 1990, the discovery of strong, visible, room-temperature PL of porous silicon, and its obvious industrial applications have fueled extensive investigation and publication in this field (see review by Cullis et al., 1997). p-Si is obtained by etching c-Si to porosities exceeding 80%, leaving a skeleton made of only tenuously connected crystalline islands.

It is now widely accepted that the high PL efficiency ($\geq 1\%$) is mainly a result of the confinement of excited electrons in the nanometric quantum wells formed by the islands (Feng and Tsu, 1995; Brus et al., 1995). It was also shown theoretically that λ_{max} must decrease with the well size, which explains why the PL shifts blueward as the porosity increases. The whole visible spectrum can thus be covered with a set of porosities (Fauchet, 1996). In particular, the brightest luminescence is obtained by porosity-tuning so that the peak PL falls in the range 600–800 nm (precisely the same as ERE!).

After preparation of the samples, the strong PL persists in open air only if the material surface is passivated, either by saturating the dangling Si bonds with H atoms or, better still, by oxidation (Brus et al., 1995). The overlayer of SiO₂ that spontaneously forms in air is usually ~ 1 nm thick and does not modify the PL spectrum.

While much insight in the PL of Si has been gained by these studies, a more fundamental understanding, as is necessary for astrophysical applications, is hindered by the fact that p-Si is a result of a very specific preparation and that the material is not homogeneous, but consists of small active regions with a distribution of sizes. Among other effects, this dispersion entails an artificial broadening of the PL spectrum. We therefore directed our efforts to the production of narrowly dispersed, nearly spherical, nanosized particles.

3. Nanocrystalline silicon

Si clusters and nanocrystals were generated by CO₂-laser-induced decomposition of silane (SiH₄) in a flow reactor (Ehbrecht et al., 1995, 1997). By introducing a conical nozzle into the reaction zone, the clusters are extracted into a molecular beam machine and analyzed with a time-of-flight mass spectrometer. As the cluster velocity is size dependent, a mechanical velocity selector is used to further narrow the size distribution and select a specific mean size. In this way, size distributions were obtained, with mean diameter in the range from 2.5 to 7 nm, and FWHMs between 1 and 1.5 nm. Such distributions were collected in the form of uniform thin films deposited on

silicon, KBr and CaF₂ substrates inserted in the molecular beam, behind the selector.

Raman scattering analysis showed that the structure is crystalline and that the particles do not fragment or change in size or coalesce after deposition (Ehbrecht et al., 1997). This could also be confirmed by high resolution electron microscopy (HREM) (Hofmeister et al., 1998).

4. Experimental procedure and results

The measuring apparatus has been designed to study the surface of a solid sample by ir and/or visible spectroscopy. The sample is mounted in a vacuum chamber and can be irradiated with H atoms and/or electrons and UV photons. It can be cooled down to 77 K and heated up to 500 K.

The PL is excited by means of a quadrupled Nd-YAG laser (266 nm, 4.66 eV). The UV output is ~ 300 mW in 6 ns pulses, 30 mJ each, with a repetition rate of 10 Hz. Before entering the vacuum chamber, the UV beam is attenuated as required, by Schott glass filters (UG 11) and a calibrated, rotatable polarizer-depolarizer system. The laser power is measured by means of a commercial calorimeter and monitored during the PL spectra measurement by a photodiode. The average power incident on the sample never exceeds 100 μ W.

Measuring the absolute value of the PL efficiency is the most delicate part of the experiment, for a number of reasons (Theiss, 1997): a) even in the simple case of a semi-infinite sample, irradiated by a monochromatic beam at 45° incidence and observed in a direction perpendicular to this, account must be taken of reflection losses of exciting and PL light at the interfaces and absorption losses along their paths inside the sample; moreover, a large fraction of the PL photons may be lost by total reflection at the internal side of the interface; b) in practice, the samples are often quite thin (optically), so that part of the exciting energy is lost or reflected on the backing substrate in uncontrolled ways.

In view of this, we adopted the following procedure. The irradiation and observation directions are 80° to each other and the normal to the sample surface is tilted at 45° to the plane of the former directions. The collecting optics images an area $S \sim 1$ mm² of the sample surface subtended by a solid angle small enough that total reflection does not occur ($\Omega \sim 5$ msr). When the sample is thin enough or the UV absorptivity of the material is large enough that essentially all the exciting light is absorbed within 1 mm of the surface, essentially all the light emitted in Ω over area S is collected. The absorbances of the naked substrate and of the nano-Si-covered substrate are measured separately, to determine the fraction of incident laser power that is absorbed in the sample.

Now, the same optical set-up is used to detect the PL of a liquid solution of the very efficient Rhodamine 6G molecule ($\eta \sim 1$), filling a rectangular parallelepiped made of quartz plates, 1 mm thick. The titration is 5 10^{-4} mole/l in ethanol, so that $\alpha_{UV} = 10$ cm⁻¹ and the photoluminescent region is confined very near to the irradiated face of the vessel, as required above. Here, there are two sources of PL loss: self-absorption ($\sim 10\%$) and

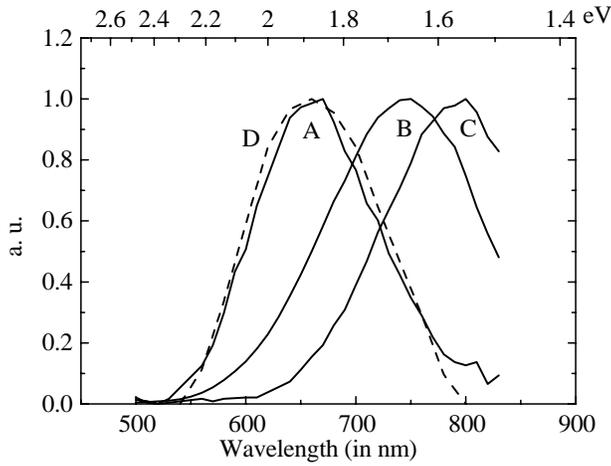


Fig. 1. Normalized PL spectra under pulsed laser excitation at 266nm. Samples A, B, C have average particle sizes of 3.65, 3.92 and 4.95nm respectively, and efficiencies $\eta=1\%$, 12% and 1.6%. The dashed curve, D, represents ERE from NGC 2023 (Witt and Boroson, 1990). The arrowed segment represents the range of observed ERE peak wavelengths.

reflection at the interfaces ($\sim 4\%$). We take a correction factor of 0.85 to account for both losses. Finally, the efficiencies are obtained by ratioing the corrected signals from the sample and the Rhodamine respectively.

Figure 1 presents the PL spectra, at a resolution of 10nm, of 3 typical samples, A, B, C, which were prepared about one year ago and stored without special precautions. The average crystallite sizes are 3.65, 3.92 and 4.95 nm, respectively, with a size dispersion of ~ 1 nm. The curves are normalized and the absolute PL quantum efficiencies are 1%, 12% and 1.6%. The corresponding peak wavelengths are 670, 750 and 800nm. The PL of sample B is the strongest of a series covering the spectral range 500-900 nm. The occurrence of a maximum as the crystallite size decreases could be the result of a compromise between 1) the increase of the band gap energy (which hinders phonon-assisted non-radiative processes) and the reduced probability of occurrence of a defect on a grain, and 2) the increase of non-radiative processes with the ratio of the volume of the outer oxide shell to the volume of the crystalline core. Thus crystallites ~ 4 nm in size are likely to dominate the PL spectrum of a distribution of nanoparticles.

When the sample temperature is lowered from 300 K to 77 K, the PL intensity increases by $\sim 50\%$ and its peak shifts by ~ 20 nm to the blue; these changes are reversible. Thus the grain temperature is not an important parameter for ERE. Neither is the excitation wavelength: excitation at 266, 300, 400, and 500nm gives essentially the same PL spectrum. Fig. 1 also shows an example of the quality of fit one can obtain between particular ERE and sample spectra.

5. Crystalline Si as a carrier of ERE

Crystalline Si in the form of nanoclusters suitably distributed in size between 3 and 5 nm, clearly satisfies the observational

constraints of ERE as regards spectral shape and position of PL, and their dependence on grain temperature and excitation wavelength. Although its efficiency is much higher than that of the other candidates, we must now consider if there may be enough silicon particles in the relevant space environments. In this respect, it should be remembered that a carbon-rich environment does not exclude silicon chemistry (see, for instance, Chan and Kwok, 1991).

The required quantity of Si can be estimated from its PL efficiency and the ratio of ERE to scattered intensities, $r = \phi_{ERE}/\phi_{sca}$, which was measured by Witt and coll., in a number of environments (Gordon and Witt, 1997; Witt and Boroson, 1990). This ratio can be written

$$r = \eta_{PL} \frac{h\nu_{PL} \phi_{*,exc}}{h\nu_{exc} \phi_{*,PL}} \frac{2\alpha_{2,exc}}{(Q_{sca}/a)_{1,PL}} \frac{M_{d2} \rho_1}{M_{d1} \rho_2}, \quad (1)$$

where PL and exc designate, respectively, the wavelength ranges of photoluminescence (600-900 nm) and excitation (100-400 nm); 1 and 2, the main and photoluminescent dust, respectively; ϕ_* , the radiative star flux falling upon the dust; α , the absorptivity of the material (cm^{-1}); Q_{sca} , the scattering efficiency of a grain of radius a ; M_d and ρ , the corresponding dust mass and specific gravity; M_{d2}/M_{d1} is the unknown, X.

From Sect. 4, we can take $\eta_{PL}=0.1$; the second factor of (1) is $\sim 1/3$. For star photospheric temperatures of 10^4 and $2 \cdot 10^4$ K, respectively, the 3rd factor ranges between 3.3 and 16. The absorptivity of pure, crystalline Si ranges between 10^5 and 10^6 in the spectral range 100-400 nm (Cullis et al., 1997). Since the specific gravity of pure Si, silicates and carbon dust are, respectively, about 2.5, 3 to 4 and 2, we take $\rho_1/\rho_2=1$. For Q_{sca}/a we start from the values tabulated by Draine (1985) for $0.1 \mu\text{m}$ grains of “astrophysical silicates” and graphite, at 700nm: 0.29 and 1.15, respectively. In the Rayleigh approximation, $Q_{sca}/a \sim a^3$. We average this quantity over a canonical size distribution in $a^{-3.5}$ between 10 and 1000 nm, and, assuming that both dust types are present in equal amounts, we obtain an overall average $(Q_{sca}/a)_{1,PL}$ of 3750 cm^{-1} . Thus, the r.h.s. of (1) ranges between 3X and 160X. Considering the range of r values observed by Gordon et al. (1997), 0.05-2, and assigning these variations mainly to star colour, we estimate that X is in the order of 1%. This must be taken as a higher limit, because anisotropy favours forward scattering rather than the usual average direction of observation (90°), so that Q_{sca} should be smaller than the adopted value; and also because account was not taken of possible excitation by recombination lines, often quite strong just outside HII regions.

Another estimate can be deduced along the same lines, but using the ERE intensity in the diffuse ISM, as measured by Gordon et al. (3% of the total energy emitted by dust, or $1.8 \cdot 10^{-25} \text{ erg/s.H atom}$), and the diffuse ISRF between 100 and 400 nm. If we take the latter to be $2 \cdot 10^{-9} \text{ W/cm}^2$ (Draine and Bertoldi, 1996), we find $X \sim 5\%$. The most plausible reason for the disagreement with the value found above is that the adopted ISRF does not apply to the excitation of diffuse ERE, being too low.

Considering that the cosmic mass abundance of Si is only one fifth that of C, it appears that the required amount for ERE can plausibly be found in the form of small nuggets, either bare, but hydrogen passivated, or embedded. Such nanocrystals have been found, for instance, in SiCN powders obtained by laser pyrolysis (Mayne et al., 1998). In CVD a-Si:H films, nanocrystallites of Si and their luminescence were observed even without any post-processing (Liu et al., 1993). Finally, pure Si has only a few mid-ir bands and they are very much weaker than the 11.3- μm band of SiC (Theiss, 1997), so that they could hardly be detected in the sky.

Further measurements on nano crystallites Si, and similar measurements of PL have been performed or are going on, with the same apparatus, on various other materials: a-C:H, a-SiC:H, coals and p-Si. They will be reported elsewhere.

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References

- Angus J. Koidl, P. and Domitz, S., 1986, in Plasma Deposited Thin Films, Chap. 4, CRC Press Inc.
- Bouree, J. et al., 1996, J. Non-Crystal. Solids, 198-200, 623
- Brus, L. et al., 1995, J. Am. Chem. Soc., 117, 2915
- Chan, J. and Kwok, S., 1991, ApJ, 383, 837
- Cullis, A., Canham, L. and Calcott, P., 1997, J. Appl. Phys., 82, 909
- Draine, B., 1985, Ap. J. Suppl., 57, 587
- Draine, B. and Bertoldi, F., 1996, ApJ, 468, 269
- Duley, W., Seahra, S., Williams, D., 1997, Ap. J., 482, 866
- Ehbrecht, M., Ferkel, H., Smirnov, V.V., Stelmakh, O.M., and Huisken, F., 1995, Rev. Sci. Instrum. 66, 3833
- Ehbrecht, M., Kohn, B., Huisken, F., Laguna, M. and Paillard, V., 1997, Phys. Rev. B, 56, 6958
- Fabisiak, K., Rozploch, F., Szatkowski, J., and Targowski, P., 1991, Phys. Stat. Sol. (a), 126, 275
- Fauchet, F., 1996, J. Luminesc., 70, 294
- Feng, Z. and Tsu, R.(edrs), 1995, Porous Silicon, World Science, Singapore
- Furton, D. and Witt, A., 1992, Ap. J., 386, 587
- Furton, D. and Witt, A., 1993, Ap. J. Lett., 415, L51
- Gordon, K., Witt, A. and Friedman, B., 1997, ApJ, in press
- Hofmeister, H., Huisken, F., and Kohn, B., 1998, to be published
- Liedtke, S., Lips., K., Bort, M., Jahn, K. and Fuhs, W., 1989, J. Non-Cryst. Sol., 114, 522
- Liu, X., Wu, X., Bao, X. and He, Y., 1993, Appl. Phys. Lett., 64, 220
- Mayne M. et al., 1998, to appear in J. Eur. Ceram. Soc.
- Perrin, J.-M. and Sivan, J.-P., 1992, A&A, 255,271
- Perrin, J.-M., Darbon, S. and Sivan, J.-P., 1995, A&A, 304, L21
- Rusli, Robertson, J. and Amaratunga, G., 1996, J. Appl. Phys., 80, 2998
- Sakata, A., Wada, S., et al. 1992, Ap. J. Lett., 393, L83
- Schmidt, G., Cohen, M. and Margon, B., 1980, Ap. J. Lett., 239, L133
- Sivan, J.-P. and Perrin, J.-M., 1993, Ap. J. 404,258
- Siebert, W., Carius, R., Fuhs, W. and Jahn, K., 1987, Phys. Stat. Sol. (b), 140, 311
- Street, R., 1991, Hydrogenated Amorphous Silicon, Cambridge U. A., Cambridge
- Szomoru, A. and, Guhathakurta, P., 1997, in press???
- Tawada, Y, Tsuge, K., Kondo, M., Okamoto, H. and Hamakawa, Y., 1982, J. Appl. Phys., 53, 5273
- Tessler, L. and Solomon, I., 1995, Phys.Rev. B, 52, 10962
- Theiss, W., 1997, Surface Sc. Rep., 29, 91
- Watanabe, I., Hasegawa, S., Kurata, Y. 1982, JJAP, 21, 6
- Witt, A., Schild, R. and Kraiman, J., 1984, Ap. J., 281, 708
- Witt, A., Schild, R., 1988, Ap. J., 325, 837
- Witt, A. and Boroson, T., 1990, Ap. J., 355, 182
- Witt, A., Ryutov, D. and Furton, D., 1996, From Star Dust to Planetesimals, Santa Clara, NASA
- Xu, S., Hundhausen, M., Ristein, J., Yan, B., and Ley, L., 1993, J. Non-Cryst. Sol. 164-166, 1127