

Efficient visible electroluminescence from porous silicon diodes with low driven voltage

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By using n-butylamine as carbon resource, diamond-like carbon film (DLCF) was deposited on the p-n porous silicon (PS) surface by means of a radio-frequency glow discharge plasma system. Electroluminescent (EL) spectra show that EL intensity of the passivated PS diodes increases by 4.5 times and 30-nm blue-shift of EL peak occurs compared with the diodes without treatment and both of them are stable while the passivated diodes are exposed to the air indoor. The current-voltage (I - V) characteristics exhibit that the passivated diodes have a smaller series resistance and a lower onset voltage. The EL intensity-voltage (I_{EL} - V) relations of the PS devices with different DLCF thicknesses show that only medium DLCF thickness is optimum. These experimental phenomena have been explained based on Raman spectra and IR spectra of the diamond-like carbon films and IR spectra of the passivated PS samples.

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The optical properties of porous silicon are currently receiving widespread interest motivated by their potential application as electroluminescent devices compatible with silicon VLSI. Although visible light from avalanche breakdown in a Si p-n junction^[1] was reported by Newman *et al.* in 1955, its low efficiency, on the order of 10^{-9} , rendered it impractical for device applications. Electroluminescence (EL), which offers greater potential for device applications, has been obtained from porous silicon in solid-state structures. The observations of efficient room-temperature photoluminescence (PL) in porous silicon (PS)^[2] and electroluminescence for anodic^[3] or cathodic^[4] bias in an aqueous electrolyte have stimulated the research aimed at the realization of practical, low-cost Si-based electroluminescent devices.

Visible EL, with emission peaks spanning the wavelength ranging from red to blue, has been observed at room temperature from Schottky diodes prepared by evaporating a semitransparent metal contact onto a PS layer^[5]. However, to date, the reported quantum efficiencies have been poor, and often involve high applied bias voltages. More efficient EL has been obtained by increasing electron and hole injection into the emitting region through the incorporation of a p-n junction. The luminescent characteristics of light-emitting diodes with a PS p-n junction have recently been reported by several groups^[6,7]. Visible EL has also been observed from n-type indium-tin-oxide (ITO)/p-PS^[8], n-SiC/p-PS^[9] and conducting polymer (CP)/p-PS^[10]. Extremely low external quantum efficiency and poor stability of EL devices, however, hampered the successful development. To improve efficiency and stability of EL from PS, a lot of the post-treated methods of PS have been reported recently^[11-15]. In this letter we will present the EL from a p-n PS light-emitting diodes which utilize the diamond-like carbon films as a surface passivated layer of PS.

The porous samples were prepared using 5.0 – 8.5 Ω

n-type crystalline silicon. Anodization was performed in an electrolyte of 1 : 40% HF and ethanol at a current density of 10 mA/cm for 10 minutes under illumination by a tungsten lamp at an optical power density of 30 mW/cm². The total PS layer thickness was approximately 6 μ m estimated from a magnified side view. The porous region consisted of a mesoporous p-layer, a nanoporous n layer and formed a p-n junction, and an ITO contact was evaporated through a shadow mask. The backside contact was formed by evaporation of Al.

The diamond-like carbon films were prepared^[16] in a capacitive couple radio frequency plasma system with a stainless reactor and were deposited onto crystalline silicon wafers and p-n PS. The source material of the DLCF was n-butylamine. The organic precursor vapor was carried into reactor by pure hydrogen. The films deposited on crystalline silicon wafers were used for Raman and infrared spectroscopy analysis and the coatings deposited on p-n PS were used for PL and EL measurement. In the process of deposition, the rate of carrying gas flow was 50 ml/min; the pressure of the chamber was maintained at 266 Pa; the apparent radio frequency power was 150 – 300 W. The analysis of Raman spectroscopy shows that the film has diamond-like structure, and IR spectroscopy measurement indicates that there are SP^2 bonding, SP^3 bonding, and amino-group in the film.

Figure 1 shows the Raman spectrum of the films deposited on crystal silicon wafer. In the spectrum a broad scattering band with two maxima at 1337 and 1599 cm^{-1} appears. The frequency of the two peaks shifts as compared with the inherent frequency of SP^3 bonding of tetrabasic carbon in diamond and SP^2 bonding of tribasic carbon in graphite^[17], approximately 5 and 14 cm^{-1} , respectively. It will be shown later that there are amine groups and hydrogen atoms in the films. It is these amine groups and hydrogen atoms that lead SP^2 and SP^3 bonding to distort, thus causing the vibration frequency of SP^2 and SP^3 bonding of the films to shift.

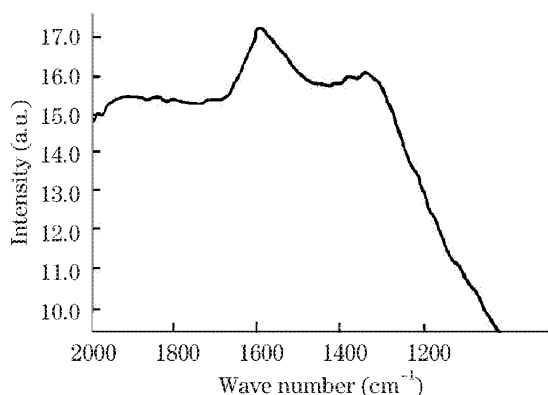


Fig. 1. Typical Raman spectrum for films grown from *n*-butylamine.

Therefore, we suggest that the 1337 cm^{-1} band is related to SP^3 bonding, while the 1599 cm^{-1} band is related to SP^2 bonding. The SP^3 - and SP^2 -type bonding are further supported by the IR spectrum of the film. The deformation of tetrabasic and tribasic carbon band also makes the peaks of Raman spectrum broadened. In addition, there are disorder distribution about the bond length and bond angle of amorphous carbon in the films. Therefore the vibration frequency of bonding is not unitary and a certain distribution appears.

Typical spectrum of the film deposited at radio frequency power of 150 W is shown in Fig. 2. The broad absorption peak at about 3400 cm^{-1} indicates the stretch vibration of N-H bonding. The peak at 3200 cm^{-1} is piled on the peak of N-H bonding. The stronger the absorption, the more the $SP^3\text{-CH}_2$ bonding in the film. The peak at 1641 cm^{-1} represents the deformation vibration of -NH bonding. Absorption at 1399 cm^{-1} is the vibration of deformed N-H bonding. The peak at 1088 cm^{-1} suggests the stretch vibration of C-N bonding. The peaks within the range from 455 to 780 cm^{-1} indicate the distortion vibration of C-H bonding to bonding and the group vibration of $R^1H = CHR^2$. The above analysis of IR spectrum shows that there exist amine groups in the film. It is the existence of amine groups and hydrogen atoms that cause the amorphous structure and the deformation of bonding to increase and lead to the Raman spectrum to form a broad absorption band.

Luminescence intensity is a main parameter to measure the device's properties. The EL spectra are obtained by

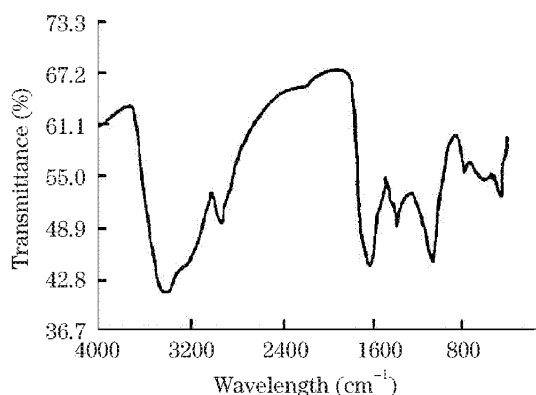


Fig. 2. Typical IR spectrum of the diamond-like carbon films.

transmission through a spectrometer onto a multi-alkali photomultiplier tube (PMT). The light is chopped and the signal from the PMT was measured with a lock-in amplifier. The excitation source is a He-Cd laser ($\lambda = 411\text{ nm}$). For freshly prepared PS devices, we note that the EL intensity of an ITO/DLCF/p-n PS light-emitting device (B) increases by 4.5 times and 30-nm blue-shift of EL occurs compared with an ITO/p-n PS light-emitting device (A). It is found that the EL intensity of the device B was reduced 5% and the EL peak are almost fixed, but the EL intensity of the device A was cut down 60% when the both devices have been exposed to the air for 60 days. According to the IR spectra of the passivated PS, the enhancement of EL intensity and stability may be due to the existence of Si-C, Si-N and Si-O bond structures on the PS surface simultaneously, and the blue-shift of the peaks may be attributed to amino-groups and hydrogen atoms in the passivated layer. It probably is the existence of amino-groups and hydrogen atoms that lead SP^2 and SP^3 bonding to distort, causing the vibration frequency of SP^2 and SP^3 bonding of thin films to shift.

Figure 3 shows the relative luminescent intensities of the device A and device B under different current densities. The luminescent intensity is approximately linear dependence on the current when the current is lower than $0.3\text{ mA}\cdot\text{mm}^{-2}$ for the device B and the device A, and deviates from linear behavior increasing drastically when the current is higher than $0.4\text{ mA}\cdot\text{mm}^{-2}$ and the higher the current, more obviously the luminescent intensity increases for the device B.

The I - V curve of an ITO/DLCF/p-n PS diodes (see Fig. 4) exhibits typical rectifying junction behavior. Similar rectifying I - V characteristics have also been observed from ITO/p-n PS diodes. The I - V curves reveal that the passivated diodes have a lower onset voltage than the one without treatment. At room temperature, the I - V characteristics in Fig. 4 indicate a relatively large value of series resistance R_s for our ITO/p-n PS diodes, basically due to nonoptimized sample preparation procedures (including the ITO deposition). We note that the presence of a series resistance in ITO/p-n PS diodes can limit the electrical-to-optical conversion efficiency since a portion of the applied voltage will be dropped across the resistance. We note that the series resistance R_s in the ITO/DLCF/p-n porous diode is reduced greatly,

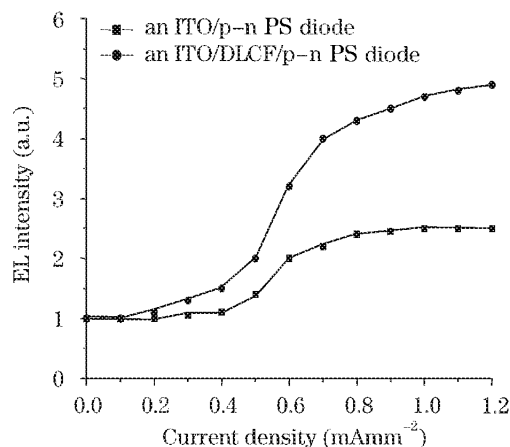


Fig. 3. The EL intensity of PS devices versus current density.

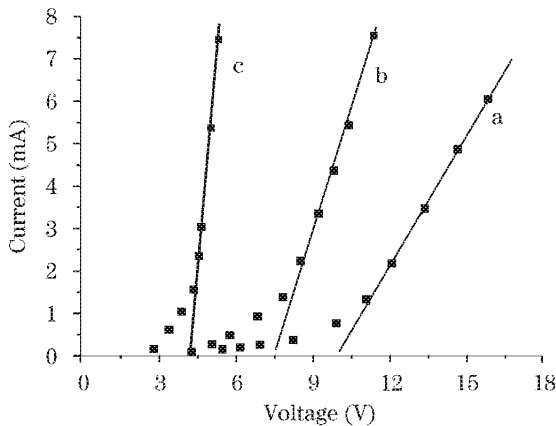


Fig. 4. Current-voltage characteristics of PS LED. Indicating presence of series resistance, the I - V curves of (a) a ITO/p-n PS LED and (b) an ITO/DLCF/p-n PS LED, (c) the corrected I - V curve of an ITO/DLCF/p-n PS LED for $R_s = 0$.

it is probably due to n-butylamine molecular permeates the pore, formed better contact between ITO and inner surface of PS.

The current-voltage relationship, including the ideality factor m , can be written as

$$I = I_0 \exp \left[\frac{q}{mKT} (V - IR_s) \right], \quad (1)$$

so that the dynamic resistance of the diodes is expressed as

$$r = \frac{dV}{dI} = \frac{mKT}{qI} + R_s. \quad (2)$$

Clearly, when V becomes larger, the first term in Eq. (2) will become negligible as compared with the second term, and the I - V characteristics will approach a straight line, with slope R_s . Relying on Eq. (2), we corrected the characteristics to obtain the dependence of the current on the junction voltage. An exponential regression analysis of the corrected data yielded curve (c) in the figure, which indicates that the device should emit light with less than 4-V applied bias, if R_s can be eliminated ($R_s \rightarrow 0$), such as by using higher doping levels in the base silicon.

When the voltage exceeds a certain value, the device will be destroyed for the heat effect. It was found experimentally that the heat makes the DLCF crackle. The destructive voltage for the device A is 90 V, while for the device B is 65 V. The different destructive voltages account for the decrease of resistance for passivation and thus the penetrating current and the heat effect increase drastically.

In order to compare the influence of different DLCF thickness on luminescence properties of PS devices, we have prepared three kinds of devices which DLCF thickness is 10, 20, and 30 nm respectively under the same experimental conditions. Figure 5 shows EL intensity-voltage relations (I_{EL} - V) of the PS devices with different DLCF thickness. All three profiles have the similar behavior, they can hardly luminescence under onset voltage and the EL intensity has linear dependence on the external voltage within the range of threshold voltage.

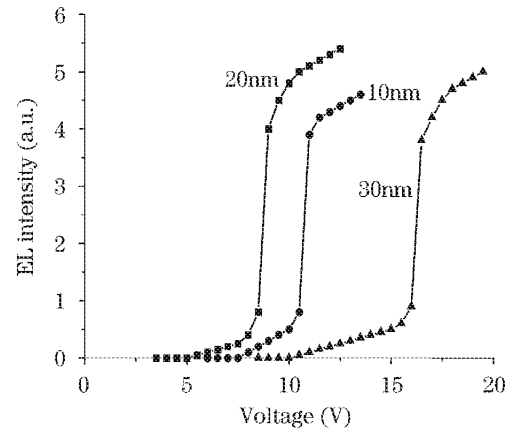


Fig. 5. EL intensity-voltage relations of the PS devices with different DLCF thickness.

The luminescence tends to be steady when keeping on increasing the voltage, but the device which DLCF thickness is 20 nm has lower onset voltage and higher luminescence intensity. If the DLCF is too thin or too thick, the onset voltage is higher and its steady luminescence intensity is lower. Only medium DLCF thickness is optimum.

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