The Contribution of sp^2- and H-bonded Carbon to the Luminescence from Diamond Films

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Introduction

Photoluminescence (PL) from diamond thin films prepared by chemical vapor deposition (CVD) has been widely studied. The observation of a sharp band at 1.68 eV [1-3] and several broad-band emissions at higher energies [4] from CVD diamond films has been reported. [4-8] It is widely accepted that the sharp emission at 1.68 eV is related to defect centers involving silicon impurity in diamond. However, the origin of the broadband emissions is still not well understood. These broad-band emissions have been attributed to phase impurities associated with sp^2-bonded carbon [4,5] and hydrogen [6,7] on the surfaces. However, luminescence originating from diamond and other impurities cannot be distinguished in the conventional PL spectra. Additionally, no direct evidence has been reported to support this model. Here, we report X-ray excited optical luminescence (XEOL) from a CVD diamond film, providing new insight into this problem.

Science

In order to study the effect of the sp^2-bonded carbon in diamond thin films on luminescence, a very thin diamond film with a high content of sp^2 carbon phase was chosen. The diamond film of interest was prepared on a Si(100) substrate by microwave plasma enhanced CVD with a 15 minute bias-enhanced nucleation followed by a 10 minute growth [9]. The film thickness is ~100 nm, which is about one absorption length of carbon at photon energy just above 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. 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). Measurements were conducted on the SGM beamline 11ID-1 at the Canadian Light Source. A JY 100 monochromator (200-850 nm) equipped with a Hamamastu photomultiplier was used to record the luminescence spectrum. C *K*-edge XANES spectra are normalized by I_0 measured with a clean photodiode, checked with ion chamber measurements. 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, the Raman spectra show that the film consists of both diamond and sp^2 non-diamond carbon.

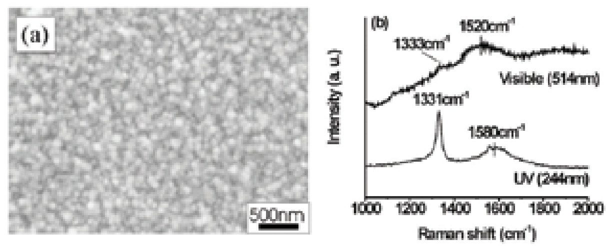

Figure 1: (a) SEM of the nanodiamond film and (b) corresponding Raman in both visible and UV region.

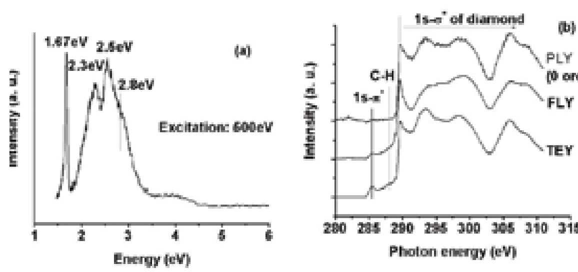

Figure 2: (a) Room temperature XEOL from the diamond film sample excited at 500 eV photon energy. (b) The C *K*-edge XANES of the diamond thin film sample obtained in TEY, FLY, and PLY.

The room temperature XEOL spectrum (Figure 2a) of the diamond film was acquired at an excitation photon energy of 500 eV. This energy, which is far above the C *K*-edge threshold, was selected so that the absorption cross-section for sp^3 and sp^2 carbon should be nearly the same (no localized resonance effects). From Figure 2a, there is 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. These emissions have been observed in the PL analyses of CVD diamond films. [5-8] The C *K*-edge XANES 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 bulk-sensitive FLY-XANES 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. A sp^2 carbon feature at 285.5 eV (the $1s \rightarrow \pi^*$ transition of sp^2 non-diamond carbon) is also observed. These observations also indicate that the film consists of sp^2 carbon and a dominant sp^3 diamond phase.

Discussion

Compared to the more bulk-sensitive FLY, the surface-sensitive TEY exhibits a more noticeable 1s → π* transition and an additional weak feature at ~288 eV (1s → σ* 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.[11] 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 σ* 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 [11,12]. 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 σ* 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-rays. 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. 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.

Conclusion

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.

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