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Blue Light Emission from Hydrogenated Amorphous Silicon Carbide Prepared by Xylene Source in Plasma-Enhanced Chemical Vapour Deposition System

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We chose xylene C_8H_{10} as carbon source instead of conventional methane CH_4 to fabricate a-$Si_{1-x}C_x$: H films using plasma-enhanced chemial vapour deposition method. The optical band gap of this material could be widened to 3.1 eV. And the infrared absorption spectra of our films manifest the existence of aromatic ring in them. Strong blue light emission with a peak wavelength of 490 nm has been observed at room temperature.

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The research on blue light emission materials has great significance in large-area flat-screen full-color display[1] and other optoelectronic device applications.[2] In such applications, hydrogenated amorphous silicon carbide (a-$Si_{1-x}C_x$: H) is one of the most attractive and promising materials since its wide band gap ranges from 1.8 to 2.6 eV or more when the carbon content in the material varies. This meets the energy requirement of visible light emission. Conventionally, methane (or other alkane or alkene, such as ethene or ethyne) is chosen to be the carbon source in silane-based reaction gas mixture to fabricate a-$Si_{1-x}C_x$: H films in rf plasma-enhanced chemical vapour deposition (PECVD) system. Making use of the dependence of the carbon content in a-$Si_{1-x}C_x$: H films on the composition of reaction gas mixture, we can optionally adjust the optical band gap (E_{opt}) by controlling the fraction of methane gas, which is defined as the methane flow rate divided by the total gas flow rate. However, a severe problem accompanies with the increase of the carbon content in the films. The electronic properties, especially photoluminescence (PL), rapidly deteriorate when E_{opt} is widened over 1.9 eV. This is attributed to the existence of plentiful carbons in form of methyl groups ($-CH_3$) that promote the formation of microvoids and Si dangling bonds, which provide main non-radiative recombination channels.[3,4] Moreover, E_{opt} of such material reaches the maximum value of about 2.6 eV at the carbon content about 60% and then decreases with increasing carbon content. It is generally considered that the band character of the material transforms from a tetrahedrally σ-bonded diamond-like type to a ($\pi - \pi^*$) graphite-like orbital type, resulting from the formation of graphitic clusters as pointed out by both theories and experiments.[5,6]

In order to reduce the ($-CH_3$) groups in the films, we used xylene (C_8H_{10}) instead of traditional methane as carbon source to prepare a series of a-$Si_{1-x}C_x$: H film samples with different xylene gas fraction by PECVD. The films were deposited on crystalline Si wafer, Corning 7059 glass, and fused quartz plate at 200°C in capacitively coupled reaction chamber at frequency 13.56 MHz. The liquid xylene source was kept at a constant temperature of 100°C and the saturated xylene vapor carried into the reactor by argon gas. The flow rates of pure [SiH_4] and [C_8H_{10}]+[Ar] mixture were finely controlled by mass flow controllers. The flow rate of xylene vapor was calculated according to the Dolton principles and E_{opt} deduced through Tauc plot.

Figure 1 shows the dependence of E_{opt} of a-$Si_{1-x}C_x$: H films on the fraction of xylene gas, which has the same definition as that of the methane gas mentioned above. Optical band gap E_{opt} obviously rises up from 2.4 to 3.1 eV with increasing fraction of xylene gas from 30 to 60%

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and then tends to saturation. Compared with that of methane-made a-$Si_{1-x}C_x$: H films (see the inset of Fig. 1), the value of E_{opt} of xylene-made a-$Si_{1-x}C_x$: H films has a great blue shift about 0.5 eV. We attribute this shift to two reasons: Firstly, it is far more easily to incorporate carbon into the alloys in the case of using xylene as carbon source than in the case of using methane. Secondly, the carbon-related radicals in xylene reaction plasma are mostly in form of C_8H_{10} or $C_8H_9^*$ groups instead of small [C–H] groups in the methane reaction plasma, which effectively reduces the formation of graphite-like cluster.[7] Consequently, the band gap of xylene-made a-$Si_{1-x}C_x$: H films is mainly determined by tetrahedrally bonded SiC atomic network in a larger range of carbon content.

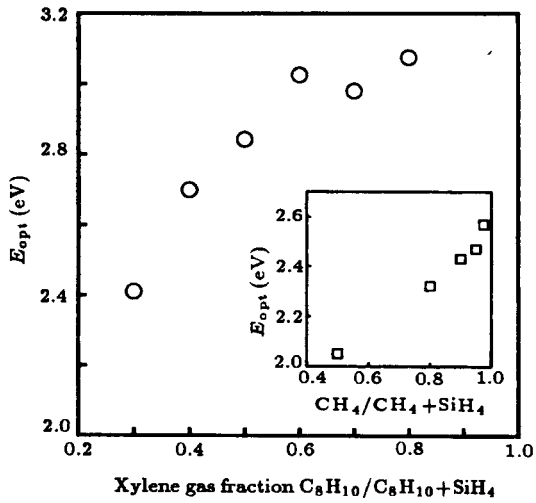

Fig. 1. Optical band gap of xylene-made a-$Si_{1-x}C_x$: H as a function of xylene gas fraction, compared with that of conventional methane-made a-$Si_{1-x}C_x$: H shown by the inset.

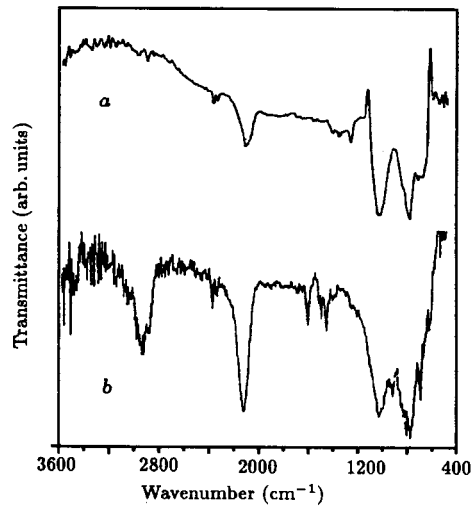

Fig. 2. Fourier-transform infrared spectra of a-$Si_{1-x}C_x$: H films prepared using methane *a* and using xylene *b*.

To get a better understanding of such character in E_{opt}, we have studied the [C–H] bonding configuration of xylene-made a-$Si_{1-x}C_x$: H films by Fourier-transform infrared spectroscopy and compared it with that of the methane-made a-$Si_{1-x}C_x$: H films. Curve *a* in Fig. 2 shows typical infrared spectrum for traditional methane-made a-$Si_{1-x}C_x$: H films. There are four prominent absorption features: the peak at 780 cm^{-1} assigned to Si–CH_3 group rocking or wagging mode and SiC stretching mode,[8,9] the peak at 1000 cm^{-1} attributed to CH_n ($n = 1, 2, 3$) group wagging mode,[10] the band at 1250–1400 cm^{-1} considered as Si–CH_3 symmetric and antisymmetric bending mode,[8] and the band at 2090–2100 cm^{-1} identified as SiH_2 groups stretching mode.[11,12] These peaks or bands manifest that carbons in traditional methane-made a-$Si_{1-x}C_x$: H films are dominantly incorporated as methyl groups while hydrogen acts as network terminators in the form of SiH_2 or methyl groups. The [C–H] bonding configuration of xylene-made a-$Si_{1-x}C_x$: H films has a remarkable difference from that of methane-made a-$Si_{1-x}C_x$: H films, as indicated by the infrared spectrum shown in curve *b* of Fig. 2. The film has an E_{opt} of 3.1 eV and xylene gas fraction is 60% in deposition. The most distinguished features are the occurrences of sp^2 C–H stretching mode at above 3000 cm^{-1}, sp^3 C–H stretching mode at 2800–3000 cm^{-1}, and the vibration mode of aromatic ring at 1400–1600 cm^{-1}, especially the sharp peak at 1602 cm^{-1} that can be recognized as distinctive vibration of the aromatic ring skeleton.[13] These peaks and bands definitely confirm the existence of a large amount of aromatic ring in our xylene-made a-$Si_{1-x}C_x$: H films. Another conspicuous character is the absence of Si–CH_3 bending mode

at 1250–1400 cm^{-1}, demonstrating the abrupt decrease of the Si–CH_3 groups in our xylene-made a-$Si_{1-x}C_x$: H films. Furthermore, in contrast with the peak at 1000 cm^{-1} in spectrum *a* of Fig. 2, the peak at 1030 cm^{-1} attributed to sp^2 C–H wagging mode also implies that carbon combination with hydrogen in xylene-made a-$Si_{1-x}C_x$: H films mainly exists in sp^2 C–H form[13] and hence gives an oblique evidence of the existence of aromatic ring in xylene-made a-$Si_{1-x}C_x$: H films.

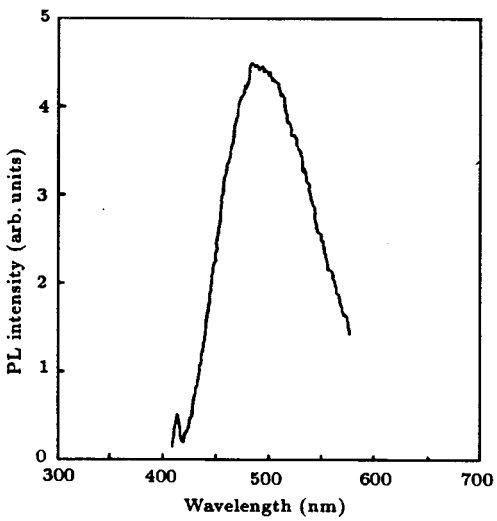

Fig. 3. PL spectrum of xylene-made a-$Si_{1-x}C_x$: H films with E_{opt} of about 3.1 eV. The excitation wavelength is 320 nm.

The modification in the bonding configuration resulted in the improvement of photoluminescence properties. The xylene-made a-$Si_{1-x}C_x$: H films can emit strong blue light at room temperature, as shown in Fig. 3. The excitation light source is Xe lamp and the wavelength of excitation light is 320 nm. The films deposited on crystalline Si substrates with an E_{opt} of 3.1 eV emit intense blue light with a peak wavelength of 490 nm (2.53 eV). When the excitation light wavelength changed from 240 to 260, 280, 300, 320, 350, 380, and 400 nm, the emission wavelength remains to be 490 nm, while the emission intensity decreased with decreasing of excitation photon energy. The study on emission mechanism in xylene-made a-$Si_{1-x}C_x$: H films is underway.

In conclusion, we chose xylene as the carbon source in place of conventional methane to fabricate a-$Si_{1-x}C_x$: H films using PECVD method, and observed intense blue light emission from such a material successfully. The infrared spectra manifest the presence of a lot of aromatic rings in these films and the absence of Si–CH_3 groups. This is obviously different from the character of conventional methane-made a-$Si_{1-x}C_x$: H films. Moreover, the E_{opt} of xylene-made a-$Si_{1-x}C_x$: H films can be widen to 3.1 eV, which is much wider than that of methane-made a-$Si_{1-x}C_x$: H films. This new properties allow this material to become a candidate in making blue light emission devices.

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