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Monolithic *n*-type conductivity on low temperature grown freestanding ultrananocrystalline diamond films

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We report monolithic *n*-type conductivity on low-temperature (<570 °C) grown ultrananocrystalline diamond (UNCD) films by Li-diffusion (about 255 nm) from $LiNbO_3$ substrates. Low resistivity of 1.2 Ω cm with carrier concentration of -2×10^{20} cm^{-3} is obtained on freestanding UNCD films. The films bonded to Cu-tape show very low turn-on field of 4.2 V/μm with emission current density of above 0.3 mA/cm^2 at a low applied filed of 10 V/μm. The *n*-type conductivity of low-temperature Li-diffused UNCD films overwhelms that of the high-temperature (≥800 °C) nitrogen doped ones and will make a significant impact to diamond-based electronics. © *2010 American Institute of Physics*. [doi:10.1063/1.3472204]

Diamond is an ideal candidate for electronic devices due to its marvelous physical and chemical properties[1–3] along with the possibilities to fabricate *p*-type or *n*-type conducting nature.[4–8] While the *p*-type doping of diamond is well established, *n*-type doping of diamond is still in its infancy. Recently, incorporation of nitrogen (N) into ultrananocrystalline diamond (UNCD) is reported to show *n*-type or semimetallic conductivity.[9–12] N-doped UNCD films also showed high electron field emission (EFE) characteristics and exhibited a potential for cold cathode emitters.[4,13,14] However, high growth temperature of above 800 °C is required to activate the dopants to produce the conductivity in the films,[14–17] which is not compatible with the Si-based device processes. Low temperature fabrication of *n*-type diamond films is required for diamond-based electronics.

Alternatively, Li-ion has been suggested as a possible *n*-type dopant into diamond.[18–20] However, the efforts for Li-doping into diamond via ion implantation, diffusion, or during growth were not very effective in making *n*-type conductivity and the reported results were contradictory.[19–22] Here, we show that by using $LiNbO_3$ substrate as a possible source of Li-doping to grow *n*-type UNCD films at very low growth temperature of about 570 °C and achieved an interesting characteristic of homojunction UNCD films. The possible mechanism of *n*-type conduction in UNCD films is presented.

UNCD films were grown on $LiNbO_3$ substrates in a microwave plasma enhanced chemical vapor deposition system with 1200 W and 110 Torr for 4–10 h. To increase the growth rate, H_2 (2%, 4%, 6%, 10%, and 15%) was added into CH_4(1%)/Ar plasma. It should be noted that, the thermal mismatch between diamond and $LiNbO_3$ substrate could make the film peel off from the substrate after growth, forming a freestanding film with the dimension of substrates. The films were bonded using epoxy to a plastic substrate and Ohmic contacts were made on the films in van der Pauw configuration to study the electrical properties.[23] It is interesting to note that, the bottom surface of UNCD films detached from the substrates possesses markedly smoother surface than the top surface (not shown) and showed very low resistivity, while the top surface of freestanding films showed insulating behavior.

The Hall measurements confirmed the *n*-type conductivity for the bottom surfaces of UNCD films. The bulk carrier concentrations and electrical resistivity vary with growth conditions and are given in Table I. Figure 1 shows that the resistivity of UNCD films first decreases monotonously with increasing H_2 percentage in the plasma, from 179 Ω cm (bulk concentration of -5×10^{15} cm^{-3}) for H_2-2% UNCD films to about 1.2 Ω cm with the bulk concentration of -2×10^{20} cm^{-3} for H_2-6% films. The resistivity reverted back for the films grown in larger H_2 percentage, i.e., 232 Ω cm (bulk concentration of -1×10^{15} cm^{-3}) for H_2-15% films. Restated, the lowest resistivity is obtained for UNCD films prepared in H_2-6% plasma. Moreover, these *n*-type UNCD films were grown without the substrate heating. The UNCD films prepared at a low substrate temperature of about 570 °C could exhibit *n*-type conductivity and carrier concentration comparable with those of high temperature (≥800 °C) grown *n*-type heavily N-doped[4,17] or *p*-type boron doped diamond films.[7]

The role of H_2 on enhancing this behavior is not understood yet. Previous reports stated that the addition of H_2 up to 10% in the plasma has no serious intervention in the C_2-based UNCD growth chemistry.[9] It is also known that the major role of increasing amount of H_2 in the plasma can lower the heterogeneous nucleation rate and therefore to in-

TABLE I. Plasma induced substrate temperature, bulk carrier concentration and resistivity measured by Hall measurements, and the turn-on field of electron field emission for the freestanding films grown on $LiNbO_3$ substrates in CH_4(1%)/Ar plasma with 2%–15% H_2.

Growth species	Substrate temperature (°C)	Bulk concentration (cm^{-3})	Resistivity (Ω cm)	Turn-on field (V/μm)
CH_4/Ar/H_2-2%	547	-5×10^{15}	179.0	6.8
CH_4/Ar/H_2-4%	553	-9×10^{16}	133.0	4.2
CH_4/Ar/H_2-6%	563	-2×10^{20}	1.2	5.2
CH_4/Ar/H_2-10%	570	-5×10^{18}	1.4	6.4
CH_4/Ar/H_2-15%	590	-1×10^{15}	232.0	8.0

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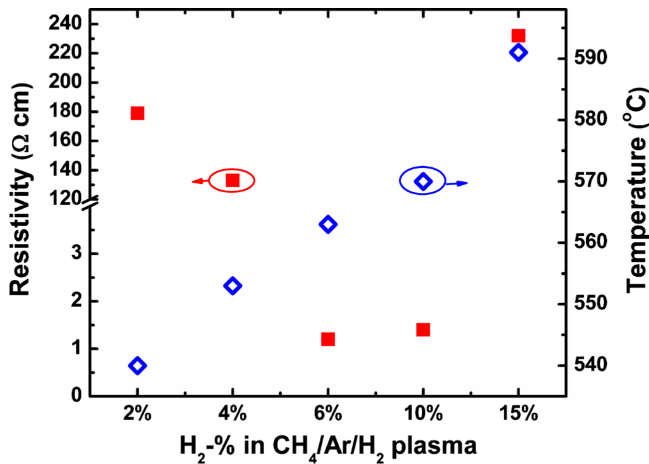

FIG. 1. (Color online) Variation in the resistivity (solid symbols) and substrate temperature (open symbols) of conducting side of the freestanding films with varying H_2 percentage in the growth medium.

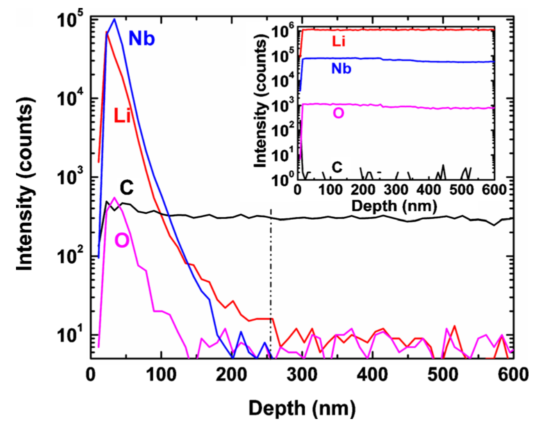

FIG. 3. (Color online) SIMS depth profile of conducting side of freestanding UNCD film grown on $LiNbO_3$ substrate in $CH_4/Ar/H_2(6\%)$. The dotted line in SIMS profile indicates the region between the doped and undoped region and the inset shows the SIMS depth profile of pristine $LiNbO_3$ substrate.

crease the crystallite size.[24,25] A thermocouple attached to below the substrate holder showed that the temperature is about 547 °C with H_2-2% and increased monotonically with H_2 percentage, reaching to about 590 °C for H_2-15% plasma (Fig. 1 and Table I). We expect that the slight increase in substrate temperature due to larger H_2 percentage in the plasma could lead to higher amount of Li-diffusion. However, it also induces the formation of large diamond grains that could hinder the Li-diffusion process, as report suggests that the doping effect of Li in MCD is limited.[21]

The sp^3 bonding nature of UNCD films is confirmed using UV-Raman spectroscopy (Renishaw, $\lambda = 328$ nm) studies on the bottom surfaces. The spectrum for H_2-6% UNCD film is shown in Fig. 2. A clear indication of sp^3 peak at about 1332 cm^{-1} is observed for all the films. In addition, transpolyacetylene (about 1185 cm^{-1}), D-band (about 1365 cm^{-1}), and G-band (about 1575 cm^{-1}) peaks are also observed due to nondiamond contents.[26] Inset in Fig. 2 shows typical high resolution transmission electron micrograph (HRTEM, Jeol-2100) near the conducting surface of H_2-6% UNCD films. The sp^3 bonded UNCD grains with size of about 5–10 nm are observed.[15] Formation of about 1 nm wide grain boundary nanochannel with mixture of sp^2 or amorphous type phases is observed.

To ensure the source of *n*-type conductivity for UNCD films, secondary ion mass spectroscopy (SIMS, Cameca-I4f) depth profile for the conducting side of the film was measured. Typical depth profile in Fig. 3 suggests that Li is diffused into UNCD to a depth of about 255 nm (H_2-6% films). For comparison, SIMS spectrum of pristine $LiNbO_3$ substrate is also shown in the inset. The initial counts for Li from UNCD layer and the substrate are similar, which suggests that highly Li-doping near the surface region of conducting side of the freestanding films. Nb and O diffusion are also observed. It is not clear yet whether the presence of Nb or O in the UNCD can influence the resistivity, which needs further investigation.

Furthermore, EFE measurements were also carried out on the conducting surface of UNCD films, bonded to a Cu-tape. A molybdenum rod with a diameter of 2 mm was used as anode and IV characteristics were acquired using Keithley 237 electrometer. The results are shown in Fig. 4 with the inset shows Fowler–Nordheim plots[27] of the corresponding data. For field emission measurements, the Cu-foil adhered to insulating side of the films was wrapped over to have a better contact with the conducting side of UNCD films. An applied field at a current density of 1 $\mu A/cm^2$ was taken as the turn-on field. The data in Table I indicates low turn-on field of about 4.2 $V/\mu m$ and 5.2 $V/\mu m$, respectively, for

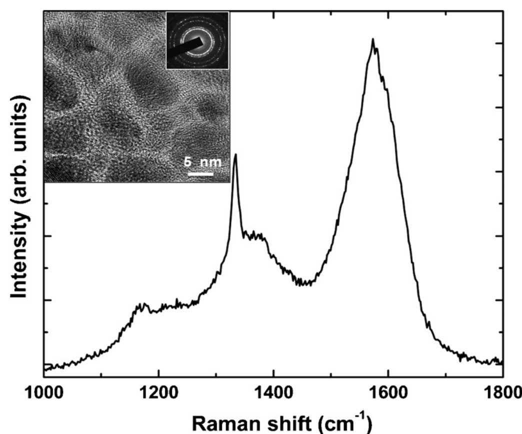

FIG. 2. UV Raman spectrum of freestanding UNCD film grown on $LiNbO_3$ substrate in $CH_4/Ar/H_2(6\%)$. The inset shows typical HRTEM image of the film and the corresponding SAD pattern.

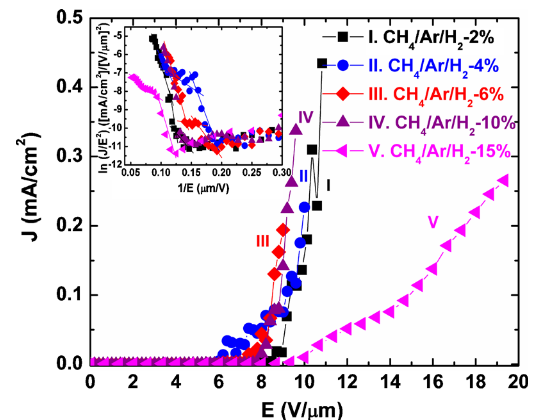

FIG. 4. (Color online) Field emission properties of conducting side of freestanding UNCD films grown on $LiNbO_3$ substrates in CH_4/Ar environment with different H_2 percentage.

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the sample grown in H_2-4% and H_2-6%. Such a turn-on field is low as compared with that for planar N-doped UNCD ever reported.[13,14] The highest level of Li-doping occurred for H_2-6% UNCD films, which exhibit the highest conductivity as well as the best EFE properties.

It is evident that the doping of Li into UNCD could provide *n*-type conductivity. The growth temperature (<570 °C) for this process is very low as compared to the required temperature for N-doping process (≥ 800 °C) to attain the same *n*-type conductivity. How the Li-doping enhances the conductivity of UNCD films is not completely understood yet. It is possibly via a mechanism similar to that of N-doping on improving the conductivity of UNCD films.[17] Presumably, the doped Li promotes the formation of disordered carbon containing nanochannels, which resides at grain boundaries and provides grain boundary transport, i.e., electron injection into interband defect levels or to π^* states that enhances the electron transport along grain boundaries.

In summary, Li-doping into UNCD is achieved via diffusion of Li from $LiNbO_3$ substrate at a low growth temperature of ≤ 570 °C. The sample prepared at $CH_4/Ar/H_2$-6% showed lowest resistivity probably due to the favorable substrate temperature and H_2-% to grow UNCD grains that can promote the maximum amount of Li-diffusion as well as grain boundary nanochannel formation. The bonding of freestanding UNCD films to substrates could make the films for device applications and may open up a pathway to the use of the low temperature grown *n*-type UNCD films for diamond electronics.

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