

A simple route to Ohmic contacts on low boron-doped CVD diamond

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Abstract

Formation and characterisation of titanium underlayer contacts (TiUL) for polycrystalline diamond grown on silicon substrates are described. The TiUL contacts are advantageous that they are easy to fabricate and permit direct probing of the electronic and electrochemical properties of the as-grown polycrystalline diamond surface. The TiUL contacts show nearly Ohmic behaviour over a wide potential range.

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1. Introduction

Silicon wafers are amongst the best substrates for the chemical vapour deposition of polycrystalline diamond [1,2]. Silicon is of low cost, possesses a suitably high melting point, a thermal expansivity sufficient to minimise delamination on cooling and forms a carbide that promotes adhesion of the polycrystalline diamond layer. However, the use of silicon as a substrate in electronic and electrochemical applications of low-doped polycrystalline diamond is compromised by the need to deposit Ohmic contacts post-fabrication. To obtain high-quality contacts, various combinations of ion implantation [3], metal deposition and annealing are performed [4–9]. For example, low-resistance contacts have been fabricated by evaporating or sputtering sequential layers of titanium, platinum and gold onto the diamond surface and then annealing at temperatures greater than 500 °C. The annealing step is necessary to promote the formation of a defective TiC junction, the Au layer serves to prevent oxidation of the Ti and the platinum layer inhibits inter-diffusion between Au and Ti. Such processing is not only time-consuming but also alters the diamond surface. A rehydrogenation step being required in order to recover the sub-surface hydrogen layer present at the as-grown surface [5]. In this letter, we describe a quick, simple technique of preparing nearly

Ohmic contacts to polycrystalline diamond grown on silicon. The process involves evaporation of a thin Ti layer onto the Si substrate prior to film growth. The TiC contact is then formed during diamond deposition. We refer to the junctions formed as Ti underlayer contacts (TiUL). The methodology not only offers the advantage of reduced processing time but also negates those problems associated with changes to the electronic properties of diamond in post-growth annealing steps.

2. Experimental

Undoped silicon $\langle 100 \rangle$ wafers, with conductivity $1 \times 10^{-3} \Omega \text{ cm}^{-1}$, of approximately $1 \times 2 \text{ cm}^2$ in dimension were employed as substrates for diamond growth. To fabricate a TiUL, a 3 mm strip along one edge of the silicon was masked using a polymer tape. Then, the exposed area was manually abraded with 1–3 μm diamond grit. After removal of the mask, the silicon was ultrasonically cleaned in propan-2-ol. A 5 mm strip of titanium of thickness 100 nm was then evaporated onto the silicon, straddling the unabraded and abraded regions. Boron-doped CVD diamond (BDCD) was then deposited onto the substrate.

The BDCD was deposited in a hot filament reactor. The film was grown at a pressure of 20 Torr and typical flow rates were 200 sccm of H_2 , 1.4 sccm of CH_4 and 4×10^{-5} sccm of B_2H_6 . These flow rates correspond to a boron to carbon ratio of 50 ppm in the chamber.

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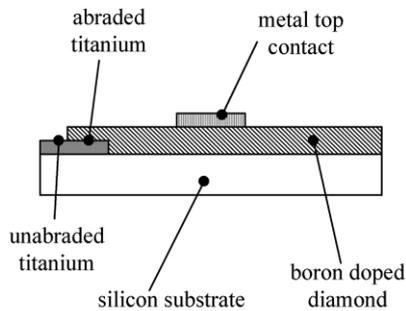


Fig. 1. Schematic of the configuration for electrical measurements. The relative thickness of the layers is not to scale.

Deposition runs of 12 h were employed to yield films of approximately $4 \mu\text{m}$ thickness. The film was allowed to cool in a hydrogen atmosphere before removal from the chamber.

The structure of the as-prepared films was characterised using scanning electron microscopy (SEM), Raman spectroscopy and optical microscopy. A JEOL JSM 5600LV was employed to obtain SEM images of the diamond surface. The Raman scattering spectrum was recorded on a Renishaw system using the 488 nm Argon ion laser line. Optical images were captured with a JVC TK-1280E colour camera attached to an Olympus BH2 optical microscope fitted with a $10\times$ eyepiece and $4\times$, $10\times$, $20\times$ and $50\times$ objective lenses.

All electronic measurements were performed on a Solartron 1250 Interface. Two contact measurements were performed between the TiUL contact and a metal top-contact, i.e. a metal contact evaporated onto the diamond surface post-growth, see Fig. 1. Three types of top-contact were considered (i) an annealed Ti–Pt–Au contact, (ii) an Au contact on the as-grown diamond and (iii) an Au contact on oxidised diamond. The Ti–Pt–Au top-contact was prepared by the sequential deposition of 100 nm of Ti (evaporated), 40 nm of Pt (sputter coated) and 100 nm of gold (evaporated), followed by annealing in a vacuum at 500°C . The gold contacts were formed by the evaporation of 100 nm of gold onto the BDCD surface. Mild oxidation of the BDCD was achieved by placing the samples in a saturated solution of chromic acid for 2 minutes. The conductivity of the BDCD was determined using a four-point probe which consisted of four spring loaded electrodes that were linearly aligned and separated by 2 mm gaps.

3. Results and discussion

The results of Raman and SEM studies have been reported previously [10]. The SEM images show crystallites of dimension approximately $1\text{--}5 \mu\text{m}$ with no evidence of graphitic regions, cracks in the film or extensive pitting. The Raman spectrum displays a sharp

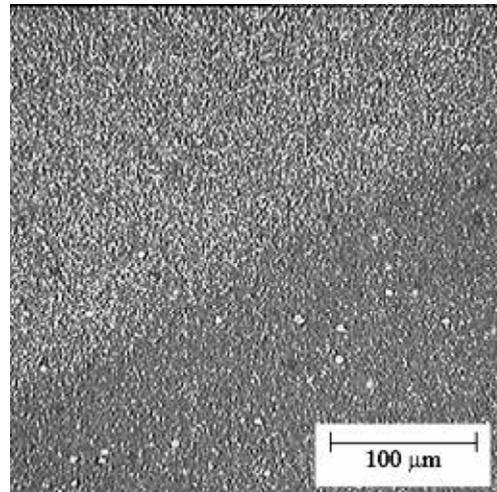


Fig. 2. An optical image of the BDCD diamond grown at the boundary between abraded Ti and Si. The boundary between the underlying metal and underlying semiconductor is clearly defined by a change in the reflectivity.

sp^3 peak at 1332 cm^{-1} and shows no evidence of sp^2 carbon lines between 1500 and 1700 cm^{-1} . Fig. 2 shows an image, recorded using the optical microscope, of the BDCD deposited at the boundary between Si and abraded Ti. The boundary between the underlying Ti and Si regions is clearly defined by the abrupt change in reflectivity. It is apparent that the BDCD film is continuous across the underlying semiconductor/metal boundary. The junction between unabraded Ti and abraded Ti is displayed in Fig. 3. It is evident that on the unabraded Ti surface, on which there was no nucleation sites, BDCD growth was extremely limited. Hence, electrical contact to the low-doped BDCD film could be easily

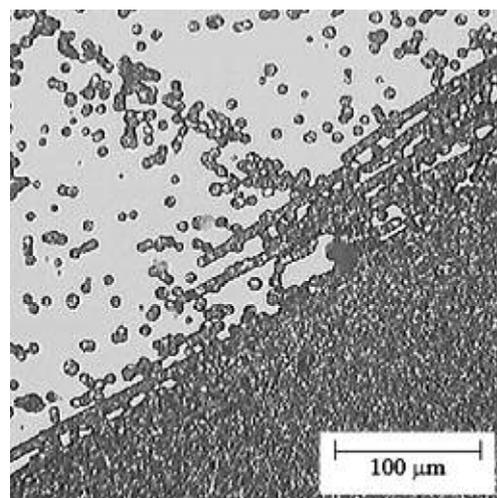


Fig. 3. An optical image of the BDCD diamond grown at the boundary between abraded Ti and unabraded Ti.

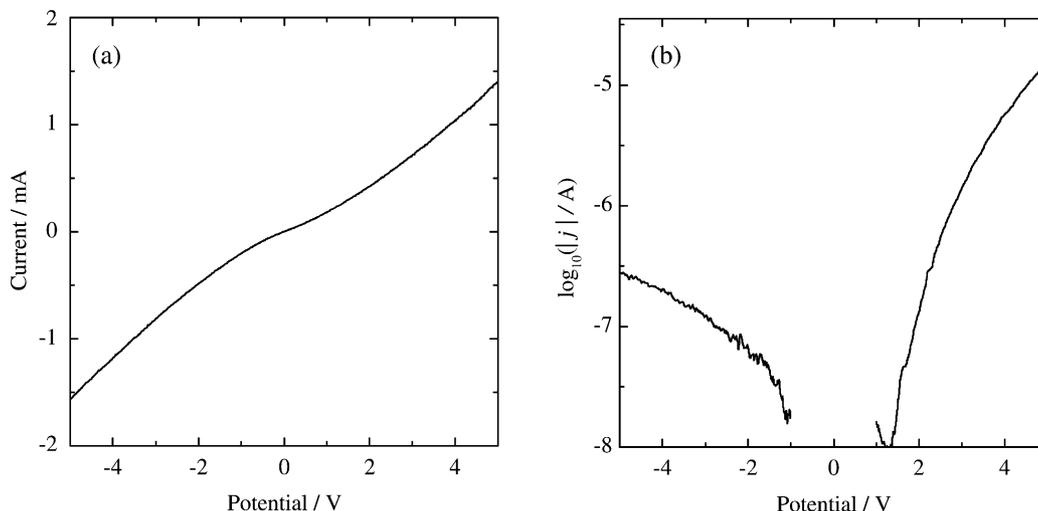


Fig. 4. j - V plots measured for the two electrode configurations; (a) TiUL/BDCD/Ti-Pt-Au; (b) TiUL/partially-oxidised BDCD/Au.

achieved by bonding a copper wire to the unabraded titanium region.

Four-point probe measurements on as-grown BDCD yielded a conductivity of $0.2 \Omega^{-1} \text{cm}^{-1}$. Fig. 4a shows the i - V curve for the TiUL/BDCD/Ti-Pt-Au configuration. The j - V curve is extremely linear with correlation coefficient of 0.998, between -5 and $+5$ V. The linearity of the j - V curve compares favourably to that reported when two annealed Ti top-contacts, formed by metal deposition onto as-grown diamond, are employed [4–9]. The j - V plot for the TiUL/as-grown BDCD/Au configuration was also linear, indicating that a gold contact onto the as-grown BDCD exhibits near Ohmic characteristics, as reported previously [4–9]. Mild oxidation of the BDCD surface prior to the deposition of the gold contact yielded a contact that was rectifying [9], as shown in Fig. 4b.

4. Conclusions

Contacts were formed for BDCD grown on silicon by evaporation of a Ti layer onto the substrate prior to diamond deposition. The formation of a TiC layer during growth of the BDCD rendered the as-prepared contact nearly Ohmic. The highly reducing atmosphere in the CVD chamber during diamond deposition removed the need to protect the Ti against oxidation. The diamond only grew on the abraded Ti, facilitating electrical contact to the metal. In addition to offering an easier route to Ohmic junction formation, TiUL contacts also permit the electronic properties of the as-grown surface

to be studied directly, as post-processing steps that alter the surface chemistry are not required. We have found this property of the contacts to be extremely useful in studies of the influence of surface chemistry on the electrochemical properties of low-doped BDCD [10,11].

Acknowledgments

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References

- [1] X.C. He, H.S. Shen, Z.M. Zhang, X.J. Hu, Y.Z. Wan, T. Shen, *Diamond Relat. Mater.* 9 (2000) 1626.
- [2] P.W. May, *Philos. Trans. R. Soc. Lond. A* 358 (2000) 473.
- [3] G.R. Brandes, C.P. Beetz, C.F. Feger, R.W. Wright, J.L. Davidson, *Diamond Relat. Mater.* 8 (1999) 1936.
- [4] C. Jany, F. Foulon, P. Bergonzo, R.D. Marshall, *Diamond Relat. Mater.* 7 (1998) 951.
- [5] H.J. Looi, L.Y.S. Pang, M.D. Whitfield, J.S. Foord, R.B. Jackman, *Diamond Relat. Mater.* 9 (2000) 975.
- [6] K.L. Moazed, J.R. Zeidler, M.J. Taylor, *J. Appl. Phys.* 68 (1990) 2246.
- [7] H. Shiomi, H. Nakahata, T. Imai, Y. Nishibayashi, N. Fujimori, *Jap. J. Appl. Phys.* 28 (1989) 758.
- [8] T. Tachibana, B.E. Williams, J.T. Glass, *Phys. Rev. B* 45 (1992) 11975.
- [9] H. Kiyota, E. Matsushima, *Appl. Phys. Lett.* 67 (1995) 3596.
- [10] G. Pastor-Moreno, D.J. Riley, *Electrochim. Acta* 47 (2002) 2589.
- [11] G. Pastor-Moreno, D.J. Riley, *Electrochem. Commun.* 4 (2002) 218.