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Narrow-band photoluminescence at room-temperature in amorphous SiC$_x$:H film

H.P. Zhou [a], M. Xu [b], D.Y. Wei [a], T. Ong [a], S.Q. Xiao [a], L.X. Xu [a], S.Y. Huang [a], Y.N. Guo [a], S. Xu [a,*]

[a] *Plasma Sources and Application Center, NIE, and Institute of Advanced Studies, Nanyang Technological University, Singapore 637616, Singapore*
[b] *Key Lab of Information Materials of Sichuan Province & School of Electrical and Information Engineering, South-west University for Nationalities, Chengdu 610041, China*

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ABSTRACT

We report strong narrow-band photoluminescence at room temperature in amorphous SiC$_x$:H films synthesized by means of high-density reactive plasma. The emission energy is found to remain constant with varying nanoparticle sizes. Detailed bond configuration analysis shows that the PL intensity strongly depends on the density of nanoparticle and Si–C bonds. On the basis of a variety of bond characterizations, the origin of photoluminescence is explained as two separated processes: photoexitation in Si nanoparticles embedded in amorphous SiC matrix and photoemission in SiC matrix or at Si/SiC interface. The contribution from the passivation behavior of amorphous SiC on Si nanoparticle surface is also proposed.

Silicon quantum dots (QDs) or nanograin silicon embedded in a dielectric host matrix (SiN$_x$, SiO$_2$ and SiC) is an increasingly attractive field because of a variety of potential applications like a CMOS-compatible integrated light source [1] and new generation of photovoltaic devices [2]. Compared with the wide band gap SiO$_2$ (~9 eV) and SiN$_x$ (5–6 eV), the hydrogenated amorphous silicon carbide (a-SiC$_x$:H) features narrower tunable band gaps in the range of 2–3 eV, suggesting this system is favorable for the carrier transport and effective luminescence of Si QDs. This is because the tunneling probability of the carriers between the adjacent Si QDs in the SiC matrix can be exponentially increased, and the radiative electron–hole recombination rate can be significantly enhanced due to the strong overlap of electron–hole wave function [3,4]. Many works have reported PL behavior from Si QDs embedded in SiO$_2$ and SiN$_x$ matrix [5–7]. In contrast, the report on PL from Si QDs embedded in SiC matrix is scarce. In our previous work, Si QDs were observed in an amorphous SiC matrix fabricated by a custom-designed low frequency (460 kHz) inductively coupled plasma (LFICP) source [8]. The Si QDs formation is regarded as a result of the ultra-high density plasma in the LFICP source and the hydrogen dilution effect on the nucleation.

In despite of intensive research, to date, there is no consensus on the mechanism of Si-based materials (e.g. nanoscale-Si particle or porous Si etc.) PL. Numerous works have suggested that the emission energy is closely dependent on the nanocrystal size [9,10], the nonradiative surface defects and radiative process [11], as described by quantum size effect (QSE) [12] and surface state model [13]. It is known that there are two crucial processes involved in the PL occurrence: the formation of photoexcited carriers (photoexcitation process), i.e., pairs of electron and hole; and the radiative recombination of the photoexcited carriers through PL center (photoemission process). In the QSE model, both photoexcitation and the photoemission concurrently take place in the Si quantum dots. In the surface state model, the photoexcitation and photoemission occur in the Si quantum dots and in a specific surface state, respectively. Indeed, various surface species related to hydrogen and oxygen have been proposed to explain the origin of observed PL [14].

In this work, photoluminescence of a-SiC$_x$:H thin films is investigated. The a-SiC$_x$:H thin films were deposited on glass and mirror-polished silicon substrates in the LFICP system with precursor gases of H$_2$ diluted SiH$_4$ and CH$_4$ [8]. The hydrogen and silane flow rate were maintained at 20 and 5 sccm, respectively. Meanwhile, the flow rate of methane was varied in the range of 0–5 sccm, corresponding to the gas ratio $R = CH_4/SiH_4$ of 0–1. The substrates located on the carrier stage (mounted with a thermal couple) were heated to a fixed temperature of 400 °C. The inductive RF discharge power density, the total working pressure in the chamber, and the deposition duration were maintained at 21 mw/cm^3, 7.8 Pa and 60 min, respectively. Raman scattering was recorded on Renishaw 1000 micro-Raman with a 514.5 nm Ar$^+$ laser for excitation. Room temperature photoluminescence was measured by using the same Raman system with incident power of 25.8 mW. FTIR measurement was performed on a Perkin–Elmer FTIR 1725X spectrometer in the mid-infrared range from 400 to 3200 cm^{-1} with increment of 1 cm^{-1}. The chemical composition and bonding states of the deposited thin films were studied ex situ by VG ESCALAB 220I-xl X-ray photoelectron spectrometer using a Mg Kα (1253.6 eV) X-ray source.

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* Corresponding author.
E-mail address: shuyan.xu@nie.edu.sg (S. Xu).

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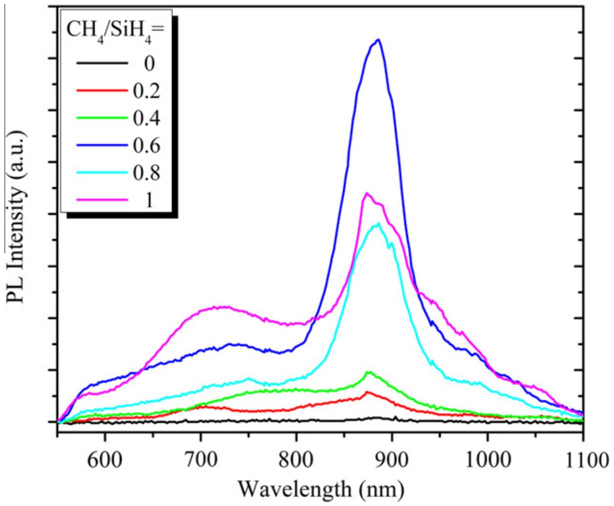

Fig. 1. Room temperature PL spectra at different gas ratios of CH_4/SiH_4. Intense PL peaks are observed at an unchanged energy of 880 nm (1.41 eV). The maximum of PL intensity is obtained at the ratio of $CH_4/SiH_4 = 0.6$.

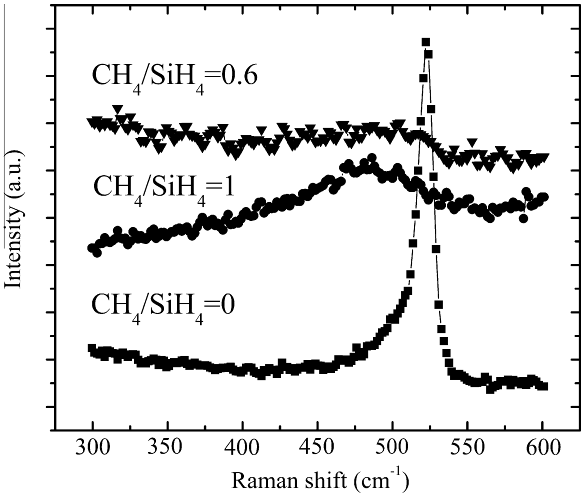

Fig. 2. The narrow range Raman spectra of Si. With increasing gas ratios of CH_4/SiH_4, The structure of silicon changes from crystal (~521 cm^{-1}) to an intermediate phase (~505 cm^{-1}) and finally to amorphous phase (~485 cm^{-1}).

The room temperature photoluminescence (PL) spectra of the thin films in the photon energy range of 550–1100 nm (1.12–2.25 eV) are displayed in Fig. 1. A peak located at 880 nm (1.41 eV) is observed in all the films deposited at various gas ratios from 0 to 1. The PL intensity is very weak in the case of pure silane with $R = 0$ followed by a slight increase in the range of $R = 0.2$–0.4. The intensity of this peak increases rapidly when R is increased to 0.6 where the maximum intensity is observed with minimum width of about 0.10 eV. It is worth noting that further increasing R beyond 0.8 leads to decrease of the PL intensity. When flow rate of methane equals that of silane ($CH_4/SiH_4 = 1$), a broad shoulder centered at 720 nm (1.72 eV) becomes pronounced.

Most of the reports on the Si-based material PL processes have been regarded as being related to the size of the Si nanograins. In the QSE model, for instance, the emission energy is widely believed to shift to higher energy orientation because of the quantum confinement effect from the reduced nano-size. The nano-size-related shift is usually indicative of the dominant pole of QSE model in a PL process [7]. In the present experiment, even though the average size of the crystal silicon particle reduces into quantum-confined size range (see the following Raman scattering result), the emission energy, however, was pinned at around 1.41 eV. As such, the QSE model should be ruled out in our experiments.

To investigate the bond structure of Si–Si in the composite system, the narrow range (400–600 cm^{-1}) micro-Raman spectra of the thin films (with thicknesses in the range of 300–1500 nm) deposited on glass substrates have been measured. The spectra for the samples with gas ratio of $CH_4/SiH_4 = 0$, 0.6 and 1 are presented in Fig. 2. It should be noted that the signals in the recorded spectra are completely from the deposited films because of the use of glass substrates. Actually, the Raman peak is located at the vicinity of 521 cm^{-1} and the peak location scarcely changes when the gas ratio R is in the range of 0–0.4. The Raman spectrum of Si consists of three components, each corresponding to different bonding configurations. The TO mode of amorphous silicon appears at about 480 cm^{-1}, the intermediate phase exists around 510 cm^{-1} due to the formation of micrograins of size no more than 30 Å [15,16], and the crystalline silicon phase is near 521 cm^{-1}. Accordingly, Si is of high crystallinity in the range of $R = 0$–0.4. Further increase of the CH_4 molecule results in a reduction of the silicon crystallinity. At the ratio of $R = 0.6$, Raman peak is shifted to around 505 cm^{-1}. As mentioned above, the occurrence of an intermediate phase indicates the formation of nano-size silicon grains in the thin films. The size of the silicon grains can be estimated by the formula: [15] $t = 2\pi\sqrt{B/\Delta\omega}$, where t is the grain size, B (~2.0 cm^{-1} nm^2) the FWHM of the Raman peak, and $\Delta\omega$ the peak shift from crystalline to nanocrystalline silicon. The obtained value of t is ~2.3 nm, which is consistent with the previous HRTEM observation [8]. Recalling the maximum PL intensity at the same ratio of $CH_4/SiH_4 = 0.6$ shown in Fig. 1, we can connect the PL behavior with the presence of silicon nanoparticles. It is worthwhile to note that, silicon becomes almost amorphous with the peak at around 485 cm^{-1} when the ratio R reaches 0.8 and above. The phase evolution of silicon and the PL process in our experiments imply the formation of an amorphous SiC phase due to the introduction of CH_4 into the feedstock gases.

In order to get the information of the SiC matrix, FTIR absorption measurements were performed as shown in Fig. 3. The peak located at ~635 and 2100 cm^{-1} corresponds to the Si–H rocking/wagging and the SiH_2 stretching modes, respectively [17]. The former is recognized to be related to the entire hydrogen bonded with Si [18]. With increasing CH_4 in the feedstock gases, this peak becomes weak, indicating the reduced Si-bonded hydrogen in the deposited thin films. As a result, the observed PL should not be related to the hydrides as stated in Ref. [19], where the PL was

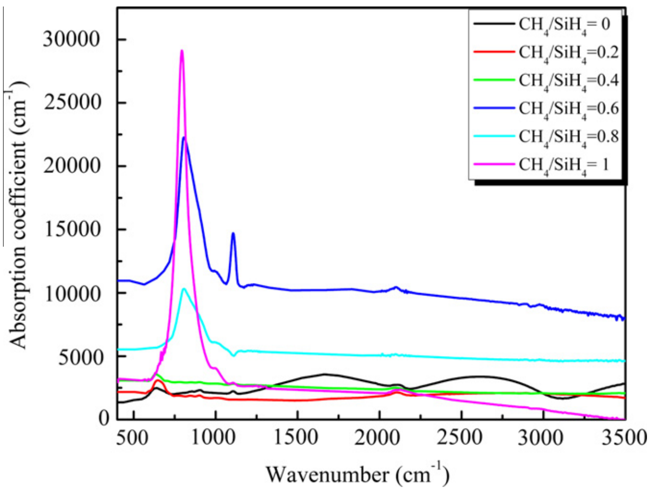

Fig. 3. FTIR absorption coefficient spectra at varying gas ratios of CH_4/SiH_4.