

Visible light emission from Si-related nanostructures and the effect of ambient atmosphere on photoluminescence

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ABSTRACT

Si-related nanostructures were prepared by vapor condensation in an Ar-5%O₂ atmosphere at various working pressures (1, 30, 50, and 100 torr). The specimen prepared at 1 torr had a nanocrystalline core sheathed by a thin oxide layer. It exhibited orange photoluminescence (PL) peaked at 800 nm in vacuum. The PL disappeared when air was introduced into the sample chamber. For the specimens prepared at higher working pressures (30, 50, and 100 torr), an amorphous chain-like nanostructure was identified, and a blue-green light emission peaked at 520 nm was observed. The intensity of this blue-green PL increased with increasing the oxygen content of the Si oxide nanostructure, and an effect of ambient atmosphere on PL was also observed. The PL mechanisms of these two different light emissions and the related ambient effects on PL are discussed.

Keywords: Si, nanostructure, photoluminescence

1 INTRODUCTION

Si-related nanostructures have attracted a lot of attention owing to the possibility to realize silicon-based integrated optoelectronic devices since highly efficient visible luminescence from porous Si was reported in 1990 [1]. Based on the PL study of Si-related nanostructures, most of the visible luminescence could be classified into two emission bands: one is the low energy band (LEB) with the peak position at 1.5 to 1.9 eV [2-5], and the other is the high energy band (HEB) with the peak position at 2.4 to 3.1 eV [6-9]. The nanostructures exhibiting emissions in the HEB are generally oxygen-related, such as oxidized porous Si [10,11], oxygen-containing Si nanostructures [9,12], and Si/SiO₂ films [7,8]. Several commonly accepted mechanisms including quantum confinement effect (QCE) [7,10,13,14], surface state model [15,16], oxygen-induced luminescent centers [17,18], and hydrogen-related species [19], etc., have been proposed to account for the luminescence from these nanomaterials. However, there are still controversy and disputation on the mechanisms, thus further study is needed to understand the detailed properties of these visible luminescence.

2 EXPERIMENTAL

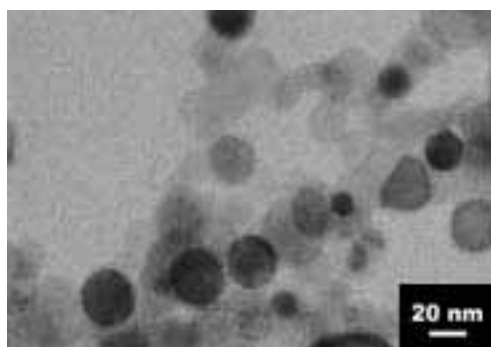
The Si-related nanostructures were prepared by vapor condensation in a thermal evaporation apparatus equipped with a liquid nitrogen trap. A gas mixture of argon/oxygen with the oxygen content fixed at 5% was introduced into the chamber as the working gas. The working pressure was set at four values: 1, 30, 50, and 100 torr. These Si-related nanostructures were grown directly on the stainless plate cooled by liquid nitrogen and then scraped off for characterization.

The crystallinity of the nanostructures were determined by X-ray diffraction (XRD, Rigaku), and the morphology and particle size were characterized by transmission electron microscopy (TEM, JEOL JEM-200 FX). Fourier transform infrared (FTIR) spectroscopy (Bomem MB-Series) was utilized to identify the composition of the nanostructures. The PL spectra were measured using a He-Cd laser with a power of 50 mW and wavelength of 325 nm. The samples were placed on a copper holder in the chamber which was equipped with a liquid helium cooling system. The chamber could be evacuated by a vacuum system, thus in-situ PL test under different ambient conditions could be conducted.

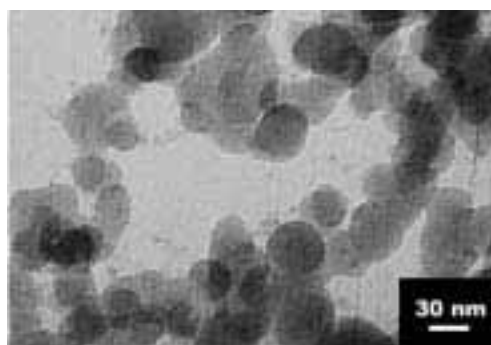
3 RESULTS AND DISCUSSION

The TEM image of Si-related nanostructure prepared at 1 torr is shown in Figure 1(a). All the nanoparticles were isolated and spherical, with a particle size ranging from 8 to 30 nm. Further characterization by HRTEM indicated that these nanoparticles had a crystalline core sheathed by a thin oxide shell which was in accordance with our previous work on Si quantum dots (SQDs).

On the contrary, the specimen prepared at 30 torr had an aggregated nanostructure of irregular morphology, as presented in Figure 1(b). The other two specimens prepared at higher working pressures of 50 and 100 torr also had the same cluster- or chain-like nanostructure. All the specimens prepared at higher pressures (30, 50, and 100 torr) were amorphous and mainly composed of Si oxide, according to the analyses of XRD and HRTEM. The structural feature of these oxygen-containing Si nanoparticles (OCSNs) is similar to that obtained by Morisaki et al. [9,12].



(a)



(b)

Figure 1: SEM images of SQDs prepared at various pressures. (a) 1 torr, (b) 30 torr.

From the FTIR analysis, a primary absorption band located at 1000 cm^{-1} to 1200 cm^{-1} and a small peak at 800 cm^{-1} were observed, that can be ascribed to the Si-O-Si and the Si-O stretching modes, respectively. Another broad band in the vicinity of 3400 cm^{-1} was caused by the Si-OH group. The peak intensity of all these absorption bands increased with increasing the working pressure, implying a higher oxygen content in the specimen prepared at a higher pressure.

An orange PL from the SQDs prepared at 1 torr was observed in vacuum, and the broad peak ranging from 500 nm to 900 nm had a maximum at around 800 nm, as illustrated in Figure 2. After air was introduced into the specimen chamber, however, the PL disappeared immediately. This PL phenomenon was basically the same as that of our previous study on SQDs in which an oxygen-related surface state was proposed to be responsible for the orange luminescence. Since the structure of the SQDs was a nanocrystalline core covered by an oxide shell, chemical bondings on surface may form certain surface localized states participating in the light emission process. Based on this model, the ambient effect on the PL performance can also be explained. The reversible quenching of PL by adsorption of air might be attributed to the redistribution of surface charge during the adsorption process [20], where resulting electrical field may break the surface-localized

excitons or affect the recombination states such that the radiative recombination is quenched.

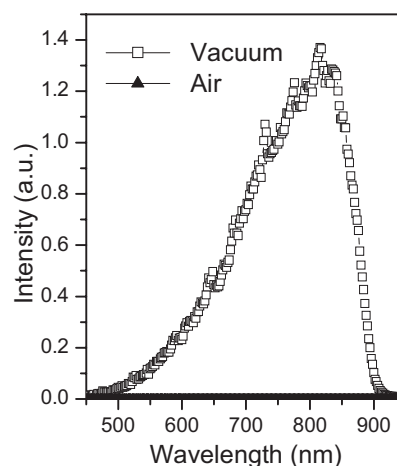


Figure 2: PL spectra of SQDs (1 torr) measured in air and vacuum.

Among all the OCSNs prepared at higher pressures (30, 50, and 100 torr), a stronger blue-green PL was observed in comparison with that of SQDs prepared at 1 torr, as presented in Figure 3. This blue-green PL ranging from 350 nm to 1000 nm had a maximum at 520 nm. The PL intensity increased with increasing the working pressure, or more specifically, with increasing the oxygen content in the OCSNs from the FTIR analysis. No peak shift with the oxygen content was observed.

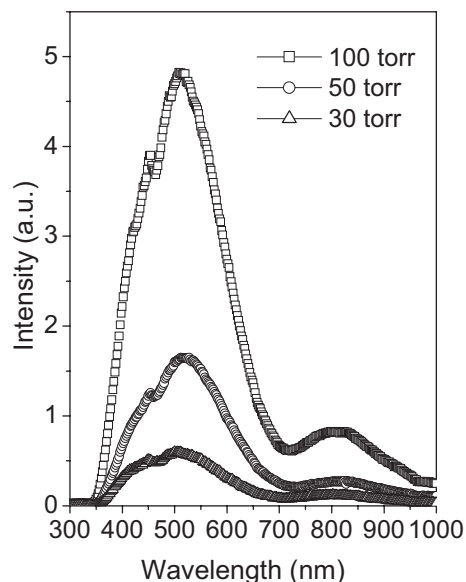
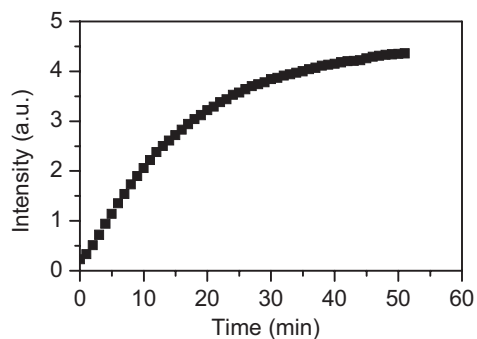
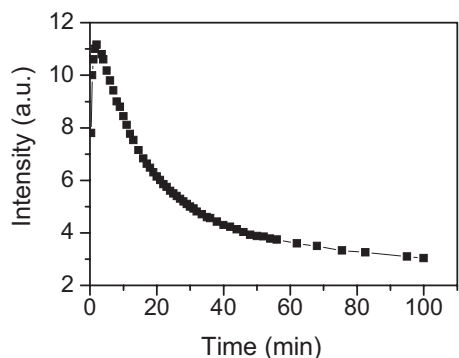


Figure 3: PL spectra measured in vacuum for OCSNs prepared at different working pressures.

The effect of ambient atmosphere on the PL of the OCSNs was also observed. Taking the specimen prepared at 100 torr as an example, the variation of peak intensity in vacuum is presented in Figure 4(a). The peak intensity at 520 nm increased at a higher increasing rate in the initial stage of vacuum process and then gradually saturated. When 1 atm air was introduced into the chamber, the peak intensity first rapidly increased in a very short interval of time and then decayed exponentially, as shown in Figure 4(b). If the chamber was evacuated again, the peak intensity went up again in the same way with very good reproducibility.



(a)



(b)

Figure 4: Ambient effect on the peak intensity at 520 nm of the OCSNs (100 torr). (a) vacuum, (b) air (1 atm).

Based on the above results and related literature [9,17,18], it is speculated that the blue-green light emission of the OCSNs is dominated by the mechanism of oxygen-induced luminescent centers. Here, both QCE and interface luminescent states are unlikely in operation because the physical dimension of the OCSNs is not small enough and there is no distinct interface between a nanocrystalline core and the Si oxide shell due to their amorphous structure. Thus, the constant peak position and the oxygen content-related intensity of PL should be ascribed to the oxygen-induced luminescent center. The amount of this luminescent

center increases with the oxygen content of the OCSNs, yielding increased PL intensity. When the transmission spectra of these OCSNs were taken, it was found that the absorption edge shifted from 300 nm to less than 200 nm as the working pressure increased. Combined with the FTIR analysis, this blue shift can be related to the increased oxygen content since SiO_2 has an energy gap of 8 eV.

The effect of gas adsorption on the PL performance can be explained by surface charge redistribution during the adsorption process [20,21]. This charge redistribution may break the excitons localized in the luminescent centers, resulting in a lower PL intensity. When the gas molecules are desorbed during the evacuation process, the configuration of charge distribution is recovered and the PL intensity increases again. That is the reason why a good reversibility by the cyclic vacuum-adsorption-vacuum process could be reached in the OCSNs.

4 CONCLUSION

Two different types of visible light emission were observed from the Si-related nanostructures prepared by vapor condensation in an Ar-5% O_2 atmosphere at various working pressures. The specimen prepared at 1 torr had a nanocrystalline core covered by a thin oxide shell. An orange PL peaked at 800 nm was observed from these SQDs in vacuum. The specimens prepared at higher working pressures had an amorphous chain-like nanostructure that exhibited a stronger blue-green light emission peaked at 520 nm. It is speculated that the orange emission of SQDs and the blue-green luminescence from OCSNs originate from certain surface states and oxygen-induced luminescent centers, respectively. An effect of ambient atmosphere on the PL was observed in both nanostructures. The different characteristics of PL in air and vacuum may be explained by surface charge redistribution during the gas adsorption and desorption process.

REFERENCES

- [1] L. T. Canham, *Appl. Phys. Lett.*, 57, 1046, 1990.
- [2] Y. H. Xie, W. L. Wilson, F. M. Ross, J. A. Mucha, E. A. Fitzgerald, J. M. Macaulay, and T. D. Harris, *J. Appl. Phys.*, 71, 2403, 1992.
- [3] Y. Kanemitsu, H. Uto, Y. Masumoto, T. Matsumoto, T. Futagi, and H. Mimura, *Phys. Rev. B*, 48, 2827, 1993.
- [4] Y. Q. Wang, G. L. Kong, W. D. Chen, H. W. Diao, C. Y. Chen, S. B. Zhang, and X. B. Liao, *Appl. Phys. Lett.*, 81, 4147, 2002.
- [5] C. Tsai, K. H. Li, D. S. Kinosky, R. Z. Qian, T. C. Hsu, J. T. Irby, S. K. Banerjee, A. F. Tasch, and J. C. Campbell, *Appl. Phys. Lett.*, 60, 1700, 1992.
- [6] A. J. Kontkiewicz, A. M. Kontkiewicz, J. Siejka, S. Sen, G. Nowak, A. M. Hoff, P. Sakthivel, K. Ahmed, P. Mukherjee, S. Witanachchi, and J. Lagowski, *Appl. Phys. Lett.*, 65, 1436, 1994.

- [7] O. Hanaizumi, K. Ono, and Y. Ogawa, *Appl. Phys. Lett.*, 82, 538, 2003.
- [8] M. Zhu, G. Chen, and P. Chen, *Appl. Phys. A*, 65, 195, 1997.
- [9] H. Morisaki, H. Hashimoto, F. W. Ping, H. Nozawa, and H. Ono, *J. Appl. Phys.*, 74, 2977, 1993.
- [10] H. Mimura, T. Futagi, T. Matsumoto, T. Nakamura, and Y. Kanemitsu, *Jpn J. Appl. Phys.*, 33, 586, 1994.
- [11] M. K. Lee and K. R. Peng, *Appl. Phys. Lett.*, 62, 3159, 1993.
- [12] S. Sato, H. Ono, S. Nozaki, and H. Morisaki, *Nanostruct. Mater.*, 5, 589, 1995.
- [13] H. Morisaki, *Nanotechnol.*, 3, 196, 1992.
- [14] J. G. Wan, M. Han, J. Zhou, and G. Wang, *Phys. Lett. A*, 280, 357, 2001.
- [15] Y. Kanemitsu and S. Okamoto, *Mater. Sci. Eng. B*, 48, 108, 1997.
- [16] F. Koch, V. Petrova-Koch, and T. Muschik, *J. Lumin.*, 57, 271, 1993.
- [17] L. Tsybeskov, J. V. Vandyshev, and P. M. Fauchet, *Phys. Rev. B*, 49, 7821, 1994.
- [18] S. Komuro, T. Kato, T. Morikawa, P. O’Keeffe, and Y. Aoyagi, *Appl. Phys. Lett.*, 68, 949, 1996.
- [19] Y. D. Glinka, S. H. Lin, and Y. T. Chen, *Appl. Phys. Lett.*, 75, 778, 1999.
- [20] T. Dittrich, E. A. Konstantinova, and V. Yu. Timoshenko, *Thin Solid Films*, 255, 238, 1995.
- [21] E. A. Konstantinova, T. Dittrich, V. Yu. Timoshenko, and P. K. Kashkarov, *Thin Solid Films*, 276, 265, 1996.