Vibrational Properties of Nitrogen-Doped Nanocrystalline Diamond Films Grown by Microwave Plasma CVD

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Polycrystalline diamond films can be grown by a variety of chemical vapor deposition (CVD) techniques from methane-hydrogen gas mixtures at high (typically >90%) H_2 concentrations. In contrast, at very low (at few, or even zero, percents) H_2 concentrations, nanocrystalline diamond films (NCD) with grain size down to 2-5 nm are produced in microwave plasma [1] or DC discharge [2] provided a noble gas (Ar) is added to the feed gas. Addition of nitrogen in the NCD films has been shown to transform the virtually nonconductive films into the highly-conductive (up to 140 ? $^{-1}$ cm^{-1}) ones [3]. In the present work the NCD films grown in an Ar-rich microwave plasma with nitrogen gas added in amounts of 0%-25% were studied by Raman spectroscopy with different excitation wavelength. Besides the Raman spectra of diamond, the first and second order Raman scattering of disordered graphite and polyacetylene were detected in the films. The position of diamond peak at 1336 cm^{-1} revealed that nanodiamond grains are under strong compressive stress. With increasing nitrogen content in the gas phase the Raman spectra of disordered graphite show: (i) an increasing intensity ratio of D mode to G mode, and (ii) an upshift of the frequency of the G mode. No dispersion with excitation energy was notified for D and G bands With surface enhanced Raman scattering (SERS) a variety of surface vibrational modes was observed: (i) CH_x stretching vibrations of sp^3 and sp^2 hybridized carbon in the range of 2800-3100 cm^{-1}; (ii) the sp^2 and sp^1 hybridized CC(CN) stretching modes in the range of 1600-2300 cm^{-1}; and (iii) lines in the range of 200-1250 cm^{-1} related to different kinds of vibrations of substituted aromatic rings. These results do not contradict to the model in which the electrical conductivity in N-doped NCD films is realized through the intergrain material with well connected mixture of predominantly sp^2 phase with some amount of sp^1 phase of carbon and nitrogen.

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