J|A|C|S
COMMUNICATIONS

X-ray Excited Optical Luminescence from Diamond Thin Films: The Contribution of sp^2- and H-Bonded Carbon to the Luminescence

Xingtai Zhou,[†] Tsun-Kong Sham,*[,†] Yu Wu,[‡] Yat-Ming Chong,[‡] Igor Bello,[‡] Shuit-Tong Lee,[‡]
Franziskus Heigl,[§] Tom Regier,[¶] and Robert I. R. Blyth[¶]

Department of Chemistry, The University of Western Ontario, London, Canada N6A 5B7, Center of Super-Diamond and Advanced Films (COSDAF) and Department of Physics and Materials Science, City University of Hong Kong, SAR, China, Canadian Synchrotron Radiation Facility, Synchrotron Radiation Center, University of Wisconsin−Madison, Stoughton, Wisconsin 53589, and Canadian Light Source, University of Saskatchewan, Saskatoon, Canada S7N 0X4

Received July 6, 2006; E-mail: sham@uwo.ca

Diamond is a very attractive wide band gap semiconductor for the fabrication of electronic and optoelectronic devices operating at high power and high switching frequency. Its electronic and optical properties are also desirable for light and electron emitting applications. For example, Koizumi et al. reported that homoepitaxial diamond p−n junction emits ultraviolet (UV) light at 235 nm with implication for the development of solid-state UV lasers.[1,2]

The photoluminescence (PL) excited by UV or visible light and cathodoluminescence (CL) excited by the electron beam from diamond thin films prepared by chemical vapor deposition (CVD) techniques have been widely studied. A sharp band at 1.68 eV[3−5] and several broad-band emissions at higher energies[6−15] from CVD diamond films have been reported. It is widely accepted that the sharp emission at 1.68 eV is related to defect centers involving silicon impurity in diamond.[3−5] However, the origin of the broad-band emissions is still not well understood. These broad-band emissions have been attributed to the phase impurities of short-range sp^2-bonded carbon[6−8,13−15] and hydrogen[9−14] on the surfaces of CVD diamond films. The sp^2-bonded carbon model can partly explain the experimental results, particularly, the increase of the intensity of some broad luminescence bands with the increase in content of the sp^2-bonded carbon in the diamond films.[8] The drawback of this model is, however, that it cannot explain the similarity of the luminescence features from diamond films, which may confine nonequivalent sp^2 carbon-bonded structures prepared by various techniques.[13] Furthermore, luminescence originating from both diamond phase and other phase impurities cannot be distinguished in the conventional PL and CL spectra. Finally, no direct evidence has been reported to support the above model.

In this work, we report the X-ray excited optical luminescence (XEOL) from a CVD diamond film. XEOL is an X-ray photon-in, optical photon-out technique that can provide site and excitation channel specificity if the excitation energy is tuned across an absorption edge.[16−18] Previous XEOL studies indicate that optical luminescence with excitations near an absorption threshold/edge depends strongly on the site and chemical environment of the absorbing atom as well as subsequent energy transfer to the luminescence chromophore, and that X-ray absorption near-edge structure (XANES) in photoluminescence yield (PLY) provides invaluable information on the origin of luminescence.[16]

The diamond film of interest was prepared on a Si(100) substrate by microwave plasma enhanced CVD with a 15 min bias-enhanced nucleation followed by a 10 min growth.[19] The experimental parameters are listed in Table 1. The film thickness is ∼100 nm, which is about one absorption length at the carbon K-edge, and the thickness effect, which can distort the spectrum recorded in photon (fluorescence X-ray and optical) yields, should be negligible in this case. The samples were analyzed by scanning electron microscopy (SEM, LEO 1530) and Raman In Via (Renishaw, wavelength = 244 and 514 nm for UV and visible light, respectively). X-ray absorption and XEOL were conducted on the spherical grating monochromator (SGM) undulator beamline (energy range = 250−1900 eV,$\Delta E/E = \sim 10^{-4}$) at the 2.9 GeV third generation Canadian Light Source (CLS). A JY 100 monochromator (200−850 nm) equipped with a Hamamastu photomultiplier was used to monitor the luminescence. The C K-edge XANES spectra are normalized by the I_0 measured with a clean photodiode to minimize contributions from carbon contamination from the optics (not a serious problem with relatively new beamline optics). The photodiode I_0 curve was checked with ion chamber measurements.

Table 1. Experimental Parameters of the Nucleation and Growth of the Diamond Film

parameters	nucleation	growth
CH_4:H_2	5%	0.5%
total flow rate (sccm)	200	200
pressure (Torr)	30	30
microwave power (W)	750	1300
substrate temp (°C)	850	800
substrate bias (V)	−150	0
duration (min)	15	10

In order to study the effect of the sp^2-bonded non-diamond carbon in the diamond thin films on the luminescence, a very thin diamond film with a high content of sp^2 carbon phase was chosen. The SEM image of the diamond film is shown in Figure 1a. The size of the diamond particle is on the order of tens of nanometers. Both UV and visible Raman (Figure 1b) exhibit a diamond peak at ∼1332 cm^{-1} and a broad sp^2 non-diamond feature in the region of 1500−1600 cm^{-1}. Clearly, relative to the visible Raman, the UV Raman spectrum shows an indisputable diamond peak at ∼1332 cm^{-1}, as UV Raman is more effective to reveal the sp^3 diamond phase in the film.[20] The Raman spectra show that the film consists of both diamond and sp^2 non-diamond carbon.

The room temperature XEOL spectrum (Figure 2a) of the diamond film acquired at an excitation photon energy of 500 eV exhibits a very sharp emission peak at 1.67 eV and broad-band emissions centered at 2.3, 2.5, and 2.8 eV as well as a weak band at 4.0 eV. No diamond near band-edge emission at 5.5 eV corresponding to the diamond band gap is observed. The disappearance of the near band-edge emission from some wide band

---

[†] The University of Western Ontario.
[‡] City University of Hong Kong.
[§] University of Wisconsin−Madison.
[¶] University of Saskatchewan.

10.1021/ja064555r CCC: $37.00

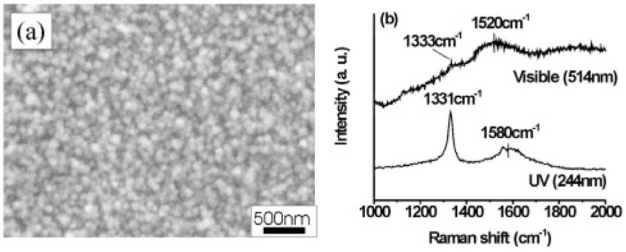

Figure 1. (a) SEM image. (b) Raman spectra of the diamond thin film sample.

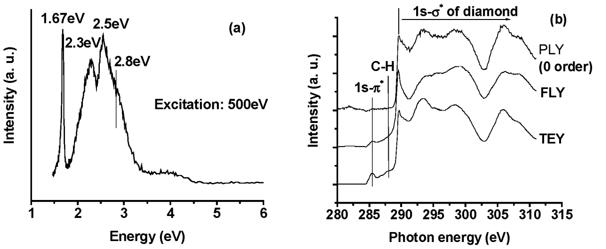

Figure 2. (a) Room temperature XEOL from the diamond film sample excited at 500 eV photon energy. (b) The C K-edge XANES of the diamond thin film sample obtained in TEY, FLY, and PLY.

gap semiconductors is not uncommon as the near band-edge emission can be quenched by the defect energy states in the band gap. These emissions have been observed in the PL[8,14] and CL[9,15] analyses of CVD diamond films. The C K-edge XANES spectra recorded in total electron yield (TEY), X-ray fluorescence yield (FLY), and PLY (zero order) are displayed in Figure 2b. Both the surface-sensitive TEY- and the more bulk-sensitive FLY-XANES spectra exhibit similar spectral patterns characteristic of diamond with a sharp edge peak at 289 eV (an excitonic transition) and a dip at 303 eV. This indicates that the film is sufficiently thin. Also observed is an sp^2 carbon feature at 285.5 eV (the $1s-\pi^*$ transition of sp^2 non-diamond carbon). These observations also indicate that the film consists of sp^2 carbon and a dominant sp^3 diamond phase.[21] Compared to the more bulk-sensitive FLY, the surface-sensitive TEY exhibits a more noticeable $1s-\pi^*$ transition and an additional weak feature at ~288 eV ($1s-\sigma^*$ transition of H-bonded carbon). The enhancement of the π^* transition feature and the appearance of the C−H bond transition in the TEY are due to the presence of diamond surface states and reconstruction.[22,23] The appearance of the C−H bond σ^* transition in the TEY confirms the presence of hydrogen at the diamond surface. The PLY shown in Figure 2b is very similar to TEY and FLY, except for the disappearance of the π^* and C−H bond transition features. Note that in the PLY spectrum there is a weak feature at ~282 eV. This feature could be due to the contribution of the defect centers involving silicon impurity in diamond phase to the luminescence as the X-ray at this energy excites the Si-bonded carbon atoms.[24] Further experiments are need to confirm this point. The similarity of the PLY to TEY and FLY for a sufficiently thin film indicates that the observed luminescence (including the sharp Si impurity-related emission at 1.67 eV and the other broad emissions) from the sample comes from the diamond phase. The disappearance of π^* and C−H bond features in PLY reveals that no noticeable change in luminescence from the sample is recorded when the sp^2 carbon and/or surface carbon atoms bonded to hydrogen in the film are preferentially excited by X-ray. This indicates that both the sp^2-bonded carbon and surface carbon atoms bonded with hydrogen contribute little to the observed luminescence. In other words, the observed luminescence from the CVD diamond film sample comes from the diamond itself and not the phase impurities such as sp^2 carbon and the surface carbon atoms bonded to hydrogen. The luminescence from diamond films should then be assigned to the defects, such as dislocations, defects near diamond grain boundaries, Si- or N-associated defects in diamond crystallites.[25] However, further research work is needed to corroborate the detailed assignment of the broad-band emissions. Thus, to reconcile with the observation that the increase in the luminescence intensity from diamond films with the increase of sp^2 carbon in the films reported in literature,[8] we propose that this observation is probably due to the increase of defect density in the diamond crystallites, resulting in the enhancement of the broad-band emissions.

In summary, we have employed XEOL and XANES to study the luminescence from a diamond thin film prepared by microwave plasma enhanced CVD technique. Our results and analyses indicate that the observed luminescence, including the broad-band emissions, from CVD diamond films is not associated with the phase impurities of sp^2- or the H-bonded non-diamond carbon, as previously reported, but it originates from the dominant diamond phase.

Acknowledgment. Research at the University of Western Ontario is supported by NSERC, CFI, OIT, and CRC (T.K.S.). The research described in this paper was performed in part at the Canadian Light Source, which is supported by NSERC, NRC, CIHR, and the University of Saskatchewan.

References

(1) Koizumi, S.; Watanabe, K.; Hasegawa, M.; Kanda, H. *Science* **2001**, *292*, 1899−1901.
(2) John, P. *Science* **2001**, *292*, 1847−1848.
(3) Rossi, M. C.; Salvatori, S.; Galluzzi, F.; Montereali, R. M.; Somma, F. *Diamond Relat. Mater.* **1997**, *6*, 1564−1567.
(4) Correia, M. R.; Monterio, T.; Costa, L. C. *J. Appl. Phys.* **1998**, *84*, 2207−2211.
(5) Rzepka, E.; Laroche, J. M.; Teukam, Z.; Franc, G.; Jomard, F.; Ballutaud, D.; Galtier, P. *Phys. Status Solidi* **2004**, *A201*, 2503−2508.
(6) Robinjs, L. H.; Farabangh, E. N.; Feldman, A.; Cook, L. P. *Phys. Rev.* **1991**, *B43*, 9102−9107.
(7) Bergman, L.; Stoner, B. R.; Turner, K. F.; Glass, J. T.; Nemanich, R. J. *J. Appl. Phys.* **1992**, *73*, 3951−3957.
(8) Bergman, L.; McClure, M. T.; Glass, J. T.; Nemanich, R. J. *J. Appl. Phys.* **1994**, *76*, 3020−3027.
(9) Yang, X.; Barnes, A. V.; Albert, M. M.; Albridge, R. G.; McKinley, J. T.; Tolk, N. H.; Davidson, J. T. *J. Appl. Phys.* **1995**, *77*, 1758−1761.
(10) Hayashi, K.; Watanabe, H.; Yamanaka, S.; Okushi, H.; Kajimura, K.; Sekiguchi, T. *Appl. Phys. Lett.* **1996**, *69*, 1122−1124.
(11) Hayashi, K.; Watanabe, H.; Yamanaka, S.; K.; Sekiguchi, Okushi, H.; Kajimura, K. *Diamond Relat. Mater.* **1997**, *6*, 303−307.
(12) Hayashi, K.; Yamanaka, S.; Watanabe, H.; Sekiguchi, T.; Okushi, H.; Kajimura, K. *J. Appl. Phys.* **1997**, *81*, 744−753.
(13) Iakoubovskii, K.; Adriaenssens, G. J. *Phys. Rev.* **2000**, *B61*, 10174−10182.
(14) Iakoubovskii, K.; Adriaenssens, G. J. *Diamond Relat. Mater.* **2000**, *9*, 1017−1020.
(15) Takeuchi, D.; Watanabe, H.; Yamanaka, S. Okushi, H. *Phys. Rev.* **2001**, *B63*, 245328.
(16) Rogalev, A.; Goulon, J. In *Chemical Applications of Synchotron Radiation*; Sham, T. K., Ed.; World Scientific Publishing Co: River Edge, NJ, 2002; pp 707−760.
(17) Sham, T. K.; Jiang, D. T.; Coulthard, I.; Lorimer, J. W.; Feng, X. H.; Tan, K. H.; Frigo, S. P.; Rosenberg, R. A.; Houghton, D. C.; Bryskiewicz, B. *Nature* **1993**, *363*, 331−334.
(18) Rosenberg, R. A.; Shenoy, G. K.; Heigl, F.; Lee, S. T.; Kim, P. S. G.; Zhou, X. T.; Sham, T. K. *Appl. Phys. Lett.* **2005**, *86*, 263115.
(19) Sun, C.; Zhang, W. J.; Wang, N.; Chan, C. Y.; Bello, I.; Lee, C. S.; Lee, S. T. *J. Appl. Phys.* **2000**, *88*, 3354−3360.
(20) Xiao, X.; Birrell, J.; Jerbi, J. E. Auciello, O.; Carlisle, J. A. *J. Appl. Phys.* **2004**, *96*, 2232−2239.
(21) Tang, Y. H.; Zhou, X. T.; Hu, Y. F.; Lee, C. S.; Lee, S. T.; Sham, T. K. *Chem. Phys. Lett.* **2003**, *372*, 320−324.
(22) Huang, L. J.; Bello, I.; Lau, W. M.; Lee, S. T.; Stevens, P. A.; DeVries, D. *J. Appl. Phys.* **1994**, *76*, 7483−7485.
(23) Hoffman, A.; Petravic, M.; Comtet, G.; Heurtel, A.; Hellner, L.; Dujardin, G. *Phys. Rev.* **1999**, *B59*, 3203−3209.
(24) Asokan, K.; Srivastava, S. K.; Kabiraj, D.; Mookerjee, S.; Avasthi, D. K.; Jan, J. C.; Chiou, J. W.; Pong, W. F.; Ting, L. C.; Chien, F. Z. *Nucl. Instrum. Methods Phys. Res., Sect. B* **2002**, *8*, 324−328.
(25) Kim, D. G.; Seong, T. Y.; Baik, Y. J.; Stevens Kalceff, M. A.; Phillips, M. R. *Diamond Relat. Mater.* **1999**, *8*, 712−716.

JA064555R