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Metallic contacts to nitrogen and boron doped diamond-like carbon films

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ABSTRACT

Hydrogenated diamond-like carbon (DLC) was deposited using a radio-frequency plasma-enhanced chemical vapor deposition method. Electrical properties of Al, Au, Ti, and Zr contacts to nitrogen and boron doped DLC films have been studied, and mechanisms of the observed current–voltage (*I–V*) characteristics are investigated. Linear *I–V* characteristics were observed for Au, Ti, and Zr contacts to both nitrogen and boron doped DLC films. A band structure model for metal–DLC contact is proposed to explain the observed ohmic contacts. Fermi level shifting at the surface of DLC films produces an ohmic resistive layer instead of a Schottky barrier for metal–DLC contacts. Al contacts to both nitrogen and boron doped DLC films show nonlinear *I–V* characteristics, which are attributed to a dielectric layer of carbide (Al_4C_3) instead of a Schottky barrier suggested by other groups. Inert elements such as Au and Pt, and transition metals such as Ti, Zr and W, which form conductive carbides, are considered good contacting metals for electrical studies of DLC films.

1. Introduction

Diamond-like carbon (DLC) is an amorphous carbon material made of random networks of sp^3 and sp^2 hybrid bonds. DLC material with high sp^3 content has similar mechanical, chemical, and electrical properties as single crystal or polycrystalline diamond and has applications in many fields [1,2]. Possible electronic applications of DLC material have attracted many interests because of its extended range of band gaps (1–4 eV), and of its room temperature and large area growth conditions. These properties make it very attractive in certain electronic applications like area detectors, displays, and solar cells [1–4]. Nitrogen doped DLC (a-C:H:N) and boron doped DLC (a-C:H:B) films have been studied by many groups to try to obtain n-type and p-type semiconducting DLC material [5–16]. Even though orders of magnitude increase of conductivity has been achieved, high doping density (1–20 at.%), reduction of optical band gap, and $T^{-1/4}$ temperature dependence of conductivity, all indicate that conductivity increase is due to increased density of localized states, and conduction mechanism is hopping among localized states [5–12,17,18] instead of band conduction. Hopping conduction can explain many of the observed linear and non-linear current–voltage (*I–V*) characteristics. Hopping conduction exhibits linear *I–V* characteristics at low electrical field, and shows nonlinear *I–V* relations at high electrical field due to mechanisms such as Fowler–Nordheim emission and Poole–Frenkel emission [13–15]. Even though advance in using DLC as traditional active semiconducting material has been slow, research groups have been reporting progresses in utilizing DLC material in many electronic applications: organic light emitting diode carrier injection enhancement [19,20], large piezo-resistive effects [21,22], room temperature electroluminance [23,24], electrode material for electrochemical applications [25], cold-cathode material [1,26,27], metal–semiconductor–metal detector [28], thin film transistors [29–31], and DLC/Si based solar cells [32–34].

Metallic contact studies are very important in researching of a semiconductor, yet there have been very few research works focusing on metallic contact to DLC material. Ohmic contacts have been reported for Ti and Cr [25,27], while Schottky contacts have been reported for Al and Ag [25,27,28]. Paul et al. [15] found rectifying Schottky contacts for sub-micron tipped Al, Au, and W metals at some areas on DLC films, while observing Poole–Frenkel emission on other areas. The goal of this study is to gain more experimental results and better theoretical understandings of metal–DLC electrical contacts.

In this study, hydrogenated DLC films doped with nitrogen and boron are prepared on quartz substrate. Planar contact patterns of Al, Au, Ti and Zr metals are deposited onto the surface of a-C:H:N and a-C:H:B films. *I–V* characteristics of coplanar type metal–DLC–metal structures are measured and analyzed. Raman spectroscopy, Auger electron spectroscopy, and UV–visible spectroscopy have been employed to characterize doped DLC films. A band-structure model is proposed to explain the observed and reported metal–DLC contact properties.

2. Experiments

A capacitively coupled parallel plate radio-frequency plasma-enhanced chemical vapor deposition system was used to deposit hydrogenated DLC on quartz substrate. Samples were mounted on the

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powered electrode. CH_4 was used as source gas, and NH_3 and BH_3 were used as doping gases. After reaching 10^{-4} Pa base pressure, Ar plasma was used to clean the sample chamber and quartz substrates. Deposition of undoped DLC films used only CH_4 gas with a flow rate of 80 sccm; deposition of a-C:H:N films used a mixture of CH_4 and NH_3 gases with flow rates of 50 and 5 sccm; and deposition of a-C:H:B films used a mixture of CH_4 and BH_3 gases with flow rates of 40 and 30 sccm respectively. Working pressure was kept at 5.0 Pa, and power was set at 200 W.

Sample thicknesses were measured using a Jobin ellipsometer and a Veeco Surface Profiler. The a-C:H:N and a-C:H:B samples were about 160 nm and 340 nm thick respectively. The a-C:H:N samples were thinner because NH_3 has a bigger etching effect on DLC films and hence leads to a lower growth rate. Raman scattering data were collected with a Renishaw System using 514 nm wavelength. Auger-electron spectroscopy data were collected on a Physical Electronics PHI 660 system, and the sputtering processes were carried out with Ar gas at 6.6×10^{-5} Pa pressure, 5 kV bias voltage, and 50 nA current. UV–visible spectra were collected and analyzed, and Tauc gaps of undoped DLC, a-C:H:N, and a-C:H:B films were calculated to be 1.20 eV, 0.70 eV, and 1.04 eV respectively.

After optical characterizations, arrays of circular metallic contacts with 1 mm diameter and 1 mm distance were deposited on the samples. Magnetron sputtering method was used to deposit Al and Au contacts, and ion plating method was used to prepare Ti and Zr contacts. *I–V* characteristics of coplanar metallic contacts with 1 mm and 3 mm distances were measured using a Keithley 6514 electrometer and 2410 SourceMeter. Special cares were taken to achieve good electrical contact between system probes and metal electrodes.

3. Results and discussions

Raman scattering spectra of undoped DLC, a-C:H:N, and a-C:H:B samples show similar structure, indicating similar sp^3/sp^2 composition (see Fig. 1). Characteristic parameters of the Raman spectra, including position of G peak, full width at half maximum (FWHM) of G peak, and $I(D)/I(G)$ (intensity ratio of D peak and G peak), are calculated by fitting two Gaussian peaks to the spectra. The results are shown in Table 1. As expected, calculated parameters are similar for all three kind of samples, with the undoped sample having slightly larger G peak width and lower $I(D)/I(G)$ ratio, which indicates that the undoped sample has slightly higher sp^3 density [35]. With a Tauc gap of 1.20 eV, undoped DLC samples have about 30% sp^3 content [35,36]. This means that a-C:H:N and a-C:H:B samples have slightly less than 30% sp^3 bonds.

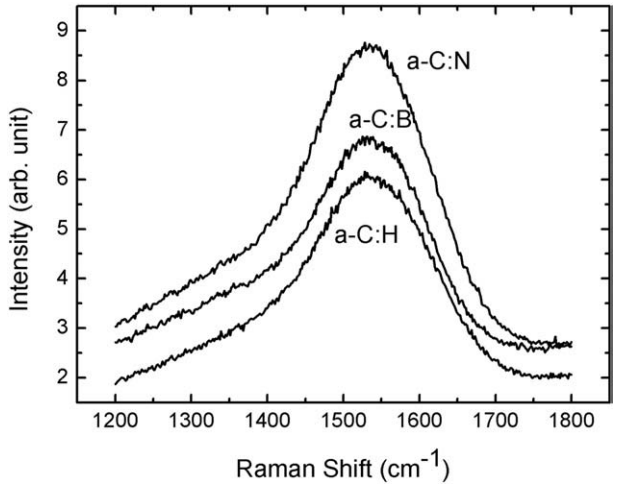

Fig. 1. Raman scattering spectra of Raman spectra results of undoped (a-C:H), nitrogen doped (a-C:H:N), and boron doped (a-C:H:B) DLC films.

Table 1
Raman spectra results of undoped (a-C:H), nitrogen doped (a-C:H:N), and boron doped (a-C:H:B) DLC films. Here Pos(G) is the position of G peak, and Width (G) is the FWHM of G peak; and $I(D)/I(G)$ is intensity ratio of the D peak and G peak.

	Pos (G) (cm^{-1})	Width(G) (cm^{-1})	$I(D)/I(G)$
a-C:H	1540	149	0.36
a-C:H:N	1540	146	0.32
a-C:H:B	1539	150	0.20

Auger-electron spectra in Fig. 2 show that nitrogen and boron have been effectively doped into DLC films. Nitrogen and boron doping density of 4.6 at.% and 2.7 at.% are obtained by fitting straight lines to the data. Nitrogen doping is more effective than boron.

I–V characteristics of a-C:H:N and a-C:H:B contacting Al, Au, Ti, and Zr metals are shown in Figs. 3 and 4. Ohmic behaviors are observed for Au, Ti, and Zr contacts to both a-C:H:N and a-C:H:B samples, while nonlinearity is observed for Al contacts. The slopes of Al contacts are smaller than that of the other metals, indicating higher resistance. Straight lines are fitted to the linear *I–V* data of Au, Ti, and Zr contacts of 1 mm and 3 mm distances. Total resistances R_T are obtained from slopes of the lines. Film resistance is estimated assuming metal contacts are connected by a rectangle slab of DLC material between the contacts. Length of the slab is same as distance between the contacts (1 or 3 mm), and the cross section of the slab is defined by diameter of the contact (1 mm) and thickness of the film. The resistivity ρ_s of doped DLC films can then be estimated from total resistance R_T at 1 mm and 3 mm contact distances. Estimated ρ_s are listed in Table 2. The average ρ_s for a-C:H:N and a-C:H:B films are estimated as $1.0\times10^5\,\Omega$ cm and $4.9\times10^5\,\Omega$ cm respectively. We can see that a-C:H:N films are more conductive, indicating higher density of localized states, which is consistent with the measurement of higher doping density (4.6 at.%) and lower Tauc gap (0.7 eV). Density of localized states of DLC can be estimated using reported mobility (10^{-6} $cm^2/(V\,s)$) [37] and obtained average ρ_s. The density of localized states for a-C:H:N and a-C:H:B samples are 6.3×10^{19} cm^{-3} and 1.3×10^{19} cm^{-3} respectively.

Several band structure models were proposed to explain observed *I–V* data for Si-DLC junctions [10,38,39]. These existing models cannot explain why metals with wide range of work functions (Au: 5.1 eV, Ti: 4.3 eV, Zr: 3.8 eV) form ohmic contacts to DLC films. We propose a new model depicting band structure changes near the metal–DLC interface (Fig. 5). Electrical conduction is carried out by carriers in localized states near the Fermi level. Shifting of Fermi level near the interface creates a layer of space charge, and hence internal electrical field (region marked by plus signs in Fig. 5(a)). However, due to

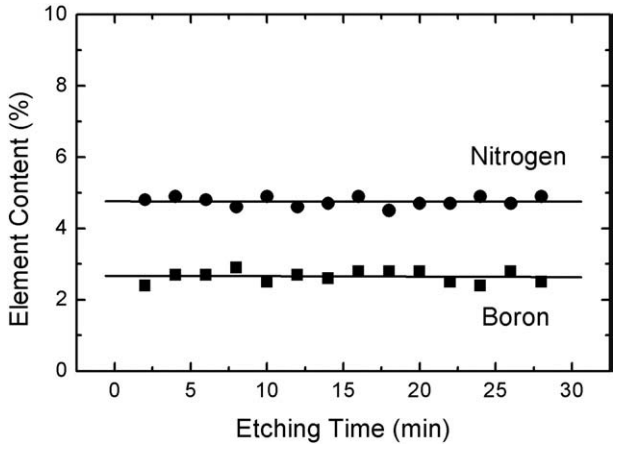

Fig. 2. Auger-electron spectra for a-C:H:N and a-C:H:B samples. Circles represent nitrogen atomic density in a-C:H:N, and squares represent boron atomic density in a-C:H:B. Solid lines are fitted straight lines indicating uniform distribution.