Synthesis and electron field emission of nanocrystalline diamond thin films grown from N2/CH4 microwave plasmas

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Nanocrystalline diamond films have been synthesized by microwave plasma enhanced chemical vapor deposition using N2/CH4 as the reactant gas without additional H2. The nanocrystalline diamond phase has been identified by x-ray diffraction and transmission electron microscopy analyses. High resolution secondary ion mass spectroscopy has been employed to measure incorporated nitrogen concentrations up to 8 × 1020 atoms/cm3. Electron field emission measurements give an onset field as low as 3.2 V/μm. The effect of the incorporated nitrogen on the field emission characteristics of the nanocrystalline films is discussed. © 1997 American Institute of Physics. [S0021-8979(97)02821-1]

I. INTRODUCTION

Nitrogen has been recognized as an important impurity in diamond, and the nature of its electronic states has been a central concern in elucidating the semiconducting properties of both natural and synthetically grown diamonds. Although substitutional nitrogen in diamond is a deep donor impurity with a level at 1.9 eV below the minimum of the conduction band, nitrogen impurities can affect the optical transparency, the thermal conductivity, and the electron field emission characteristics of diamond. Incorporation of nitrogen impurities into chemical vapor deposit (CVD) diamond films has been extensively investigated by directly adding nitrogen to the reactant gas during the film deposition process. However, substitutional doping of CVD diamond with nitrogen has proven extremely difficult, presumably because the reactant gas used for film growth is atomic hydrogen rich, which has a strong etching effect on any non-diamond phase deposition.

Because of their low (or negative) electron affinity and their chemical stability, diamond and its related materials have been intensively studied as cold cathode electron field emitters. Recently, field emission has been demonstrated from mesa-etched diodes using carbon ion implantation into p-type diamond substrates, CVD polycrystalline diamond thin films, and pulsed laser deposited diamondlike carbon thin films. Due to its wide band gap, diamond has a very high electron resistivity. It is therefore difficult to transport electrons to the emitting surface, thus limiting the development of diamond-based materials as cold cathodes for flat panel displays. Although p-type doping can greatly improve the conductivity of diamond, it has no effect on the emission characteristics, except that structural defects caused by the doping process (such as ion implantation), which may provide some gap states, enhance the electron emission. Unlike the doping impurities or dopant-related defects (point defects), however, the density and the gap states provided by the structural (linear or planar) defects in the CVD diamond films are difficult to control. By contrast, n-type doped diamond films should be able to overcome these limitations and enhance electron field emission properties. Unfortunately, n-type doped diamond films have not been available up to now.

In this article, synthesis of nitrogen-incorporated nanocrystalline diamond thin films and their electron field emission properties are reported. The films have been prepared by microwave plasma enhanced CVD with a mixture of CH4 and N2 as the reactant gas. The nanocrystalline diamond phase in the resulting films has been identified by x-ray diffraction (XRD) and transmission electron microscopy (TEM) as well as electron energy loss spectroscopy (EELS). High resolution secondary ion mass spectroscopy (SIMS) analysis (monitoring CN− negative secondary ions) reveals a high concentration of nitrogen with a uniform depth profile throughout the film. Electron field emission measurements show that the nitrogen impurities or nitrogen-related defects strongly enhance the electron field emission from the films. Based on the microstructural characterization and the field emission measurement, the influences of nitrogen impurities on the electron field emission properties are discussed.

II. EXPERIMENTS

The effects of nitrogen as an addition or impurity in the reactant gas on the properties of the resulting CVD diamond films have been extensively studied. Up to now, nitrogen has not been successfully incorporated into diamond films to act as a donor impurity. In this study, a mixture of CH4 (2 sccm) and N2 (48 sccm) has been employed as the reactant gas for the microwave plasma enhanced CVD thin film preparation. N-type single crystal silicon wafers with...
(100) orientation were used as the substrates, and mechanical polishing with fine diamond powder (0.1 μm) was employed to provide nucleation sites for film growth. During the deposition process, the substrate temperature, input microwave power, and total ambient pressure were kept under 800 °C, 1100 W, and 35 Torr, respectively. The films prepared in this work were one micrometer thick, as determined by using an in situ laser reflectance interferometer to monitor modifications of the surface reflectivity during the film growth. In order to obtain some information on plasma chemistry, optical emission spectroscopy was employed to monitor the N₂/CH₄ plasma. The characterization of the as-grown films was then carried out by using XRD, TEM, EELS, and high-resolution SIMS.

The electron field emission properties of the samples were investigated by the cold cathode electron field emission test apparatus. The anode with 1.8 mm in diameter was flat except for a slight rounding at the corners to eliminate sharp edges. The gap between the anode (probe) and the cathode (sample) was computer controlled via a stepping motor. The initial gap between the electrodes was determined by an optical microscope attached to a CCD camera and a TV monitor. Characteristics of emission current versus applied field were then obtained by scanning the applied potential between the electrodes from 0 to 3000 V with a series of increasing gap distances. The emission current was converted to a 0–10 V signal by an electrometer that was typically operated to provide maximum output for an emission current of 10 μA. The cathode voltage was applied by an analog programmable 5 kV power supply under computer control, and the measured emission current was logged at each voltage. The measurements were carried out under a low 10⁻⁸ Torr ambient pressure.

III. RESULTS AND DISCUSSION

Figure 1 shows an optical emission spectrum of the N₂/CH₄ plasma used for the film deposition. As the labels in the spectrum indicate, the optical emission from the plasma consists mainly of the N₂ second positive system, the CN violet system (B²Σ – X²Σ), the C₂ Swan system (d 3Πg – a 2Πu), and the CN second-order violet system. We have observed that the growth rate of the films is proportional to the density of C₂ dimer in the plasma, but independent of the concentration of CN molecules. Therefore, the C₂ dimer appears to be the major growth species from the N₂/CH₄ plasma. C₂ as a growth species for diamond film in Ar–C₆₀ plasma was first proposed by Gruen et al., and details of the growth mechanism with C₂ dimer have been discussed in the literature.

The x-ray diffraction spectrum of the as-grown film is shown in Fig. 2. The diffraction peaks can be indexed on the basis of the cubic diamond structure (see the labels in Fig. 2) with no evidence of hexagonal stacking or a graphite phase. Note that the diffraction peaks are significantly broadened, meaning that the diamond crystals in the film have very small grain sizes. The silicon diffraction peak from {400} planes is due to the substrate. X-ray diffraction is not sensitive to noncrystalline phases, and thus no information on amorphous carbon is available with this method. Further characterization of the films has been conducted using TEM. Figure 3(a) shows a plane view TEM image, indicating that the film contains very fine grains with sizes ranging from 10 to 30 nm. The insert image shows a ring pattern from a selected area (over 10 μm in diameter) electron diffraction, illustrating that the diamond grains have a random orientation. EELS was employed as a diagnostic for amorphous or disordered carbon with sp² bonding. It is known that different carbon phases (graphite or amorphous carbon, and diamond) have very distinct K-shell absorption edge structures. Diamond has a single EELS feature with an onset at 289 eV due to its σ* electronic states, while graphite or amorphous carbon has an additional EELS edge starting at 284 eV, owing to its lower-lying antibonding π* states. Figure 3(b) shows an EELS spectrum of the nitrogen incorporated nanocrystalline diamond film acquired over an area of ~10 μm in diameter, displaying only an EELS edge at 289 eV, characteristic of diamond. No energy loss feature at 284 eV has been observed, suggesting a lack of amorphous or graphite phases in the film.

For conventional SIMS analysis, characterization of incorporated nitrogen in diamond thin films is difficult because of the interference of hydrocarbon masses with positive ni-
trogen secondary ions (very low ion yield) and because of no stable negative nitrogen ions. In this study, \( \mathrm{CN}^- \) negative secondary ions with a mass of 26.0031 amu have been measured by high resolution SIMS for the characterization of incorporated nitrogen.\(^{21}\) A mass spectrum of the as-grown film shown in Fig. 4(a), illustrative of the nature of the SIMS data, demonstrates a \( \mathrm{CN}^- \) secondary ion peak with a mass of 26.0030 amu. Figure 4(b) displays the depth profiles of carbon, nitrogen, and silicon through the film, illustrating that the concentration of the incorporated nitrogen in the as-grown nanocrystalline diamond thin film is as high as \( \sim 8 \times 10^{20} \) atoms/cm\(^3\) with a uniform distribution through the film which is 1 \( \mu \)m thick. Note that besides nitrogen, the film also contains significant amounts of hydrogen, which may be trapped at the grain boundaries to terminate the carbon dangling bonds. Oxygen impurity has also been observed in the film, which may be due to the Si substrate containing some SiO\(_2\) at the surface even after the mechanical polishing for seeding. All elements in the depth profiles were detected as negative secondary ions (under 14.5 keV Cs\(^+\) ion bombardment). The concentration scale is established using relative sensitivity factors derived from implantation standards. Note that 1.8 \( \times 10^{23} \) atoms/cm\(^3\) is used as the average carbon concentration of diamond for the calibration.

It is of interest to test the electron field emission properties of the films because the high concentration of incorporated nitrogen impurities or the nitrogen related defects may offer electron gap states, and thus enhance the electron field emission from the surface. Figure 5(a) shows plots of emission current density versus applied voltage with gap distances between the electrodes of 30, 130, and 230 \( \mu \)m. These measurements demonstrate that for the nitrogen incorporated diamond film, the onset field for the field emission with a current of 4 \( \mu \)A/cm\(^2\) when a 1.8 mm diam probe has been used is about 3.2 V/\( \mu \)m, while a field of \( \sim 6 \) V/\( \mu \)m is required to obtain an emission current density of 0.4 mA/cm\(^2\). Fowler–Nordheim plots of \( \ln(J/F^2) \) vs \( 1/F \) are shown in Fig.
the sample and nitrogen plasma, C2 appears to be the major growth species, terminating dangling bonds with hydrogen. By contrast, in a nitrogen radical stream, atomic radicals reach the growth surface during deposition, atomic hydrogen abstraction reaction is not required for the growth with C2, which may make the incorporation of nitrogen into diamond films possible.

It is well known that nitrogen is a deep donor impurity in diamond, resulting in a complex defect-related band structure with a high density of gap states. Based on photoluminescence (PL) and cathodoluminescence (CL) spectroscopy measurements, the major nitrogen-related defect centers include a vacancy trapped at a substitutional nitrogen atom (1.94 eV), a vacancy and a nitrogen atom (2.15 eV), vacancies trapped at A centers (2.30 and 2.46 eV), vacancies trapped at nitrogen B centers (2.49 eV), and so on. These nitrogen related defect centers may play an important role in enhancing electron field emission from the surface of the nanocrystalline diamond thin films, because without the nitrogen incorporation, the Fermi level of the diamond films is about 4.5 eV deep. Note that some planes of diamond have a negative electron affinity, meaning that the minimum energy state in vacuum is lower (about 0.7 eV) than the minimum energy state in the conduction band. Consequently, the energy barrier between the nitrogen-related defect centers listed above and the minimum of the vacuum energy level will be reduced to 1.0–1.8 eV. As a result of reducing the surface energy barrier by nitrogen impurity or nitrogen related defects, electrons from the nitrogen donor states may more easily tunnel into vacuum under the influence of a local electric field. A detailed study of the microstructure and defect features of our nitrogen incorporated nanocrystalline diamond film is under way.

IV. CONCLUSION

Microwave plasma enhanced CVD with a mixture of N2 and CH4 as the reactant gas has been employed to synthesize nitrogen incorporated diamond thin film. X-ray powder diffraction, TEM, and EELS characterizations demonstrate that the films prepared from the N2/CH4 plasma consist of a pure nanocrystalline diamond phase. High-resolution SIMS analysis shows that nitrogen with a concentration of 8 \times 10^{20} \text{atoms/cm}^3 has been incorporated into the nanocrystalline diamond thin films when the reactant gas with 96 vol. % N2 and 4 vol. % CH4 has been used. Electron field emission measurements reveal that the onset field of the emission from the nitrogen incorporated nanocrystalline diamond films is about 3.2 V/\mu m. It has been suggested that the electron gap states provided by the incorporated nitrogen play an important role of enhancing the electron field emission from the surface of the nanocrystalline thin film.

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