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Ohmic contacts to epitaxial and natural diamond*

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Abstract

We have used the circular transmission line test structure of Reeves (*Solid State Electron*, 23 (1980) 487–490) in order to determine the specific contact resistance of various metals to semiconducting diamond. Sample types included highly doped epitaxial films on <100> and <110> type IIa substrates, type IIb diamonds 0.25 mm thick, and type IIb diamonds thinned to 0.05 mm in thickness. Metallizations tested include the carbide forming refractory metals Ti and Mo, as well as Al, Ni, Au, Pt, and Pd. Measured specific contact resistances ranged from 2×10^{-5} for contacts to highly doped layers to 1×10^{-2} Ω cm^2 for contacts to natural bulk type IIb diamonds. Ohmic contact behavior was not observed for non-carbide forming metallizations on lightly doped type IIb diamond, either in the as-deposited state, or after annealing.

1. Introduction

The unique material and electronic properties of diamond make it a potentially very important candidate for use in high power or high frequency applications, as well as in high temperature and corrosive environments. A requirement for any successful application of semiconducting diamond devices is the development of suitable electrical contacts. Ohmic contacts must possess a low contact resistance and be able to withstand the operating conditions, such as high temperatures, for which diamond devices are intended. Ideally, the contacts would be compatible with conventional device processing techniques, and finally, they should be strongly adherent to the diamond surface. Ohmic contacts produced via a solid state annealing process have been studied extensively and are believed to satisfy all four conditions [1]. In this process a thin film of a transition metal carbide forming metal is deposited on the diamond surface. Annealing at high temperature (950 °C) leads to the formation of a carbide layer at the interface. This layer provides an intimate contact to the diamond and promotes good adhesion. Annealing the contact produced a decrease in total resistance of several orders of magnitude. Auger electron spectroscopy studies indicated that the decrease was associated with the formation of a carbide phase. Similar results have been observed for Ti and Ta contacts.

Ohmic contacts are characterized by measuring the series resistance arising at the contact–semiconductor junction, and then normalizing the contact resistance to the contact area to determine the specific contact resistance, r_c. Various techniques have been developed in order to determine r_c. In this work we use a circular test pattern consisting of a central dot and concentric ring contacts. An advantage of this technique is that no mesa etch is required. The measurements are interpreted using a circular transmission line model. For the details of the analysis, the reader is referred to ref. 2.

Our previous work [3] has shown that carbide forming metallizations can yield low specific contact resistance ohmic contacts to type IIb diamond. In the case of highly doped epitaxial films, reliable and reproducible contacts with $r_c = 2 \times 10^{-5}$ Ω cm^2 were observed. In this paper we address the issue of carbide forming metallizations *vs.* non-carbide forming metallizations for ohmic contacts.

2. Experimental procedure

Seven different diamond samples were used in this study. The first sample consisted of a diamond film with a high boron concentration and about 4 μm in

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thickness grown epitaxially on a <100> type IIa insulating diamond substrate with the dimensions of $5 \times 5 \times 0.25\ mm^3$. The second sample consisted of a 6 μm thick diamond film with a high boron concentration grown epitaxially on a <110> substrate. These films were grown at MIT Lincoln Labs using the procedure outlined in [4] on natural diamond substrates provided by Druker International, B.V. The third sample was an irregularly shaped type IIb diamond 50 μm thick. The fourth sample was identical to the third, except that it was 0.25 mm thick. The other samples were type IIb diamonds with the dimensions of $5 \times 5 \times 0.25\ mm^3$.

The samples were cleaned using decontam, deionized water, and ethanol, sequentially. The samples were then coated with photoresist and patterned using standard photolithographic techniques. Samples were baked at 120 °C for 20 min following photoresist patterning and loaded into an ion pumped ultrahigh vacuum system (base pressure 5×10^{-9} Torr). Electron beam evaporation was used for deposition of the carbide forming metals (Ti or Mo). The thickness of the carbide forming metal was about 100 Å. Subsequently, 1500 Å of Au was deposited from a resistively heated boat onto the surface of the Ti or Mo without breaking vacuum to prevent oxidation prior to annealing. Pt, Pd, and Al were also deposited by electron beam evaporation, with a thickness of about 1500 Å. No Au cap was used for these metals. The pressure during evaporation was 2×10^{-7} Torr. Film thicknesses were determined using a crystal monitor during deposition. After deposition a lift-off process was used to remove undesired metal, leaving contact structures with the geometry shown in Fig. 1. The dimensions (in the notation of Reeves) were $r_1' = 1.65 r_0$, $r_1 = 2.74 r_0$, $r_2' = 4.34 r_0$, and $r_2 = 5.45 r_0$ with $r_0 = 11.7$ μm.

Following patterning, the contact structures were probed first with a curve tracer. If ohmic behavior was observed, then a current source and electrometer were used to determine the specific contact resistance. The measurements consisted of placing tungsten probes on the inner dot, the central ring and the outer ring. The total resistance between the central ring and the inner dot, and the central ring and the outer ring were measured. The end resistance was determined by passing a current through the central ring and the inner dot and measuring the voltage between the central ring and the outer contact. This result was checked by switching contact pairs and remeasuring. Using these three results, the specific contact resistance can be calculated in the manner of ref. 2. After probing, the samples were baked at 120 °C for approximately 20 min and then annealed in a purified hydrogen ambient at elevated temperatures (960 °C for Mo, Ti, and Au, 900 °C for Ni, 725 °C for Pt and Pd, and 425 °C for the Al films). Anneal times were in 2 min increments. After annealing, the samples were remeasured. Total anneal times of up to 8 min have been investigated.

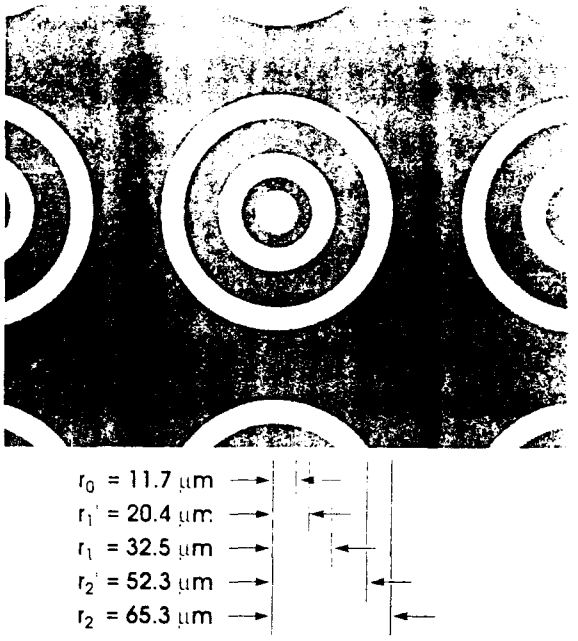

Fig. 1. Geometry of the circular transmission line structure.

3. Results and discussion

Table 1 shows the values of specific contact resistance determined in this experiment. It is interesting to note that contacts to the epitaxial layers (epi-<100> and epi-<110>) showed excellent behavior as deposited. Contacts formed by placing either tungsten or gold probe tips on the diamond surface showed only a slight deviation from linearity. Contacts formed by the Ti films were highly linear. This may be due to the highly doped nature of these layers. Heavily doping a semiconductor induces a decrease in barrier thickness, allowing tunneling of the charge carriers. Increasing the doping in natural semiconducting diamond is a non-trivial task, but may be accomplished rather easily during epitaxial growth of diamond. The measured value of specific contact resistances after annealing are more than satisfactory for device fabrication.

Lightly doped diamond (represented by the "thin" and "thick" samples) are much more difficult to contact. Non-ohmic behavior was observed for all as-deposited contacts in these samples. Upon annealing, however, Mo contacts were ohmic in nature, with a specific contact resistance of $1.4 \times 10^{-2}\ \Omega\ cm^2$ for the 0.25 mm thick diamond, and $1.2 \times 10^{-3}\ \Omega\ cm^2$ for the 50 μm thick diamond. The actual value is probably lower, since correct interpretation of the transmission line measure-

TABLE 1. Specific contact resistance results for various samples

Sample	Conducting layer thickness (μm)	Metal	N_A (cm^{-3}) at 300 K	r_c (Ω cm^2) as deposited	r_c (Ω cm^2) post anneal
epi-⟨100⟩	4	Ti	2×10^{19}	3.2×10^{-6}	1.8×10^{-5}
epi-⟨110⟩	6	Ti	7×10^{19}	7.6×10^{-5}	2×10^{-5}
thin type IIb	50	Mo	10^{14} *	Over-ranged	1.2×10^{-3}
thick type IIb	250	Mo	10^{14} *	Over-ranged	1.4×10^{-2}
thick type IIb	250	Pt	10^{14} *	Over-ranged	Rectifying
thick type IIb	250	Pd	10^{14} *	Over-ranged	Rectifying
thick type IIb	250	Al	10^{14} *	Over-ranged	Rectifying

*Representative value from other type IIb diamond samples.

ments requires two dimensional current flow. For the epitaxial layers this condition may be assumed to be approximately true, but for the 50 μm and 250 μm (0.25 mm) thick samples there is a large component of vertical current flow. This component gives rise to a spreading resistance which increases the measured contact resistance.

Linear I–V curves have also been observed for annealed Ti [1], and Ta [5] contacts to lightly doped diamond. Ni films consistently delaminate from the diamond surface, while Au contacts did not appear to wet the diamond surface but instead broke into many small balls of Au on the surface. In addition, Pt, Pd, and Al all failed to show ohmic behavior either in the as-deposited state, or after annealing. The lack of ohmic contact formation in the cases of Al, Au, Ni, Pd, and Pt might be explained by their lack of carbide formation. The solubility of C in molten Al is practically zero even in the temperature range 1000–1100 °C, but with some carbide formation in the range 1300–1500 °C. Ni does appear to form a carbide above 2000 °C, but it decomposes to Ni + C at lower temperatures. Au, at its boiling point, does dissolve a small amount of C (about 0.3 wt.%) which crystallizes in the form of graphite upon cooling of the melt. Pd and Pt both will dissolve appreciable amounts of C when in the molten state, but again the C precipitates in the form of graphite upon cooling. No diffusion of C was observed in Pt even in the temperature range 800–900 °C. (Reference 6 was used to obtain all phase information cited above.) Ohmic contacts have been produced previously with non-carbide forming metals by utilizing these liquid phase reactions (see ref. 1 and references cited therein). Thus, it seems reasonable to conclude, at least for ohmic contacts formed by the solid state reaction process, that carbide formation is necessary.

4. Conclusions

Specific contact resistance for the Ti and Mo refractory metal carbide contacts to diamond have been measured. Contacting highly doped diamond films is relatively easy, with nearly ohmic behavior observed for both W and Au probes on the bare diamond surface. An apparent correlation between ohmic contact formation on lightly doped type IIb diamonds and the use of a carbide forming metallization has been observed in solid state reactions. Non-carbide forming metallizations suffer from either poor adhesion or rectifying behavior.

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