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Silicon quantum dots in diamond matrix: a new synthesis route†

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Light-emitting layers of silicon quantum dots embedded in a diamond matrix have been prepared by using a new hybrid chemical vapour deposition–powder flowing technique. The polycrystalline diamond matrix is grown by thermal activation of CH_4–H_2 mixtures. The silicon nanoparticles used for the synthesis of the diamond-based composites were prepared by CO_2 laser pyrolysis of SiH_4–He mixtures in a gas flow reactor with controlled atmosphere. During the matrix deposition, the powder-flowing apparatus drives the silicon nanoparticles across the active area of the substrate, where diamond is growing. A strong room temperature emission is observed from composite films with characteristics dependent on the size distribution of the inserted silicon particles. We report details of the synthesis procedure and emission features of composite diamond films, whose properties promise high technological impact. Copyright © 2001 John Wiley & Sons, Ltd.

Keywords: nanoscale silicon; diamond; chemical vapour deposition; photoluminescence spectroscopy

INTRODUCTION

Crystalline silicon is the dominant material in microelectronics, but until now it has not been suitable for the realization of active optical devices, due to its poor light emission at room temperature ascribed to a band structure with an indirect gap and a small exciton binding energy.

In silicon science and technology the desire for the integration of optoelectronic devices with silicon microelectronics has led to the search for silicon-based structures that emit light with a high quantum efficiency. Among the different approaches used by researchers, the most recent is the fabrication of silicon nanostructures (porous silicon, quantum dots, quantum wells, nanoclusters, …), which exhibit strong room temperature photoluminescence.[1–5] This emission is observed only after a drastic size reduction of silicon and has been related to a quantum confinement effect that occurs only when the particle size is smaller than the exciton radius in bulk silicon (5 nm). The quantum confinement widens the band gap and extends the wave function in the momentum space, relaxing the *k*-selection rules.[6–9] Two different mechanisms are actually considered for the electron–hole radiative recombination: the first assumes that the recombination occurs across the nanostructured gap, the other hypothesizes that the electron excited across the widened gap relaxes in the low-lying energy surface states.[10,11] In this latter case a small photoluminescence peak energy shift with the particle size is observed, whereas in the other case the band gap energy scales as an inverse power of particle diameter.

However, nanoscale silicon is a complex material with regard to its stability, because its optical properties show environmental and ageing degradation with resulting ambiguity in device performance evaluation.

Our approach to overcome these difficulties was to incorporate the light-emitting silicon nanoparticles inside a matrix material that exhibits both

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chemical inertness and a band gap suitable for quantum confinement, viz. polycrystalline diamond.

We used a modified hot-filament chemical-vapour deposition (HFCVD) reactor equipped with a powder-flowing apparatus designed for controlled particles injection.[12]

The silicon nanoparticles were synthesized by laser-induced decomposition of silane in a gas flow reactor. This technique provides a unique opportunity to fabricate nanosilicon grains whose size is scalable and can be controlled by the reaction parameters in a reproducible way.[13,14]

Here we present some significant examples of such composite systems and discuss their structural and optical properties.

EXPERIMENTAL

The deposition of composite diamond films was made using a modified HFCVD reactor by using a methane–hydrogen mixture activated by a Joule-heated tantalum filament. The experimental conditions were those typical of CVD diamond synthesis: CH_4–H_2 mixtures (1% CH_4) flowing at 200 sccm, total pressure 40 Torr, temperature of the tantalum filament 2200 ± 10 °C, substrate temperature 650 ± 5 °C. The deposition was restricted to an area of about 1 cm^2. To drive the nanopowders a properly designed apparatus was used in order to assure homogeneous powder distribution.[15] The silicon nanoparticles were carried by the inert gas to the substrate during the deposition of the diamond film. To produce these samples, flow rates ranging between 10 and 50 sccm were used. The composite layers were deposited on Si(100) and polycrystalline titanium substrates.

The silicon nanoparticles were produced by continuous wave CO_2 laser heating of SiH_4–He mixtures in a gas flow reactor. By changing the ratio between SiH_4 and He it was possible to obtain particles with sizes in the 3–50 nm range.[13,14,16] The size distributions of laser-synthesized nanoparticles were deduced from small-angle neutron scattering and were found to be in fair agreement with transmission electron microscope observations.[16,17] For our experiments we used different silicon samples, characterized by particle size distributions centred between 3.6 (FWHM = 1.5 nm) and 6.2 nm (FWHM = 3.3 nm).[17,18]

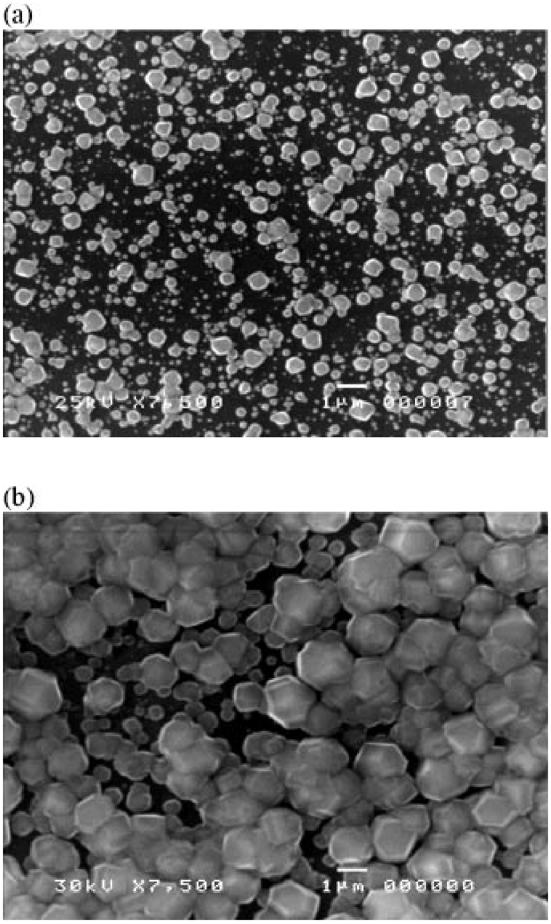

Figure 1 SEM micrographs of composite film obtained by inserting silicon nanoparticles with $\langle d \rangle = 3.2$ nm; (a) sample obtained with 1 h deposition time; (b) sample obtained with 3 h deposition time.

The structural characterizations of these films were performed by reflection high-energy electron diffraction (RHEED) using AEI EM6G apparatus equipped with a high-resolution diffraction stage (acceleration voltage of 60 kV).

The morphological and topographical information was obtained using a Jeol 5400 (SEM) scanning electron microscope, which had a resolution of 3 nm at an accelerating voltage of 30 kV.

The photoluminescence and excitation spectra were performed at room temperature on cold-pressed pellets and silicon-containing diamond films with a PTI spectrofluorimeter with extended red response to about 850 nm (spectral resolution of 3 nm). The wavelength sensitivity of the measuring system was calibrated with a standard tungsten lamp. We also evaluated the reflectance of composite film at quasi-normal incidence with a Lambda 9 Perkin Elmer spectrophotometer.

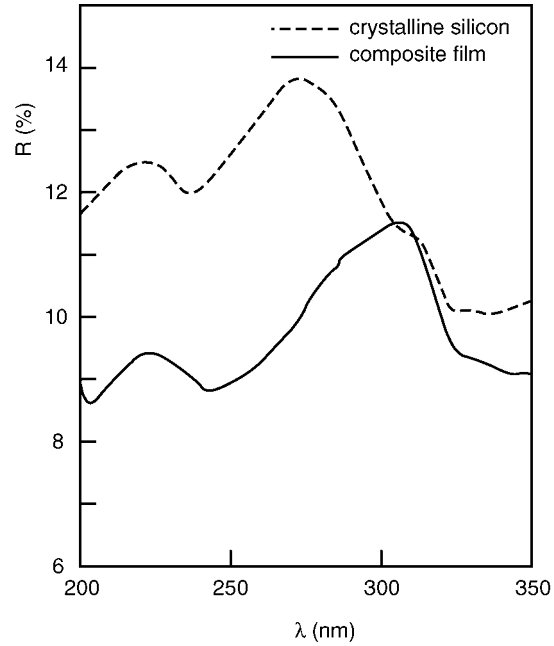

Figure 2 Reflectance spectra at normal incidence of composite film (solid line) and crystalline silicon wafer (dotted line).

RESULTS AND DISCUSSION

Composite film characterization

The structural characterization performed by RHEED shows a set of homogeneous diffraction rings belonging to the cubic diamond lattice, indicating that the highly crystalline state of the diamond matrix is also maintained in the presence of silicon nanoparticles.

SEM micrographs of the composite film are shown in Fig. 1. When the deposition time is 1 h the faceted nature of the diamond particles is clearly recognized and is accompanied by smaller spherical particles, most likely silicon (Fig. 1a). By increasing the deposition time a complete coverage of the substrate is obtained in which the silicon particles are not detectable at low magnification (Fig. 1b)

Figure 2 shows the reflectance spectra of the composite film and silicon wafer. We can observe a very similar behaviour in the UV region, which indicates that silicon is present in the diamond matrix.

Photoluminescence spectroscopy

The room temperature photoluminescence spectra

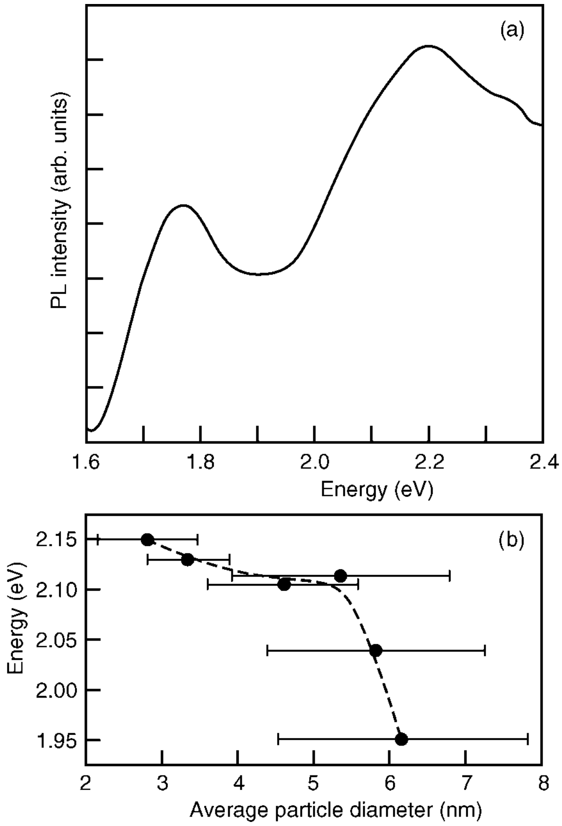

Figure 3 (a) Average energy of silicon nanoparticles emission band as a function of average diameter. (b) Room temperature emission of laser-synthesized nanosilicon with average diameter <*d*> = 3.2 nm. The excitation wavelength is 350 nm.

of silicon nanoparticles show two main emission bands in the visible region, one peaking at 1.7 eV and the other in the range 2.0–2.4 eV (see Fig. 3a).

The emission intensity decreases drastically when the average particle size exceeds 6 nm.[17] This critical size is comparable to the exciton radius in bulk silicon. However, as shown in Fig. 3b, the broad band position is slightly sensitive to the particle size.

Figure 4 shows the room temperature emission of composite films excited under UV pumping. The composite films have emission signals with a double structured band quite similar to that of inserted nanosilicon grains. As expected, the band of composite films containing smaller silicon nanoparticles is more extended towards the high energy region (Fig. 4b). The samples obtained with a higher particle carrier flow have a broader energy

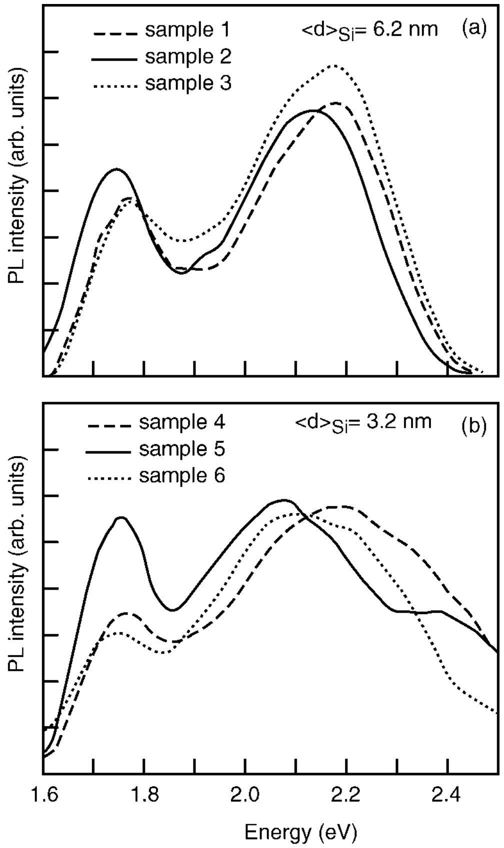

Figure 4 Room temperature emission from composite films: (a) sample 1 carrier flow rate 50 sccm, sample 2 carrier flow rate 30 sccm, sample 3 carrier flow rate 50 sccm, average diameter of inserted silicon grains 6.2 nm; (b) sample 4 carrier flow rate 50 sccm, sample 5 carrier flow rate 50 sccm, sample 6 carrier flow rate 30 sccm, average diameter of inserted silicon grains 3.2 nm.

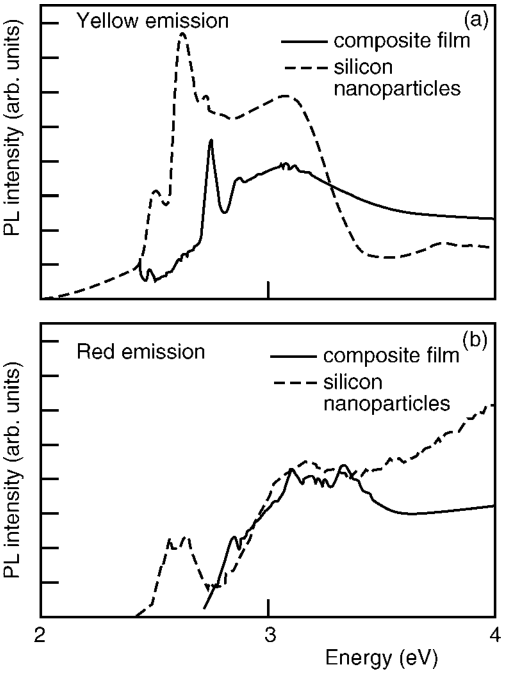

Figure 5 Excitation spectra of yellow and red emissions from silicon nanograins (dashed line) and composite films (solid line). The average diameter of the silicon nanoparticles is 3.2 nm.

band with a more pronounced shoulder on the blue side. This finding can be explained by supposing that, when the flow is relatively low, only the particles with the larger particle size can reach the active zone.

The excitation spectra of the yellow and red emissions of silicon nanoparticles and composite films are reported in Fig. 5.

The excitation spectra show sharp resonances, followed by broad absorption, which has been ascribed to the presence of excited states located at about 1 eV above the state responsible for luminescence.[17] The irradiation of energy greater than 2.5 eV induces radiative transitions across the opened gap, which are followed by non-radiative transitions to the lowest-lying excited states responsible for luminescence. The radiative recombination originates from interface states,[17] and the similarity between the excitation spectra suggests that their electronic configuration is not affected by the diamond matrix.[17]

The emission was found to be stable on storing the samples in ambient atmosphere after a period of observation of 1 year.

CONCLUSIONS

A new technique utilizing an HFCVD reactor coupled with a powder-flowing apparatus was used to fabricate light-emitting layers of silicon quantum dots embedded in a diamond matrix. Our investigation on the structural and optical properties of the composite films revealed that the insertion in the matrix does not affect the energy range of the emission band, and that the emission properties of the silicon nanoparticles are stable and do not suffer from environmental degradation.

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