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Engineering low resistance contacts on p-type hydrogenated diamond surfaces

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Abstract

Gold is expected to form a relatively low barrier on hydrogenated thin film diamond, and this metallisation has therefore been widely used as the 'ohmic' contact for electronic devices fabricated using this material. However, gold contacts are not truly 'ohmic' and suffer from reliability problems associated with poor adhesion to the diamond surface. Furthermore, the contact properties of this system have not been studied in any detail.

For the first time we report the results of a study, carried out using the circular transmission line method, to explore the specific contact resistance (SCR) of differing metallisation schemes on hydrogenated p-type CVD diamond. Gold, aluminium and reacted metal-carbide (Au/Ti, Al/Ti) contacts have been characterised. The effects of sample/contact pre- and post-treatments have been studied, including annealing to 600°C, acid and plasma treatments. Our measurements show that the simple gold contacts exhibit an SCR of $0.04\,\Omega\,cm^2$ with an associated barrier height of 0.39–0.44 eV. These values were obtained for films displaying carrier concentrations of 10^{17}–$10^{19}\,cm^{-3}$. Low specific contact resistance is important for effective device operation, especially in high power situations; previously, on boron doped material, a reacted (carbide) interface has been shown to improve contact resistance and mechanical integrity — typically Au/Ti is used. Our studies show that Au/Ti contacts can be formed on hydrogenated diamond but display rectifying characteristics up to annealing temperatures of 250°C. However, a low resistance reacted ohmic contact (SCR $\sim 0.02\,\Omega\,cm^2$) can be formed if the anneal temperature is increased to 600°C and is then followed by a careful rehydrogenation step to replace the carriers which are lost during the annealing.

Keywords: Gold; Hydrogenated diamond; Ohmic contact; P-type diamond

1. Introduction

Diamond is unique compared to other semiconductors as it does not have a native oxide, therefore the properties of metallisation contacts on diamond are strongly dependent on the surface terminating species [1,2]. The surface pre-treatment, growth technique and the quality of the diamond are critical factors determining the properties of metallisation contacts [1–3]. By modifying the properties and chemistry of diamond surfaces, the electrical behaviour of metal contacts can be controlled and either rectifying or ohmic characteristics can be obtained. It is usually difficult to fabricate good ohmic contacts on moderately doped wide band-gap materials (such as diamond) because of the large difference in work function between the metal and the semiconductor; contacts with Schottky characteristics typically result. On boron doped (p-type) diamond the usual approach used to fabricate devices is to produce a surface suited to the formation of Schottky contacts and then to selectively generate regions suited to ohmic contact formation by either high dose boron incorporation [4,5] ($>10^{20}\,cm^{-3}$) or by forming a defective interface which results in a lower barrier height [6,7]. A third approach of choosing a metal which forms a low barrier height junction has not generally been successful on oxidised boron doped diamond because the very high surface defect density encountered leads to Fermi level pinning resulting in barrier heights which are independent of the chosen metal [2,3].

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On boron doped diamond these approaches have been explored extensively, and it has been shown that reliable, low resistance ohmic contacts can be routinely formed by high dose ion implantation [5]. This type of contact can be further improved by reducing the barrier height at the interface. The usual approach is via a multilayer contact metallisation which utilises a carbide forming metal as the first layer (e.g. Ti/Au) [4,6,7]. On annealing, a metal carbide interface forms which is highly defective and exhibits near ohmic current–voltage characteristics. However, boron doped diamond devices only exhibit useful performance characteristics at high temperatures due to activation energy considerations [8]. More recently, very promising electronic behaviour has been observed for surface conducting p-type diamond associated with surface or near surface hydrogen. This effect has also been reported for the CVD form of the material, and a number of electronic structures (MSM, diode, FET) with promising *room temperature* performance have been reported [9–13]. Hydrogen termination of the diamond surface considerably reduces the problem of Fermi level pinning and allows the junction barrier height to be usefully influenced by the metal chosen for contact fabrication. Thus aluminium shows near ideal Schottky characteristics, while gold provides reasonable ohmic *I–V* behaviour and can be used to form the source and drain contacts for surface channel MESFETS [10–12] or as the ohmic contacts in high power devices [11]. However, both diamond and gold are rather unreactive and the adherence and mechanical integrity of pure gold contacts is rather poor and, in some cases, under high power conditions, destruction of the contact has been observed [11]. So far no systematic study of the properties of gold ohmic contacts to hydrogen terminated, surface conducting diamond has been reported in the literature, and improvement of ohmic contact properties by incorporation of defective reacted interfaces has not been explored. This information is needed if reliable high performance devices are to be routinely fabricated on this type of semiconducting diamond.

In this paper we report the results of studies carried out to address these points and to develop an alternative to gold for use as a low resistance ohmic contact on hydrogenated surface conducting diamond. We have used the circular transmission line method (c-TLM) of Reeves [14] together with an additional end resistance measurement to study the properties of Au, Au/Ti and Al/Ti contacts on hydrogenated CVD diamond. This method is commonly used with wide bandgap materials and allows the sheet and contact resistances to be accurately determined together with the transfer length of the test structure. The end resistance measurement allows both the bulk sheet resistivity and the sheet resistivity beneath the contact to be determined from the c-TLM measurements. We have also examined the effects of a range of treatments (acid, high temperature anneal and hydrogen plasma exposure) on the properties of these metallisation schemes.

2. Experimental

To investigate the properties of metal contacts, circular TLM structures were defined using a photolithographic lift-off procedure for gold, aluminium/titanium and gold/titanium metallisations deposited onto the surface of as-grown CVD diamond. The samples were randomly aligned free standing polycrystalline material with a grain size of 10–30 μm. The Raman spectra, measured by a He–Ne laser at 632 nm, revealed a single sharp peak at 1332 cm^{-1} with no other structure apparent, indicating the material to be primarily sp^3. Further details of the Raman spectra and the surface morphology of the CVD material used here have been given elsewhere [15]. Prior to removal from the growth reactor, the diamond substrates were cooled in a hydrogen plasma to ensure that the surfaces were hydrogen terminated. *I–V* and Hall measurements show the as-grown surface to exhibit p-type conductivity with a sheet carrier concentration of approximately 10^{13} cm^{-2}; further details of the nature of this conducting surface layer have been given elsewhere [13,15]. The dimensions and structure of the c-TLM test pattern appropriate to the Reeves method are shown in Fig. 1a, together with the equivalent circuit used to represent the contact pattern, Fig. 1b. By measuring R_{in}, the total resistance between contacts C_1 and C_2, and then R_{out}, the total resistance between contacts C_2 and C_3, and combining these with a transmission line treatment of the equivalent circuit shown in Fig. 1b, it is possible to extract values for the contact resistance, sheet resistance and contact transfer length from the measurement data. An additional measurement, called the contact end point resistance (defined

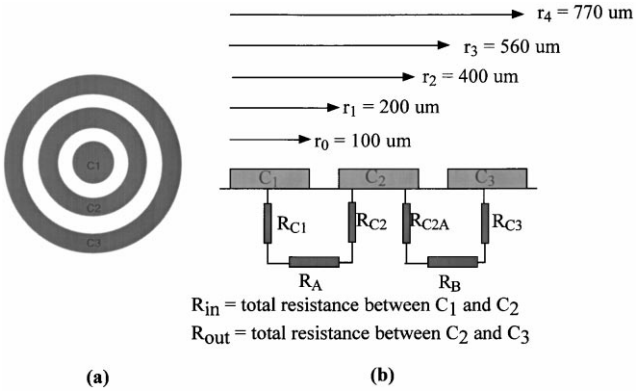

Fig. 1. (a) Schematic showing the arrangement of the concentric metal contact pattern used to carry out the Reeves c-TLM method for making contact resistance measurements. (b) Equivalent circuit used to represent the c-TLM contact pattern.

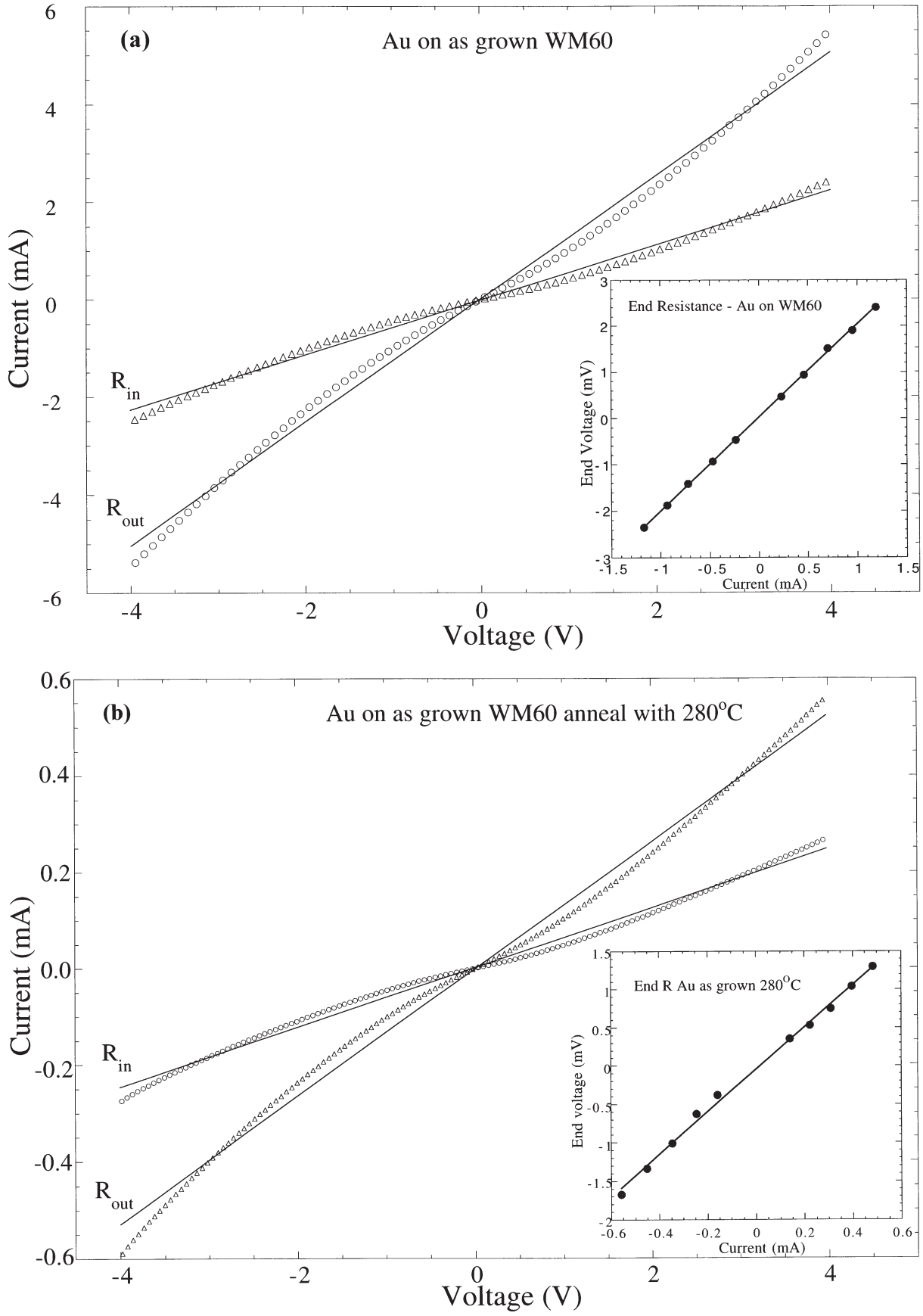

Fig. 2. (a) The *I–V* characteristic of Au deposited on as-grown films without any treatment. The inset shows the end resistance measurement. (b) The *I–V* characteristic of Au deposited on as-grown films after a 280°C anneal in air. The inset shows the end resistance measurement.

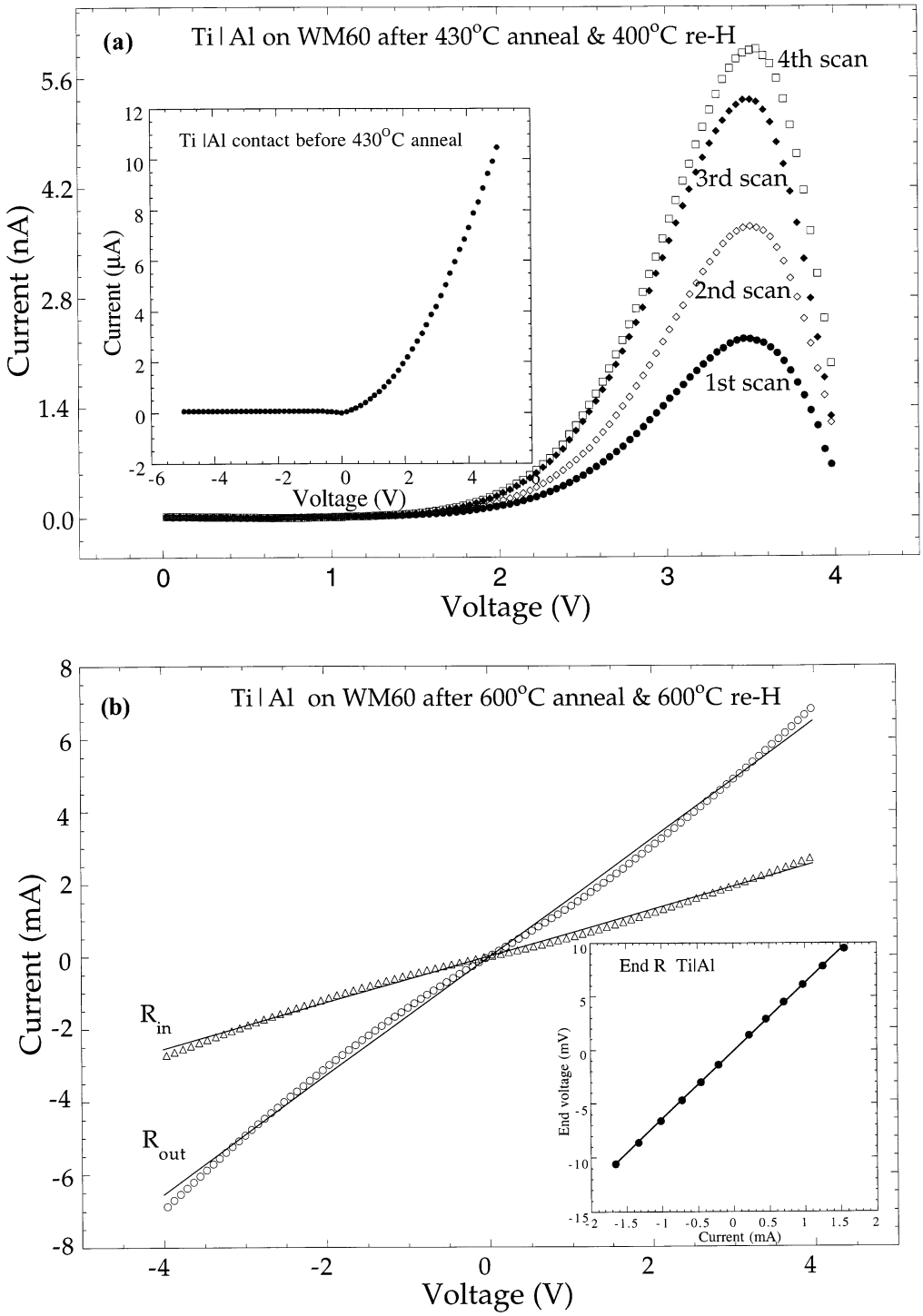

Fig. 3. (a) Different consecutive *I–V* scan of Ti/Al contact deposited on as-grown film after a 430°C and 30 min anneal in air followed by a 400°C exposure to hydrogen plasma for 5 min; the changing current levels indicate that the junction is not stable — this may be due to significant charging at the interface. The inset graph shows the rectifying Ti/Al contact before the anneal. (b) The improvement of the *I–V* characteristic of Ti/Al contact deposited on as-grown film after a 600°C and 20 min anneal in air followed by a 600°C exposure to hydrogen plasma for 5 min. The inset shows the end resistance measurement.

as $R_{\text{end}23} = V_{23}/I_{12}$ and $R_{\text{end}12} = V_{12}/I_{23}$), allows both the bulk sheet resistivity and the sheet resistivity beneath the contact to be determined. The solution of the transmission line problem is difficult and requires the use of numerical techniques, a more detailed description of the experimental techniques and numerical methods used here can be found in the original paper by Reeves [14]. To realise the method, concentric circular metal

contacts suited to the c-TLM method were deposited by thermal evaporation. The contact thicknesses were: gold contacts, 200 nm; Au/Ti contacts, 200/100 nm; Al/Ti contacts, 200/100 nm. *I–V* measurements were carried out using a Hewlett-Packard HP4145B, Keithly 2000 multimeter and Keithly picoammeter, and were carried out at room temperature. Low temperature annealing was carried out using a programmable hot-plate, high temperature anneals (>400°C) were carried out in a Carbolite furnace under flowing nitrogen at atmospheric pressure. Extraction of the contact and material parameters from the current–voltage measurements was performed numerically using MATLAB software. Additional surface hydrogenations on the samples were carried out in a conventional 2.45 GHz microwave diamond growth reactor (RFA) using a pure hydrogen plasma.

3. Results

3.1. Gold contacts

Fig. 2a shows the *I–V* curves for the Au test structure deposited on as-grown material at room temperature. The *I–V* curves display near linear characteristics with current levels in the milliamp range recorded between ±4.0 V. Close inspection shows there is a slight curvature of the characteristics, with the data points lower than the value of the best fit line between ±3.0 V and above the best fit line for voltages greater than 3.0 V. This indicates that the conductivity between the two contacts is slightly voltage dependent over this voltage range. The inset graph shows the results of the end resistance measurement of the test structure.

The sample was then annealed at 280°C in air for 2 h and allowed to cool to room temperature prior to further characterisation; the results are shown in Fig. 2b. It can be seen that the annealing treatment increases the series resistance between the contacts and increases the curvature of the *I–V* characteristics, implying that modification to either the material or the contact interface has occurred. A further gold contact pattern was fabricated which was subjected to a 600°C anneal and rehydrogenation for direct comparison with the Ti/Al and Ti/Au contacts described in the next section; all the measurements are summarised in Table 1.

3.2. Ti/Al and Ti/Au contacts

A Ti/Al contact was investigated to see if the hydrogen terminated interface was reactive to this system (resulting in the formation of TiC), or whether the electronic characteristics would be dominated by the Ti layer itself. The bilayer contacts were deposited on as-grown diamond and then annealed at 430°C for 30 min followed by a rehydrogenation treatment in hydrogen plasma for 5 min to replace the lost surface carriers expected from the annealing step. Fig. 3a shows the results of *I–V* measurements on the Ti/Al contact; the inset shows the expected rectifying behaviour from Ti/hydrogenated diamond junction prior to the anneal step. However, the main plot indicates that the contact is not stable following the 430°C anneal and the current level depended on the number of *I–V* scans carried out. The results indicate that considerable charging may be occurring at the junction, leading to unreliable contact characteristics. Following a higher temperature anneal (20 min at 600°C) and subsequent rehydrogenation, the contact properties became more stable, as shown in Fig. 3b, and did not depend on the number of *I–V* scans. Very similar plots were obtained in the case of the Ti/Au contact metallisation.

Additional experiments carried out on as-grown and oxidised surfaces (acid treatment at 200°C comprising a mixture of concentrated sulphuric acid and ammonium persulphate) showed that both surfaces resulted in similar contact properties provided the 600°C anneal and rehydrogenation step were carried out following contact formation. Table 1 summarises the results obtained from a full numerical analysis of the c-TLM measurements carried out for the different metallisations and contact treatments examined during this work. The values of specific contact resistance, bulk sheet resistance, contact

Table 1
Electrical properties of the material and different contact metallisation schemes used in this experiment

Metallisation scheme	Material treatment	Bulk sheet resistivity (kΩ/square)	Sheet resistivity below contact (kΩ/square)	Specific contact resistance (Ω cm^2)	Transfer length (μm)	Barrier height (eV)
Au	as-grown	17	1200	0.04	14	0.41
Au	as-grown, anneal 200°C	36	1460	0.06	13	0.42
Au	as-grown, anneal 280°C	180	7850	0.13	9	0.44
Au	as-grown, anneal 600°C, rehydrogenation	12	15	0.01	7	0.36
Ti/Al	as-grown, anneal 600°C, rehydrogenation	13	1300	0.07	22	0.42
Ti/Au	as-grown, anneal 600°C, rehydrogenation	10	120	0.02	16	0.39
Ti/Au	oxidised, anneal 600°C, rehydrogenation	14	77	0.03	14	0.40

sheet resistance and transfer length obtained from the analysis are given. The determination of barrier height (ϕ_b) was made using the equation

$$\mathrm{SCR} = \frac{k}{qA^*T}\exp\left(\frac{q\phi_b}{kT}\right)$$

[16] where k is the Boltzmann constant, A^* is the Richardson constant and T is the temperature together with the following assumptions: (i) the dominant current injection mechanism in the ohmic contact is thermionic emission; (ii) a hole effective mass of 0.7; and (iii) the contact resistance is dominated by the interface resistance — other contributions are assumed to be negligible. The first of these is reasonable as in the case of aluminium a highly rectifying junction is obtained on the hydrogenated surface and Hayashi et al. [13] have shown that thermionic emission dominates its characteristics. Kiyota et al. [17] have used similar effective hole mass for barrier height calculations on hydrogenated diamond. The third assumption is justified by the high specific conductivity of metals.

4. Discussion

The results of the full analysis of the c-TLM measurements presented in Table 1 show that a barrier height of between 0.38 and 0.45 eV exists for Au contacts deposited on hydrogenated diamond. This is in contrast to the near zero barrier height which has previously been generally assumed to be the case for this metal [1,12]. The low value arises from treating the *I–V* characteristic as linear rather than taking account of the curvature shown in Fig. 2. The higher values obtained from the c-TLM analysis are consistent with UPS measurements of the gold barrier height previously published in the literature [18]. A more detailed analysis (to be published elsewhere) of the c-TLM data obtained here allows a detailed equivalent circuit model to be developed which characterises the contact pattern in terms of individual resistance components. The model shows that the interface resistance comprises less than 5% of the bulk resistance for the case of gold, indicating that it should perform satisfactorily as an ohmic contact for dimensions similar to those used for the test structure. However, as has been noted, the mechanical integrity of gold contacts is rather poor on diamond, and this is particularly true for the smoother surfaces [e.g. (100)-oriented/polished/smoothed material] which will be needed for higher performance device structures. The significant decrease in the contact sheet resistivity following the 600°C anneal, Table 1, is most likely due to migration of gold into the grain boundaries beneath the contact, which would considerably increase the effective contact area. It is interesting to speculate that, if this is the case, then the adhesion of the gold contact could be expected to show significant improvement, although so far we have not tested this possibility.

To date, other metals deposited on hydrogenated diamond have exhibited non-ohmic rectifying characteristics, such as those shown in Fig. 3a for unannealed Ti/Al contacts. High temperature annealing provokes a reaction forming a defective TiC interface with the diamond. The present work shows that an annealing treatment of around 20 min at 600°C is needed to stabilise the electrical properties of the contact, compare Fig. 3a and b. Heating the diamond is already known to cause a drastic loss of surface carriers and an increase in sheet resistance [15]. However, the carriers can easily be restored by a suitable post-anneal rehydrogenation treatment in a microwave hydrogen plasma. After such a treatment, the Ti/Al contact then displays an SCR of $\sim 0.07\ \Omega\,\mathrm{cm}^2$ as shown in Table 1. Comparison of the results obtained for Ti/Al and Ti/Au contacts strongly suggests that the junction properties can be attributed to formation of a defective TiC junction, although in the case of Ti/Au the SCR is about a factor of 3 lower at $\sim 0.02\ \Omega\,\mathrm{cm}^2$. The higher SCR value in the case of the Ti/Al contact may be due to some oxidation of the aluminium occurring during annealing. For the Ti/Au reacted contact the contribution of the interface resistance still forms less than 10% to the total resistance between the contacts, indicating that the contact can perform satisfactorily as an ohmic for the dimensions used here.

5. Conclusions

The properties of ohmic contacts on the surface conducting layer present on hydrogenated as-grown CVD diamond have been investigated using the c-TLM method. Three metallisation schemes have been explored, together with various treatments to identify an alternative low contact resistance metallisation approach to gold which is currently used but suffers from poor mechanical integrity. Numerical analysis of measurements obtained from the c-TLM structure has allowed the specific contact resistances of these metallisation schemes on surface conducting hydrogenated CVD diamond to be compared for the first time. The results show that a two-layer titanium/gold metallisation can be deposited on the as-grown hydrogenated surface, and following a 20 min 600°C anneal in flowing nitrogen yields an electrical performance similar to that of a single-layer gold contact. This process yields a reacted carbide interface which has previously been shown to exhibit superior stability and mechanical integrity compared to single-layer gold contacts. The one drawback associated with the Au/Ti contact is the loss of carriers from the surface layer which occurs during the high

temperature anneal. However, this work has shown that the carriers can easily be restored without affecting the contact properties by a short 'rehydrogenation' treatment in a microwave hydrogen plasma.

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