Photoluminescence of silicone oil treated by fluorocarbon plasma*

Chen Tian(陈 天)[a], Ye Chao(叶 超)[a]†, Yuan Ying(袁 颖)[a], Deng Yan-Hong(邓艳红)[a], Ge Shui-Bin(葛水兵)[a], Xu Yi-Jun(徐轶君)[a], Ning Zhao-Yuan(宁兆元)[a], Pan Xiao-Pin(潘小平)[b], and Wang Zhen-Ming(王振明)[b]

[a] *School of Physics Science and Technology, Jiangsu Key Laboratory of Thin Films, Soochow University, Suzhou* 215006, *China*
[b] *Joint Research Laboratory of Jiemei Biomedical Engineering Instrument, Soochow University, Suzhou* 215006, *China*

(Received 1 December 2011; revised manuscript received 23 February 2012)

We investigated the photoluminescence characteristics of the silicone oils treated by C_2F_6 and CHF_3 plasma. The silicone oil treated by the C_2F_6 plasma emitted a white light mainly composed of 415 nm, 469 nm, and 554 nm emissions, while that treated by the CHF_3 plasma emitted a pink light (415 nm). Fourier transformed infrared spectroscopy and Raman spectroscopy studies showed that the photoluminescence correlated with the Si–C bond, the carbon-related defects, and the oxygen vacancies. It was suggested that the light emitting at 554 nm was related to the Si–C bond and the carbon-related defects, while the pink emission at 415 nm was related to the oxygen vacancies.

Keywords: photoluminescence, fluorocarbon plasma, silicone oil

PACS: 78.55.–m, 78.66.Qn, 52.77.–j **DOI:** 10.1088/1674-1056/21/9/097802

1. Introduction

Development of a light source for applications in display and lighting technologies makes the Si-based light emission materials be of interest.[1−10] The carbon-incorporated silicon oxide is one of the promising candidates, because its photoluminescence (PL) covers the visible spectral range of 350–800 nm.[1] Recently, various carbon-incorporated silicon oxide light emitting materials have been developed, including amorphous Si:C:O:H films,[2] amorphous silicon oxycarbide (a-SiC_xO_y) films,[3−4] hydrogenated amorphous silicon carbide (a-SiC:H) films,[5,6] and silicon-incorporated diamond-like carbon films.[7] These films are usually fabricated via thermal vapor deposition,[3] reactive dc-magnetron sputtering,[2,6] melt-spinning,[4] and plasma enhanced chemical vapor deposition (PECVD).[5,7]

Silicone oil is also a kind of carbon-incorporated silicon oxide material. However, to our knowledge, no photoluminescence from the silicone oil is reported. How to fabricate light emission materials using the silicone oil is also interesting. Recent investigations on the light emission in carbon-incorporated silicon oxide materials showed that the bonds, the defects, the nanoparticles, and the clusters in the films were possible factors related to photoluminescence characteristics.[2,3,6,7] In our previous work, we have found that the bonding configurations of the silicone oil can be changed directly by Ar plasma treatment.[11] If we use the fluorocarbon plasma to treat the silicone oil and modify its bonding configurations, photoluminescence from the post-treated silicone oil may be achieved. Therefore, in this work, we investigate the photoluminescence of the silicone oil modified by C_2F_6 and CHF_3 plasma treatments.

2. Experiment

In the experiment, the silicone oil with a viscous coefficient of 500 $mm^2 \cdot s^{-1}$ was used as the original material. A thin layer of silicone oil at the quartz wafer was prepared by using the spin-on method at 4500 rpm. Its thickness was about 0.5 mm. Then the samples were treated by 60 MHz(HF)/2 MHz(LF) dual-frequency capacitively coupled plasma (DF-CCP).[12] A high-frequency (HF) power of 165 W (Comdel, CV500) was applied to the top electrode to produce the plasma. The thin layers of silicone oil were placed at the bottom electrode, and a (low-

*Project supported by the National Natural Science Foundation of China (Grant Nos. 10975105 and 11075114).
†Corresponding author. E-mail: cye@suda.edu.cn
© 2012 Chinese Physical Society and IOP Publishing Ltd

frequency) LF power of 100 W (Comdel, CX600) was applied to the bottom electrode, which controlled the ion energy to the samples.[13,14] The base pressure and the work pressure were 5×10^{-4} Pa and 50 Pa, respectively. Hexafluoroethane (C_2F_6, 99.99%) and trifluromethane (CHF_3, 99.999%) with a flow rate of 30 sccm were used as the discharge gas. The plasma treatment lasted for 30 min.

The photoluminescence measurements were carried out with a JASCO FP-6500 spectrofluorometer in the wavelength range of 250–600 nm with the resolution of 1 nm. The wavelength of the excited light was 220 nm. The bonding configurations of the original and the post-treatment silicone oils were measured by a Nicolet MagNa-IR550 Fourier transform infrared (FTIR) spectroscopy in the wavenumber range of 600–4000 cm^{-1} with the resolution of 3 cm^{-1}. The Raman spectra of the samples were recorded with a JY HR800 Raman spectrometer in the Raman shift range of 100–4000 cm^{-1} with the resolution of 1 cm^{-1}. The laser excitation line was 514 nm. The optical emission spectroscopy (OES) (AvaSpec-2048 fiber optic spectrometer) equipped with a CCD detector was used to measure the plasma characteristics in the wavelength range from 200 nm to 800 nm with a resolution of 0.05 nm to 0.13 nm.

3. Results and discussion

The photoluminescence spectra of the original silicone oil and the silicone oils treated by C_2F_6 and CHF_3 plasma are shown in Fig. 1. In Fig. 1(a), the photoluminescence spectrum includes two peaks at 299 nm and 386 nm from the quartz wafer and two weak peaks at 326 nm and 335 nm from the silicone oil. A very weak photoluminescence of silicone oil is observed. When the silicone oil is treated by the C_2F_6 plasma, its photoluminescence changes. In the photoluminescence spectrum of the silicone oil treated by the C_2F_6 plasma, five luminescence peaks located at 415 nm, 469 nm, 482 nm, 492 nm, and 554 nm are found, as shown in Fig. 1(b). The intensities of pink (415 nm), blue (469 nm), and green-yellow (554 nm) emissions are nearly the same. Therefore, the silicone oil treated by the C_2F_6 plasma can emit a white light. When the silicone oil is treated by the CHF_3 plasma, the emission intensity of pink light (415 nm) increases greatly, while that of green-yellow light (554 nm) decreases, as shown in Fig. 1(c). Therefore, the silicone oil treated by the CHF_3 plasma can emit a pink light. The results show that the silicone oil treated directly by the plasma can emit light, and the photoluminescence behavior is related to the plasma used in the process.

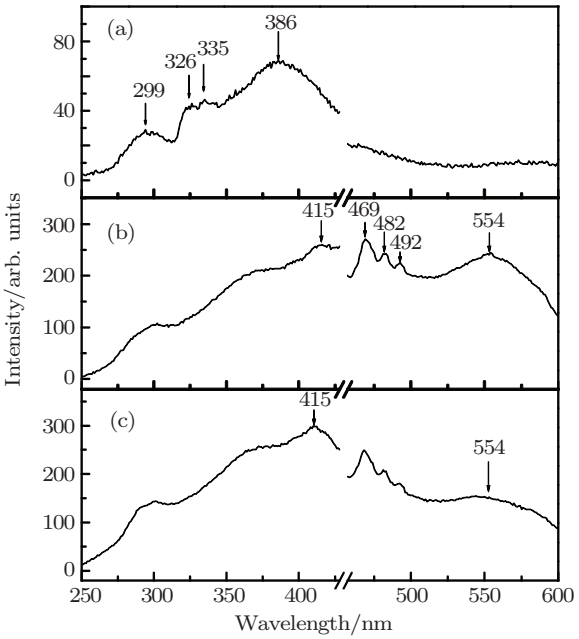


Fig. 1. Photoluminescence spectra of (a) the original silicone oil and the silicone oils treated by (b) C_2F_6 and (c) CHF_3 plasma.

To analyze the possible mechanism of light emission, the bonding configurations of the original silicone oil and the silicone oils treated by C_2F_6 and CHF_3 plasma were measured by FTIR. In the FTIR spectrum of the original silicone oil shown in Fig. 2(a), the bondings include the Si–O–Si (1021.86 cm^{-1} and 1092.15 cm^{-1}), Si–C in $SiMe_2$ and $SiMe_3$ (799.13 cm^{-1} and 863.86 cm^{-1}), Si–CH_3 (1261.28 cm^{-1}), Si–C–H (668.98 cm^{-1}), C–H (684.99 cm^{-1}), Si–O (700.99 cm^{-1}), Si–CH=CH_2 (1412.32 cm^{-1}), sp^2 C=C (1447.12 cm^{-1} and 1591.19 cm^{-1}), sp^3 C–H_2 (2904.84 cm^{-1}), and sp^3 C–H_3 (2962.56 cm^{-1}). The Si–O bonds form the main chain of the silicone oil molecule. The Si–CH_3, Si–C, and Si–C–H form the side chains, while C–H_3, C–H_2, and C–H are the terminal groups. The Si–CH=CH_2 and C=C may be from the impurity in the silicone oil. Because the silicone oil molecule is a macromolecule, the long Si–O chain leads to the Si–O–Si absorption splitting into two peaks.[15]

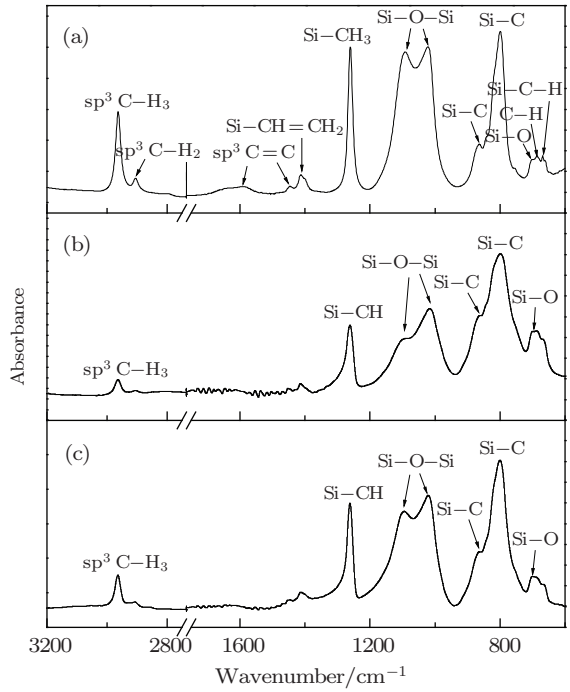


Fig. 2. FTIR spectra of (a) the original silicone oil and the silicone oils treated by (b) C_2F_6 and (c) CHF_3 plasma.

When the silicone oil is treated by the C_2F_6 plasma, the Si–O–Si vibration shifts to 1013.50 cm^{-1} from 1021.86 cm^{-1}, the Si–O–Si vibration at 1092.15 cm^{-1} appears as a peak shoulder of the Si–O–Si vibration at 1013.50 cm^{-1}, and two Si–O–Si peak intensities both decrease, as shown in Fig. 2(b). Additionally, Si–C–H (668.98 cm^{-1}) and C–H (684.99 cm^{-1}) disappear, Si–C in $SiMe_2$ (799.13 cm^{-1}), Si–O–Si (1092.15 cm^{-1}), Si–CH_3 (1261.28 cm^{-1}), and sp^3 C–H_3 (2962.56 cm^{-1}) all decrease. No CF_x-related bonding is found. The intensity decrease of the Si–O–Si peaks and the formation of the peak shoulder mean the broken of the long Si–O chain and the formation of short the Si–O chains,[15] while the intensity decrease of C–H_3 and C–H_2 peaks means the removal of some terminal groups. The stronger Si–C peak indicates the small loss of the Si–C structure. Therefore, the C_2F_6 plasma treatment leads to the formation of short the Si–O chains and more loss of C–H groups.

When the silicone oil is treated by the CHF_3 plasma, Si–C–H (668.98 cm^{-1}) and C–H (684.99 cm^{-1}) also disappear, Si–C in $SiMe_3$ (863.86 cm^{-1}), Si–O–Si stretching vibration (1021.86 cm^{-1} and 1092.15 cm^{-1}), Si–CH_3 (1261.28 cm^{-1}), and sp^3 C–H_3 (2962.56 cm^{-1}) all decrease, as shown in Fig. 2(c). Therefore, the CHF_3 plasma treatment also leads to the broken of the long Si–O chain and the removal of some CH_3 groups. However, the two splitting Si–O–Si stretching vibrations mean that the Si–O short chains formed in the CHF_3 plasma treatment are longer than those in the C_2F_6 plasma treatment.

Because the photoluminescence behavior of the carbon-incorporated silicon oxide is also related to the defects, the C-related structures are further studied with the Raman spectra shown in Fig. 3. For the silicone oil treated by the C_2F_6 plasma, except for Si–CH_3 (1263 cm^{-1}) and CH_2 (1412 cm^{-1}) peaks, which are also seen in the silicone oil,[16,17] a weak defect peak (D band at 1326 cm^{-1}) appears.[18,19] Therefore, the C_2F_6 plasma treatment leads to the formation of carbon-related defects. When the silicone oil is further treated by the CHF_3 plasma, the defect peak (D band at 1326 cm^{-1}) also exists, however, its intensity is very small. Therefore, the CHF_3 plasma treatment leads to small carbon-related defects in the silicone oil.

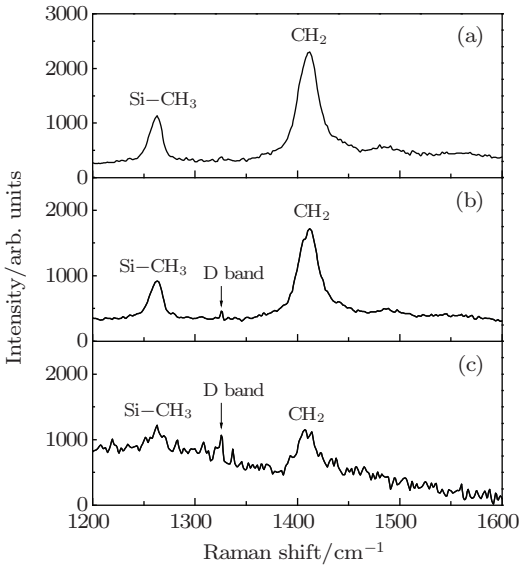


Fig. 3. Raman spectra of (a) the original silicone oil and the silicone oils treated by (b) C_2F_6 and (c) CHF_3 plasma.

The light emissions covering the spectral range of 400–700 nm from a-Si:C:O:H, a-SiC_xO_y, a-$Si_{1-x}C_x$:H films and silicon-incorporated diamond like carbon films have been reported.[2,3,6,7] However, the origins of light emissions are considered to be different, mainly related to the bonds, the defects, the nanoparticles, and the clusters in the films. The green-yellow emissions between 542 nm and 582 nm are attributed to the defects,[6] the c-SiC nanoparticles,[20] or the Si–O–C bond[3] in a-Si:C:O:H films. In our work, no Si–O–C absorption (at 437 cm^{-1})[3] in the FTIR is observed. However, a correlation between the light emission and the Si–C bond and the carbon-related

defects is found. For the silicone oil treated by the C_2F_6 plasma, the light emission at 554 nm shows a strong peak. Meanwhile, a strong Si–C peak in the FTIR and the carbon-related defects (D band) in the Raman spectrum are observed. While for the silicone oil treated by the CHF_3 plasma, the light emission at 554 nm decreases a little bit. Meanwhile, the D band in the Raman spectrum decreases, while the strong Si–C peak in the FTIR remains. Therefore, the photoluminescence peak at 554 nm may be related to the Si–C bond and the carbon-related defects.

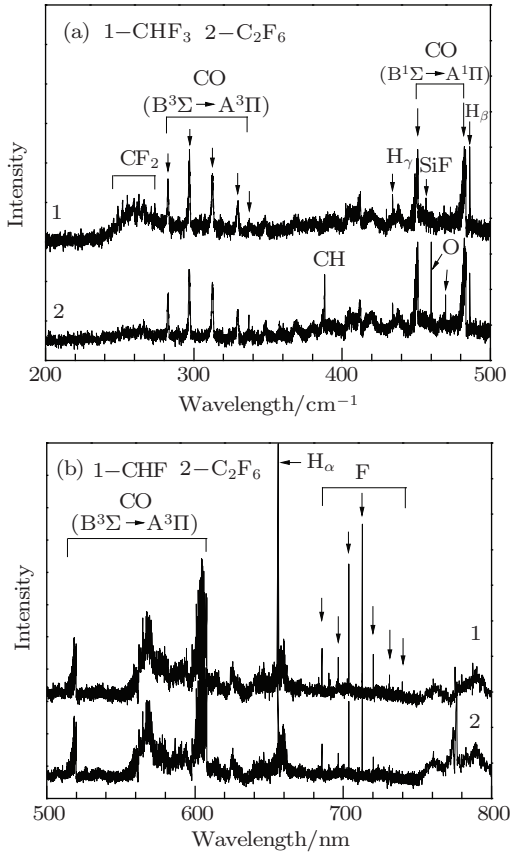


Fig. 4. OES spectra of (a) C_2F_6 and (b) CHF_3 plasma during treating silicone oils.

The light emission at 420 nm is attributed to the band to band recombination in the quantum confined β-SiC nano-crystals,[21] or the oxygen-deficient defect centers in a-SiO_xC_y.[4] The oxygen vacancy is formed by the dangling Si resulting from the removal of C and O atoms.[4] In our work, the light emission at 415 nm may be related to the oxygen-deficient defect centers. Under the action of fluorocarbon plasma, the Si–O chains break, and some terminal C–H_3 and C–H_2 groups remove from the Si atoms. The removal of the C atoms and the broken of the Si–O chains lead to the formation of dangling Si, resulting in the oxygen vacancies. Due to the difference in C_2F_6 and CHF_3 discharge plasma characteristics, the oxygen vacancies in the post-treated silicone oils are different. Figure 4 shows the optical emission spectra of CHF_3 and C_2F_6 discharge plasma during treating the silicone oils. In the OES spectrum of the CHF_3 plasma, the identifiable radicals include CF_2 (245–280 nm), CO ($B^3\Sigma\rightarrow A^3\Pi$ emissions at 282.05 nm, 296.78 nm, 312.78 nm, 329.80 nm, 336.91 nm, and $B^1\Sigma\rightarrow A^1\Pi$ emissions at 451.16 nm, 482.22 nm, 518.54 nm, 567.32 nm, 604.15 nm), H (656.22 nm, 486.08 nm, 486.08 nm), F (685.69 nm, 696.61 nm, 703.73 nm, 712.74 nm, 720.11 nm, 731.16 nm, 739.92 nm), and SiF (437.76 nm). In that of the C_2F_6 plasma, however, the new O (459.99 nm, 469.46 nm) and CH (388.27 nm) radicals appear. When using the C_2F_6 plasma to treat the silicone oil, the plasma is an O-contained environment, which is benefit for eliminating the oxygen vacancy in the post-treated silicone oil. Therefore, the light emission at 420 nm in the silicone oil treated by the C_2F_6 plasma is not as strong as that with the CHF_3 plasma.

4. Conclusion

The photoluminescence characteristics of the silicone oils treated by C_2F_6 and CHF_3 plasma were investigated. The silicone oil treated by the C_2F_6 plasma could emit a white light composed mainly of 415 nm, 469 nm, and 554 nm emissions, while that treated by the CHF_3 plasma emitted a pink light (415 nm). Fourier transformed infrared spectroscopy, Raman spectroscopy, and optical emission spectroscopy studies showed that the photoluminescence correlated with the Si–C bonds, the carbon-related defects, and the oxygen vacancies. It was suggested that the light emitting at 554 nm was related to the Si–C bonds and the carbon-related defects, while the pink emission at 415 nm was related to the oxygen vacancies. Therefore, C_2F_6 (CHF_3) plasma treating silicone oils could be used as white (pink) light emission materials.

References

[1] Ishikawa Y, Vasin A V, Salonen J, Muto S, Lysenko V S, Nazarov A N, Shibata N and Lehto V P 2008 *J. Appl. Phys.* **104** 083522

[2] Vasin A V, Ishikawa Y, Kolesnik S P, Konchits A A, Lysenko V S, Nazarov A N and Rudko G Y 2009 *Solid State Sci.* **11** 1833

[3] Gallis S, Nikas V, Suhag H, Huang M and Kaloyeros A E 2010 *Appl. Phys. Lett.* **97** 081905

[4] Yao R Q, Feng Z D, Zhang B J, Zhao H R, Yu Y X, Chen L F and Zhang Y 2011 *Opt. Mater.* **33** 635

[5] Ma T F, Xu J, Du J F, Li W, Huang X F and Chen K J 2000 *J. Appl. Phys.* **88** 6408

[6] Keffous A, Cheriet A, Belkacem Y, Gabouze N, Boukezzata A, Boukennous Y, Bright A, Cherfi R, Kechouane M, Guerbous L, Menous I and Menari H 2010 *Appl. Surf. Sci.* **256** 4591

[7] Ahmed Sk F, Banerjee D, Mitra M K and Chattopadhyay K K 2011 *J. Luminescence* **131** 2352

[8] Zhang X W, Lin T, Xu J, Xu L and Chen K J 2012 *Chin. Phys.* B **21** 018101

[9] Hu W X, Cheng B W, Xue C L, Zhang G Z, Su S J, Zuo Y H and Wang Q M 2012 *Chin. Phys.* B **21** 017805

[10] Xu H J, Chan Y F and Su L 2011 *Chin. Phys.* B **20** 107801

[11] Yuan Y, Ye C, Huang H W, Shi G F and Ning Z Y 2010 *Chin. Phys.* B **19** 065205

[12] Ye C, Xu Y J, Huang X J and Ning Z Y 2010 *Thin Solid Films* **518** 3223

[13] Georgieva V and Bogaerts A 2005 *J. Appl. Phys.* **98** 023308

[14] Li X S, Bi Z H, Chang D L, Li Z C, Wang S, Xu X, Xu Y, Lu W Q, Zhu A M and Wang Y N 2008 *Appl. Phys. Lett.* **93** 031504

[15] Feng Y J, Zhang J, Li M J and Zhu Q Z 2004 *Organosilicon Macromolecule & its Application* (Beijing: Chemical Industry Press) (in Chinese)

[16] Ke Y Kand Dong H R 1998 *Handbook of Analytical Chemistry*: *Optical Spectroscopy Analysis* (2th edn.) (Beijing: Chemical Industry Press) (in Chinese)

[17] Montejo M, Wann D A, Ortega P G R, Robertson H E, Márquez F, Rankin D W H and González J J L 2010 *J. Raman. Spectrosc.* **41** 1323

[18] Zhang W Y, Sun Y, Wu A Y, Xing J and Li J Y 2009 *Anal. Chem.* **81** 2912

[19] Zhang S L 2008 *Raman Spectroscopy & Low-dimension Nano-semiconductor* (Beijing: Science Press) (in Chinese)

[20] Chung C K, Chen T Y and Lai C E 2011 *Scripta Materialia* **65** 432

[21] Fan J Y, Wu X L, Kong F, Qiu T and Huang G S 2005 *Appl. Phys. Lett.* **86** 171903