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Cathodoluminescence experiments on isotopic clean diamond with carbon isotopes ^{12}C and ^{13}C

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Abstract

High-quality homoepitaxial diamond films grown by microwave plasma-assisted chemical vapor deposition from ^{12}C, ^{13}C and $^{natural}C$ containing methane (CH_4) gases have been studied by cathodoluminescence (CL) spectroscopy. Near-band-gap CL spectra at low temperatures were characterized in two isotopically enriched C diamond (^{12}C, ^{13}C) films. We observe an energy shift of the free-exciton recombination radiation with a change of the isotope composition from ^{12}C to ^{13}C. This result is in good agreement with both theoretical prediction as well as experimental results reported in the literature. In addition, strong excitonic emiss ion is detected from the isotopic clean ^{12}C diamond films at 79 K.
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Keywords: Isotopic clean diamond; Excitons; Cathodoluminescence

1. Introduction

Diamond in natural form consists out of an isotope mixture of 98.9% ^{12}C and 1.1% ^{13}C. This affects a variety of properties like thermal conductivity [1] which is in ^{12}C diamond significantly larger than in natural isotope mixtures, spin-lifetimes due to different nuclear spins which will ultimately affect quantum computing applications of diamond and exciton lifetimes which affects possible deep-UV light emitting devices. Isotopic compositions also affect band gaps through a change of lattice constant [2] and through changes in electron–phonon interactions. Several groups have reported about variation of the indirect band gap of natural and isotopically controlled single crystalline diamonds. For the first time, Collins et al. in 1990 [3] used cathodoluminescence experiment to characterize single crystalline diamonds, composed out of pure ^{12}C and ^{13}C. They showed that ^{13}C has a larger indirect band gap shifted by $\Delta E_g = 13.6$ meV than of ^{12}C. Moreover, Ruf et al. in 1998 [4] showed that ΔE_g is linearly depend on mixtures of $^{12}C^{13}_{1-x}C_x$.

However, up-to-now nearly all studies of diamond are related to natural isotope mixtures produced either by chemical vapor deposition (CVD) or high-pressure and high-temperature (HPHT) technique. Most of the data on isotope effects have in deed been deduced by measurement on HPHT synthetic diamond [5–7]. While the growth by plasma-assisted CVD of diamond has been optimized over recent years [8,9], no attention has been dedicated up-to-now to the growth of isotopically enriched CVD diamond films.

In this paper we report about cathodoluminescent data detected for the first time on isotopically clean ^{12}C and ^{13}C films grown by microwave plasma-assisted CVD. We use these experiments to characterize exciton properties with respect to phonon interactions, line widths and peak energy positions.

2. Experiment

The samples investigated in this work were grown by a 1.5-kW ASTeX 2.45 GHz microwave plasma-assisted CVD reactor system, contained in a stainless-steel vacuum chamber using a methane (CH_4) and hydrogen (H_2) gas mixture. Homoepitaxial diamond films were deposited on HPHT synthetic type Ib (001) single-crystal diamond plates with 3.0 mm × 3.0 mm × 0.5 mm and a misorientation angle of less than 0.5° as detected by X-ray diffraction. The chamber pressure was maintained at 25 Torr with a gas mixture 0.025% CH_4 in H_2, at a total flow rate of 400 sccm.

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The gas composition was determined from the flow rate of each gas. The applied microwave power was 750 W, and the substrate temperature was kept constant at 800 °C during growth. Isotopically pure methane either from ^{12}C or ^{13}C was obtained from Tokyo Gas Chemicals Co. The gases show purities greater than 99.9% for ^{12}C and greater than 98.7% for ^{13}C. The thicknesses of grown films are in the range of 3–7 μm.

The cathodoluminescence (CL) measurements were performed on diamond thin films using a custom-built electron beam source with 13 kV acceleration voltage and 2-μA beam current. The electron beam spot size is about 100 μm and the penetration depth is about 1.4 μm. Please note that the thickness of CVD diamond films is about 3 μm, so that the electron beam is fully absorbed in the these layers. The measurements were made in a UHV environment under a typical pressure of $<2\times10^{-10}$ Torr. The electron beam current and beam diameter were monitored by a Faraday cup detector assembled in the sample holder. The current signal and the secondary electron signal collected by the assembled detector were used to calculate the integrated profile. The spectral properties of the cathodoluminescence emission are detected using a specially designed and optimized mirror system, where the light is focused on an optical fiber bundle which guides the light into a 0.55-m monochromator with 1200 grooves/mm, blazed at 250 nm. An UV-enhanced CCD detector was used to detect photons. The spectral resolution was 0.04 nm (0.89 meV). The measurements were performed at a sample holder temperature (T_{ob}) of 79 K.

3. Results and discussion

Fig. 1 shows the near-band-gap CL spectra in the energy range be tween 4.9 eV and 5.45 eV for CVD diamond films d eposited with $^{12}CH_4$ and with $^{13}CH_4$, which will be denoted in the following as ^{12}C diamond and ^{13}C diamond, respectively. The applied temperature was $T_{ob}=79$ K. The data of Fig. 1 are normalized to the peak intensity labeled as FE^{TO} and shifted vertically for better comparisons. Five emission lines are observed. The CL spectra consist of a prominent free exciton–TO recombination line and four relative weaker emission maxima. These show exciton–phonon recombination features arising by interactions of excitons with transversal (TO) and longitudinal (LO) optical phonons and transverse acoustical phonons (TA). These emission lines, labeled as FE^{TA}, FE^{TO} and FE^{LO} are produced by exciton recombination in combination with TA phonons, TO phonons and LO phonons at energies (in ^{12}C diamond) of 87±2 meV, 141±1 meV and 163±1 meV, respectively [10–13]. The lines labeled $FE^{TO+O\Gamma}$ and $FE^{TO+2O\Gamma}$ arise

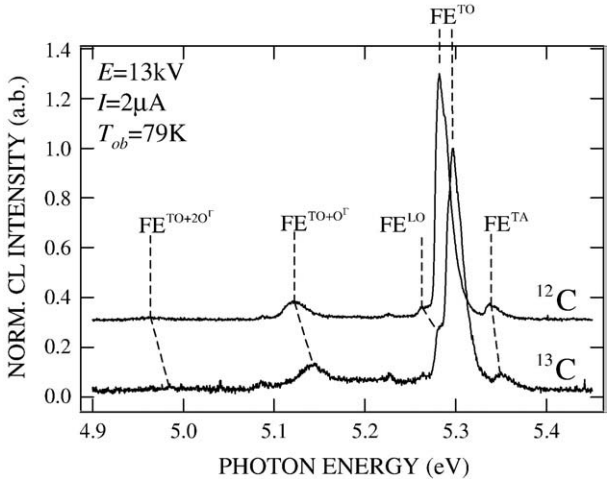

Fig. 1. Near-band-gap cathodoluminescence spectra of a homoepitaxial grown isotopic ^{12}C and isotopic ^{13}C diamond recorded at 79 K. The spectra show free-exciton emission with momentum conserving phonons (FE^{TA}, FE^{TO}, FE^{LO}) and phonon replicas ($FE^{TO+O\Gamma}$, FE^{TO+2O}). The spectra are normalized to the peak intensity labeled as FE^{TO} and shifted on the intensity axis for clarity.

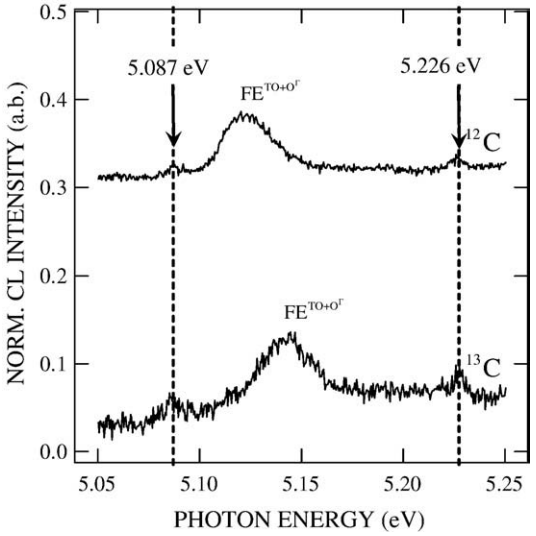

Fig. 2. Detailed the cathodoluminescence spectra in the energy rang 5.05–5.25 eV for the sample with ^{12}C and ^{13}C of the Fig. 1.

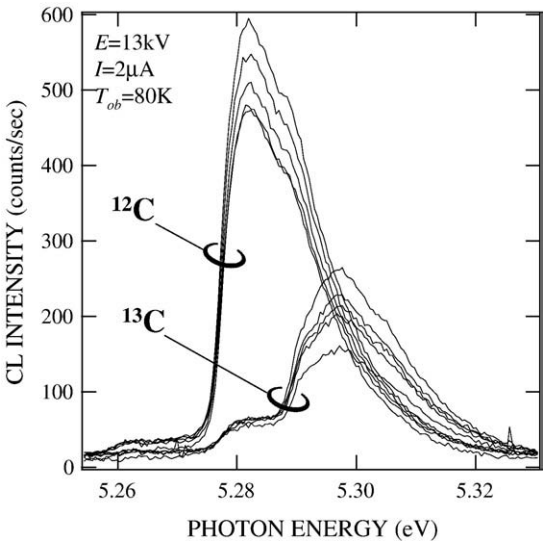

Fig. 3. CL spectra measured at different locations on the film.

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