Electrical contacts to ultrananocrystalline diamond

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The contact behavior of various metals on *n*-type nitrogen-doped ultrananocrystalline diamond (UNCD) thin films has been investigated. The influences of the following parameters on the current–voltage characteristics of the contacts are presented: (1) electronegativity and work function of various metals, (2) an oxidizing acid surface cleaning step, and (3) oxide formation at the film/contact interface. Near-ideal ohmic contacts are formed in every case, while Schottky barrier contacts prove more elusive. These results counter most work discussed to date on thin diamond films, and are discussed in the context of the unique grain-boundary conductivity mechanism of the nitrogen-doped UNCD. © *2003 American Institute of Physics.* [DOI: 10.1063/1.1609043]

Diamond thin films are a promising platform material for a large number of electronic applications, including chemical sensors,[1] bioimplantable electronics, and high-power radiation hard field effect transistors. However, many limitations exist which hinder the commercial application of diamond films, for example: High cost, lack of reliable *n*-type doping, high surface roughness, and high film stress. In addition, a crucial limitation for the materials integration of diamond is the lack of reliable low contact resistance ohmic contacts which can be fabricated at low temperatures.

Ultrananocrystalline diamond (UNCD) films have a set of unique structural and tribological characteristics which obviate many of the limitations just mentioned.[2–6] Deposited via microwave plasma-enhanced chemical vapor deposition (MPECVD) with unique Ar-rich plasma chemistries, UNCD is an extremely fine-grained (2–5 nm), smooth (24 nm root-mean-square roughness), 98% sp^3 diamond film with atomically abrupt grain boundaries. Strikingly, UNCD films can be doped with nitrogen to produce very highly conductive *n*-type diamond,[3] which is fully active at room temperature and demonstrates reasonable mobilities. Substitutional donor nitrogen in bulk diamond does not result in conduction due to its 1.7 eV activation energy, but the mechanism of nitrogen doping in UNCD is quite different. Theoretical calculations[7] indicate that nitrogen is preferentially incorporated into grain boundaries, which consist of a combination of sp^2, sp^3, and other bonded carbon. This nitrogen is energetically favored to form bonding states which result in a lone electron pair and a carbon dangling bond, promoting grain boundary conductivity. The conductivity of nitrogen-doped UNCD is correlated with the amount of nitrogen in the films as measured by high mass resolution secondary ion mass spectroscopy. Initial measurements indicate a room-temperature conductivity of $140\,\Omega^{-1}\,\mathrm{cm}^{-1}$ at a nitrogen content of 0.2 at. %. Temperature dependent conductivity measurements indicate a range of thermally activated conduction mechanisms.[3]

The conductive UNCD/contact system is thus a complicated one, as the grain boundaries—not diamond grains—form the conductive pathways. The same electrically active states which promote conduction may exist in significant numbers at the UNCD/contact interface, strongly affecting the contact characteristics. This work presents initial results of the behavior of metal contacts on conductive UNCD, including the influence of acid treatments, work function, and electronegativity of various metals, and a thin interfacial oxide layer.

Contacts to conductive diamond films have been fabricated with a wide range of metals.[8–11] The behavior of these contacts is complex, and seems to depend on a wide range of factors: Type of doping (bulk boron doping versus "*p*-type surface layer" on intrinsic diamond); morphology (homoepitaxial vs. microcrystalline); surface termination (as-grown vs. oxidizing acid treated); and the work function (W) or electronegativity (E_n) of the contact metal. The following cases seem to be typical. For "*p*-type surface" conductive diamond films, which rely on a H-terminated surface, Au forms ohmic contacts and Al near-ideal Schottky contacts.[8] For as-grown boron-doped diamond films, no contacts are ohmic without the formation of a carbide or other graphitic interface layer produced via the high-temperature annealing of a carbide-forming metal (e.g., Ti or Mo);[9,10] with an oxidizing acid cleaning step, contacts become even more rectifying, perhaps due to the removal of any residual "*p*-type surface" conductive layer. Initial work with bulk phosphorous-doped diamond films indicate that ohmic contacts are impossible without the use of an ion bombardment damage step that produces a surface layer of graphite.[11] It should be emphasized that the only films which seem to easily form high-quality ohmic contacts are the *p*-type surface conductive layer films, which have interesting but limited uses for integrated diamond electronics.

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Thin films ($\sim 1-2$ μm) of conductive nitrogen-doped UNCD were deposited on insulating substrates (Si wafers with 1000 nm of thermal oxide) in two types of MPECVD reactors—an ASTEX (Woburn, MA) PDS-17 or IPLAS (Stuttgart, Germany) Cyrranus I large-area reactor, which can fully coat 100 mm diameter wafers. Depositions were performed with the following conditions: for a "15% N" film, 84.2 sccm of Ar, 0.8 sccm of CH_4, and 15 sccm of N_2 were used at a pressure of 100 Torr; for a "20% N" film, 79.2 sccm of Ar, 0.8 sccm of CH_4, and 20 sccm of N_2 were used at a pressure of 100 Torr. The 15% N and 20% N films deposited in the IPLAS reactor had nitrogen concentrations of 0.50 at. % and 0.55 at. %, respectively. In all cases, the substrate temperature was between 700 and 800 °C as measured with a calibrated *in situ* thermocouple.

Before metal deposition, a selected number of substrates were treated for 30 min. in an oxidizing acid bath (concentrated HCl). Such treatments are often used either to remove surface graphitization or to oxidize the surface, removing any as-grown H termination. Either effect may impact the electrically active states at the UNCD grain boundaries. This issue is crucial, as a number of applications for functionalizing thin diamond films may require the existence of a fully H-terminated surface;[1] thus, it is important to fabricate high-quality ohmic contacts on diamond with various surface terminations, including as grown. Two as-grown UNCD samples were also exposed to an additional post-growth hydrogen plasma cleaning treatment in the IPLAS growth chamber to ensure hydrogen termination.

Contact metals were deposited by rf magnetron sputtering in a system with a background pressure of 10^{-7} Torr. The target–substrate distance was 8 cm, and Ar was used (26 sccm) at a pressure of 3.0 mTorr. The substrates were not heated during deposition, and the following metals were deposited: Al, Au, Cr, Cu, Pt, and Ti, all at a thickness of 200 nm. Circular contacts were formed by simple shadow masking, and were 0.8 mm in diameter, 1.2 mm from center to center. The metals all adhered acceptably to the UNCD films, as measured by an informal "tape test." Al_2O_3 was also deposited in the same system using reactive magnetron sputtering, adding 10 sccm of O_2 to the process, at a deposition temperature of 350 °C.

Current–voltage ($I-V$) characteristics at room temperature were performed on probe stations at Argonne National Laboratory and the University of Louisville using voltages up to 50 V, which was the limit of the measurement equipment. It should be noted that the simple resistances calculated from the slopes of these curves include the resistance of the UNCD plus the resistance of the metal contacts themselves ($R_{\text{total}} = R_{\text{contact}} + R_{\text{film}}$). When the contacts are all deposited on the exact same UNCD film, the difference in slope of the $I-V$ curve can be considered to be due to the change in R_{contact} alone, although the absolute value is not calculated. $I-V$ characteristics of all contacts on various conductive UNCD films were measured, including both identical and dissimilar contact pairs.

The most striking feature of the entire series of measurements is that every metal forms a high-quality ohmic contact on every conductive UNCD film as evidenced by strongly linear $I-V$ characteristics, regardless of the metal or cleaning step used. A sample of representative curves is shown in Fig. 1 for an as-grown 20% N film; linearity is demonstrated even throughout this low-voltage range. While R_{contact} changes slightly with respect to metal and the use of an acid or plasma treatment, the curves are linear in all measurement ranges used. In addition, R_{contact} does not scale directly with E_n or W of the metals; Fig. 2 shows the lack of any monotonic dependence of R_{contact} on W for similar contact pairs on a different as-grown and acid cleaned 20% N film. The lack of monotonic dependence on E_n was similar.

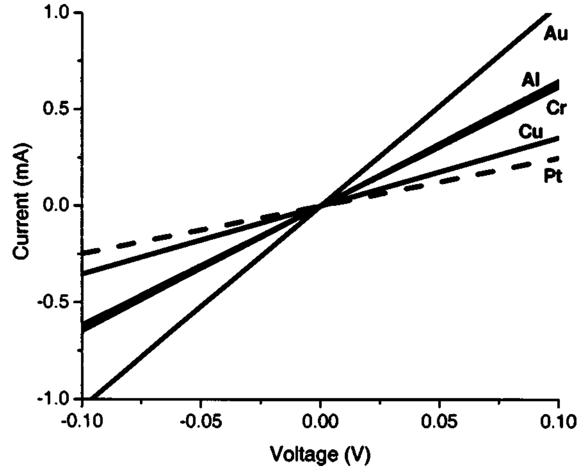

FIG. 1. $I-V$ characteristics for various metals on an as-grown 20% N UNCD film. The size and spacing of the contacts are identical in all cases.

An independent measurement of contact resistance was performed at room temperature for a 15% nitrogen-doped UNCD film. Au probes were used in the van der Pauw geometry. Contact resistivities of 140–180 Ω were obtained, with a conductivity of 166 $\Omega^{-1}\,\text{cm}^{-1}$ for the UNCD film.

These measurements indicate that there is certainly a large number of electrically active defect states at the metal/UNCD interface, even after acid cleaning. This is expected, as it is this kind of state which contributes to the extremely high n-type conductivity of UNCD with concurrent low activation energies.[7] We emphasize that the metal–to–UNCD contact system is, in essence, a metal–to–semimetal contact system.

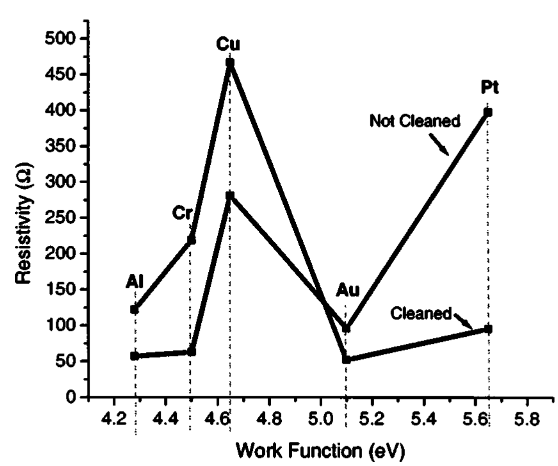

FIG. 2. Summary of $I-V$ characteristics for contacts deposited on both as-grown UNCD and acid cleaned UNCD. The same 20% N sample was used for all measurements shown here. The size and spacing of the contacts are identical in all cases. This shows the lack of monotonic dependence of R_{contact} on W. Results were similar for E_n.

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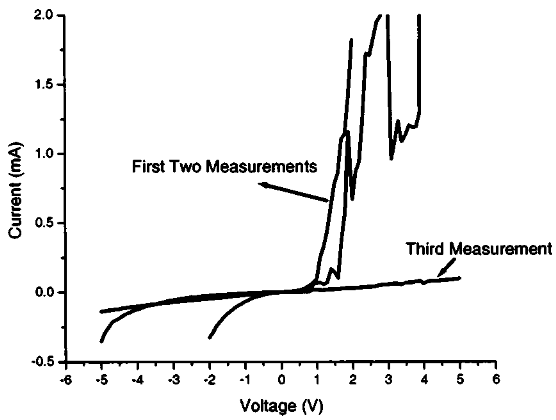

FIG. 3. Influence of an intentionally deposited aluminum oxide interface layer on the $I-V$ characteristics of Al contacts. The sample was a 15% N ASTEX-grown film. Measurements were performed in succession on the same pair of contact pads.

We should note that initial results measuring Al contacts on UNCD did, in fact, indicate rectifying behavior on UNCD.[12] This was surprising, as even if no electrically active interface states were present, Al is the most likely choice to exhibit ohmic behavior on n-type material due to its low W. Obviously contradictory to the current results, the difference may have been due to the formation of an unintentional Al_2O_3 layer at the UNCD/Al interface, if the base pressure of the growth system was not sufficiently low. We tested this theory by intentionally depositing a thin layer of Al_2O_3 under Al contacts on both ASTEX- and IPLAS-grown nitrogen-doped UNCD without breaking vacuum.

Results for a 30 nm Al_2O_3 layer capped with 300 nm of Al are shown in Fig. 3, measured against an Au contact. Results were similar for films deposited in both deposition systems, at both 15% N and 20% N doping ranges.

Indeed, the thin oxide layer results in rectifying characteristics, indicating that the oxide may reduce the influence of the UNCD surface states to a certain extent. However, remeasuring these contacts causes the thin oxide to readily break down, demonstrating nonrepeatable behavior which eventually becomes linear. This underlines the importance of removing oxygen from the Al contact deposition environment in order to adequately characterize the contact behavior of the metal.

In summary, high-quality ohmic contacts have been deposited on n-type conductive nitrogen-doped UNCD. All contacts demonstrated extremely linear $I-V$ characteristics, regardless of oxidizing treatment or metal used. The presence of Al_2O_3 at the UNCD/Al interface was shown to mimic the behavior of Schottky contacts via thin insulator breakdown. We have not yet identified a reliable candidate for Schottky contacts; however, a large number of electronic devices is still possible with ohmic contacts alone.

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[1] W. Yang *et al.*, Nat. Mater. **1**, 253 (2002).
[2] D. M. Gruen, Annu. Rev. Mater. Sci. **29**, 211 (1999).
[3] S. Bhattacharyya *et al.*, Appl. Phys. Lett. **79**, 1441 (2001).
[4] J. Birrell, J. E. Gerbi, J. A. Carlisle, O. Auciello, D. M. Gruen, and J. M. Gibson, J. Appl. Phys. **93**, 5606 (2003).
[5] A. R. Krauss *et al.*, Diamond Relat. Mater. **10**, 1952 (2001).
[6] J. Birrell, J. A. Carlisle, O. Auciello, D. M. Gruen, and J. M. Gibson, Appl. Phys. Lett. **81**, 2235 (2003).
[7] P. Zapol, M. Sternberg, L. A. Curtiss, T. Frauenhein, and D. M. Gruen, Phys. Rev. B **65**, 045403 (2002).
[8] H. J. Looi, L. Y. S. Pang, M. D. Whitfield, J. S. Foord, and R. B. Jackman, Diamond Relat. Mater. **8**, 966 (1999).
[9] D. Takeuchi, S. Yamanaka, and H. Okushi, Diamond Relat. Mater. **11**, 355 (2002).
[10] K. L. Moazed, J. R. Zeidler, and M. J. Taylor, J. Appl. Phys. **68**, 2246 (1990).
[11] T. Teraji, S. Koizumi, and H. Kanda, Appl. Phys. Lett. **76**, 1303 (2000).
[12] I. M. Abdel-Motaleb (personal communication).

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