

Carbide contacts on homoepitaxial diamond films

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Abstract

We present experimental investigations of the structural and electrical properties of carbide contacts on homoepitaxial p-type diamond films in order to achieve Schottky diodes working at high temperatures with highly adhesive ohmic and Schottky contacts on diamond. For ohmic contacts, the reaction of molybdenum deposited by magnetron sputtering on homoepitaxial diamond layer is studied through X-ray diffraction and Rutherford backscattering. The formation of hexagonal α - Mo_2C begins at 700 °C. However, the residual oxygen is exodiffused only at 900 °C and for undoped diamond. Nevertheless, ohmic contacts are achieved after annealing at 900 °C, with a low contact resistivity at a boron concentration of $1.6 \times 10^{21} \text{ cm}^{-3}$. For Schottky contacts, the in-situ reaction under ultra-high vacuum between Er and a non-oxidized diamond surface begins at 700 °C. A potential barrier height of 1.9 eV and a rectification ratio larger than 10^3 at 4 V at least up to 500 °C are obtained. In each case, coating layers intended to protect carbides against oxidation are assessed. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Carbides; Homoepitaxial diamond; Ohmic contact; Schottky diode

1. Introduction

Schottky diodes need both rectifying and ohmic metallic contacts. This is usually obtained by metal deposition on either a lightly (less than 10^{17} cm^{-3}) or highly doped (more than 10^{20} cm^{-3}) semiconductor, respectively. As p-type diamond is studied here for high-temperature operation (at least 500 °C), its metallic contacts will have to withstand more severe conditions and therefore to comply with additional requirements: (1) good adhesion on the diamond substrate; (2) chemical inertness and stability at elevated temperatures, typically higher than 500 °C for activating all the boron acceptors; (3) for the rectifying contacts, structural damage near the metal–diamond interface has to be avoided as this would induce localized states in the space charge zone.

The purpose of this paper is to show that optimal choices can be made in order to fulfil all of these conditions for p-type homoepitaxial diamond films: (1) a good adhesion of the metallic contact with diamond requires a chemical reaction between the metal and diamond and leads naturally to carbide contacts; (2) the formation of carbides by thermal annealing of the

metal deposited on diamond must be carefully studied, and the inhibition of the reaction by oxygen and doping atoms has to be addressed. The molybdenum carbide is chosen here because the Mo_2C phase forms at the relatively low temperature of 700 °C and is stable up to 1100 °C in contrast to other transition metals, M, which show evolution towards the MC phase [1]. In previous studies, Mo was deposited by e-beam evaporation under ultra-high vacuum (UHV) on weakly B-doped natural crystals [2–4,8], undoped [5] and B-doped polycrystalline [5–7] films, and highly B doped (hot filament) monocrystalline films [8]. Annealing was performed mainly under purified hydrogen [2–4,8] or UHV [5]. These studies focused mainly on the electrical properties of the contacts [2–4,6–8], whereas the formation of the carbide was studied only on undoped or weakly B-doped polycrystalline diamond [1,5]. On the contrary, we concentrate here on the formation and stability of the carbide under more realistic conditions which include annealing sputtered Mo films deposited on homoepitaxial diamond films containing $0\text{--}1.6 \times 10^{21} \text{ B cm}^{-3}$ and their effect on the contact resistance. The oxygen level in Mo and, unexpectedly, the boron concentration in diamond will be shown to have a great effect on the formation of the carbide and on the contact resistance. Finally, it will be demonstrated for the first time that Schottky contacts working up to 500 °C can be obtained on diamond with a carbide of a rare earth metal.

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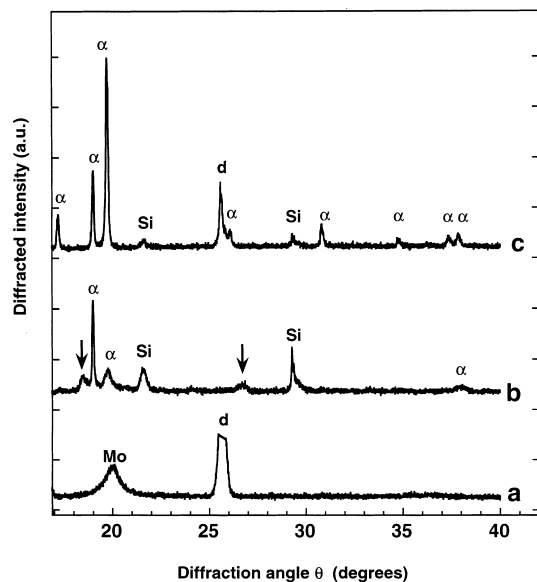


Fig. 1. Intensity of X-rays diffracted by a metallic layer deposited on a homoepitaxial undoped diamond film: (a) as deposited molybdenum (Mo); (b) after a first anneal at 700 °C, 2 h; (c) after a second anneal at 900 °C, 2 h. With the Ib synthetic diamond substrate being stuck on silicon, several silicon (Si) and diamond (d) peaks appear. In (b), arrows indicate peaks related to an oxygenated compound that does not exist after the second anneal. After annealing, only the peaks of the hexagonal carbide α -Mo₂C, labelled α , are visible, apart from the aforementioned.

2. Formation of Mo₂C contacts on homoepitaxial diamond

Molybdenum films (200–300 nm thick) are deposited at room temperature by magnetron sputtering on homoepitaxial diamond films grown by microwave chemical vapor deposition (MWCVD) on synthetic Ib (100) diamond crystals [9].

When Mo is deposited on undoped films, X-ray diffraction shows the diamond peak and a broad Mo peak (Fig. 1a), but Rutherford backscattering spectroscopy (RBS, Fig. 2a) shows that 25% of oxygen is incorporated in the as-deposited Mo film. It remains within the film after the first annealing step of 2 h at 700 °C (Fig. 2, curve a and b), and the carbon edge at 500 keV still superimposes to the oxygen plateau below 740 keV, whereas the Mo signal broadens due to the expansion of the Mo₂C unit cell in comparison to that of Mo. X-ray diffraction shows that Mo is partially transformed into polycrystalline α -Mo₂C (the hexagonal form of molybdenum carbide) after 2 h of annealing at 700 °C (Fig. 1, curve b). Some X-ray diffraction peaks marked by arrows in Fig. 1b cannot be assigned to any known compound of oxygen, carbon and molybdenum, but are related to the presence of oxygen since they disappear as the oxygen does in the RBS spectrum after the second annealing step of 2 h at 900 °C (Fig. 2, curve c). This second annealing step has transformed the

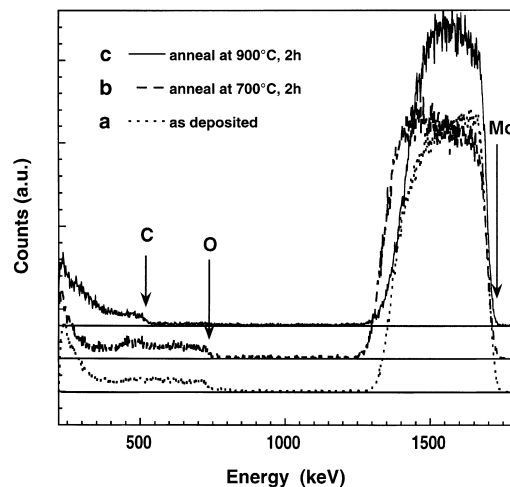


Fig. 2. Rutherford backscattering spectra of the same sample as in Fig. 1. Mo, O and C arrows display the energy thresholds corresponding, respectively, to molybdenum, oxygen and carbon at the surface of the sample. Oxygen has disappeared after the treatment in (c).

whole Mo film in α -Mo₂C with a good crystallinity, as evidenced from the sharp peaks in the diffraction pattern (Fig. 1, curve c). At the same time, the Mo plateau of the RBS spectrum shrinks, and the carbon step at 500 keV becomes clear (Fig. 2, curve c). From X-ray photoelectron spectroscopy (XPS), the binding energy of the C 1s peak (not shown here) shifts very distinctly from 285.2 eV in diamond to 283 eV for Mo₂C [10]. Such a shift of about -2 eV, towards smaller binding energies, is characteristic of carbon in carbides, in contrast to all other chemical shifts observed when carbon is bonded with any other elements [11].

The carbide formation here is slower than that observed when Mo is deposited on polycrystalline diamond, where the first annealing step of 2 h at 700 °C makes oxygen diffuse out of the metallic layer and molybdenum to transform completely into Mo₂C [12].

The same set of experiments has been carried out for Mo deposited on homoepitaxial diamond films containing 10^{18} boron atoms per cm³. This time, oxygen is still present within the α -Mo₂C layer after the second annealing step of 2 h at 900 °C, as evidenced from the extra peaks in the X-ray diffraction data and oxygen signal in the RBS spectrum.

The oxygen is not exodiffused from the metallic film when the homoepitaxial diamond film is boron-doped, and the carbide formation is even slower than in undoped film. It is increasingly slower as the boron concentration in the diamond film increases.

3. Mechanical and chemical stability, and electrical properties of the α -Mo₂C contacts

Even with residual oxygen, ohmic contacts have been achieved on diamond films doped with boron concen-

trations up to 1.6×10^{21} atoms cm^{-3} . For all doping levels, the adhesive tape does not tear off the metallic layer, and this test shows that its adherence on homoepitaxial diamond films is satisfactory.

The $\alpha\text{-Mo}_2\text{C}$ layer can be etched by aqua regia, hot H_2SO_4 and the sulfo-chromic mixture but withstands $\text{HF}/\text{NH}_4\text{F}$ (1:1) well at 70°C over a period of 15 min. Heating the sample in air leads to oxidation of the carbide as soon as 430°C is reached. An evaporated gold coating prevents oxidation only up to 520°C in air. Above 535°C , the molybdenum oxide evaporates. Consequently, a metallic layer acting as a barrier against oxygen must be deposited over the carbide layer. As proposed by several authors [13,14], transition or noble metals such as titanium and/or platinum should play such a protective role when inserted between the carbide and the gold layer. The Au layer is useful for soldering gold wire on to the top of the contact.

The Table 1 indicates the electrical characteristics of contacts made on three samples with a 90-nm-thick p+ homoepitaxial diamond film of various B-doping levels. Their current–voltage characteristics measured between two separated golden Mo_2C contacts are linear, even at ambient temperature, so that the total resistance, R_t , can be easily measured. This resistance, R_t , results from the sum $R_1 + 2R_c$, where R_1 is the resistance from the p+ layer and R_c that of the contact. From R_t and the calculation of R_1 from the film resistivity, R_c is extracted. As the B incorporation level increases, R_c decreases more rapidly than R_1 as can be seen in Table 1. For the highest boron incorporation, i.e. 1.6×10^{21} B cm^{-3} , above the threshold for metallic conductivity in the boron impurity band in diamond [15], which corresponds to a positive thermal coefficient for R_1 (Fig. 3), R_t and R_1 drop dramatically to reach roughly the same value (Table 1). From the error bar on R_c , only an upper limit of the specific contact resistivity can be estimated as a few 10^{-3} $\Omega \cdot \text{cm}^2$ at ambient temperature, which is higher than the value obtained in a previous study [8] when oxygen-free Mo is deposited under ultra-high vacuum. In conclusion, the presence of boron in homoepitaxial diamond films slows down both the ex-diffusion of oxygen from the metallic layer and the formation of the carbide, and increases the contact resistance of ohmic contacts.

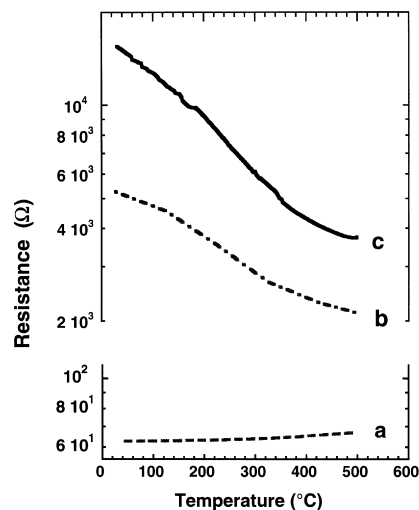


Fig. 3. Total resistance between two golden $\alpha\text{-Mo}_2\text{C}$ contacts on a $3 \mu\text{m}$ homoepitaxial diamond layer doped, respectively, with (a) 1.6×10^{21} , (b) 4×10^{20} and (c) 2.4×10^{20} B cm^{-3} as a function of temperature.

4. Rare earth metal Schottky contacts on diamond films

Another issue of high-temperature devices on p-type homoepitaxial diamond is to achieve Schottky contacts with large potential barrier heights. One must look for metals or metallic compounds with a low work function (which is expected to give a high potential barrier height on p-type semiconductors) and able to withstand high temperatures. Rare earth metals or rare earth compounds seem to be well suited for such purposes. Erbium, which is chosen here has a work function of 2.9–3 eV [16,17] and therefore appears suitable for such a purpose.

Under ultra-high vacuum, after in-situ annealing at 700°C for hydrogen desorption of the subsurface ‘H-doped’ layer obtained after the growth in a H_2/CH_4 microwave plasma, erbium is deposited at room temperature on lightly doped (10^{17} B cm^{-3}) diamond films. From the XPS spectra of Fig. 4, there is no significant carbide formation after deposition of one monolayer of Er. From the emergence of a second C 1s peak with the characteristic shift of carbides [11], erbium carbide appears after 10 min of in-situ annealing at 700°C . Although its volume increases rapidly after 15 min of annealing of two monolayers of Er at 800°C ,

Table 1

Calculation of the contact resistance of the $\alpha\text{-Mo}_2\text{C}$ dots from the measured resistance and the characteristics of the doped diamond films

[B]/[C] in the gas phase (%)	0.12	0.2	0.8
[B] in diamond (cm^{-3})	2.4×10^{20}	4×10^{20}	1.6×10^{21}
Diamond resistivity ρ ($\Omega \cdot \text{cm}$)	2×10^{-2}	6×10^{-3}	9×10^{-4}
Total resistance, R_t , measured at 300 K	17 k Ω	4.5 k Ω	62 Ω
Calculated resistance of the p+ layer alone	1300 Ω	400 Ω	62 Ω
Calculated contact resistance, R_c , at 300 K	7.9 k Ω	2.05 k Ω	\leq few Ω

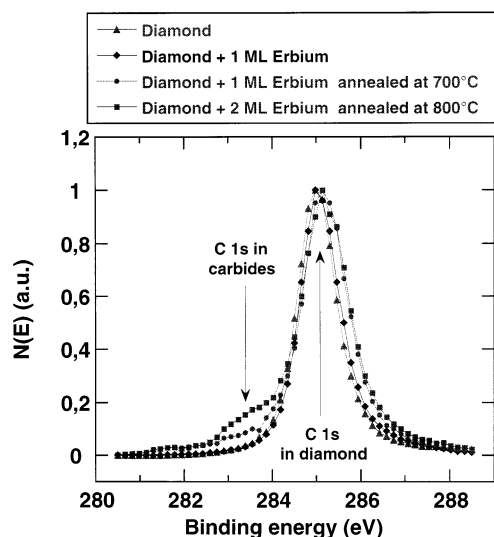


Fig. 4. X-ray photoemission spectra close to the C 1s binding energy for a homoepitaxial diamond layer, either clean or covered with one or two Er monolayers. The peak that appears as a shoulder on the lower binding energy is characteristic of the carbide formation.

the reaction involves only a fraction of the Er monolayer and therefore is not complete. Carbides like ErC_2 are highly reactive with water and oxygen. Thus, a layer of erbium silicide $\text{ErSi}_{1.7}$ annealed for 30 min at 700 °C has been deposited over the two Er monolayers to act as a protective coating. Photolithography with an electronic beam and etching in $\text{HF}/\text{NH}_4\text{F}$ mixture allows contacts to be defined with different areas. The current density as a function of voltage clearly displays rectification at room temperature and at least up to 500 °C (Fig. 5).

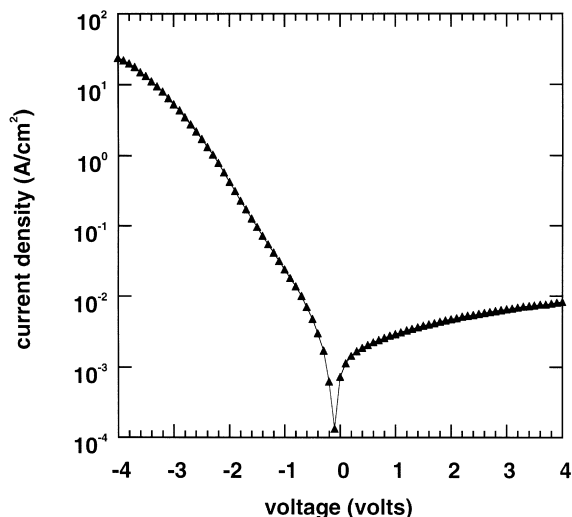


Fig. 5. Current density of a diode made of two Er monolayers annealed at 800 °C and coated with a $\text{ErSi}_{1.7}$ protective film on a homoepitaxial diamond layer doped with $10^{17} \text{ B cm}^{-3}$ as a function of the applied voltage on the Schottky contact at 773 K. Series resistance limits the forward current for the highest negative voltages because the back contact is taken in the same way as the Schottky contact but with a much larger area.

The quantum yield of internal photoemission has been measured as a function of photon energy and leads to a typical potential barrier height of 1.9 eV. This value is significantly higher than those (1 eV) obtained with a ‘H-doped’ superficial layer on the diamond surface [18], still higher than those obtained on the oxidized surface (1.2 eV [19], 1.5 eV [20]), and reaches the highest value (1.9 eV) obtained on the oxidized surface of I Ib crystals [21]. Moreover, a large rectification ratio ($>10^3$ at 4 V) is kept at least up to 500 °C. This temperature is higher than the highest temperature (400 °C with Au), which has been reported previously to give a high rectification ratio on diamond films [19], whereas a rectification ratio well below the present one has been shown up to 700 °C with W on a natural I Ib crystal [22].

We show for the first time that a Schottky contact with a high rectification ratio up to at least 500 °C can be obtained with a diamond film covered by a rare earth metal (here, Er) with an interfacial erbium carbide in the submonolayer range. It displays a potential barrier height of 1.9 eV, equal to the highest value, which was obtained (with non-reactive metal) on oxidized natural I Ib diamond. The adherence of carbide metallic layers is much better than that of non-reactive metals. However, erbium carbide formation is not expected to damage the diamond depletion zone since the reaction involves about one monolayer or less.

5. Conclusions

Sputtered Mo films contain a high concentration of oxygen. Analysis of the composition and structure of the contacts obtained after annealing at 700 °C under argon of Mo sputtered on homoepitaxial crystalline diamond shows that polycrystalline $\alpha\text{-Mo}_2\text{C}$ has been grown. However, oxygen is exodiffused only when annealing is performed at 900 °C, while oxygen exodiffusion occurred at 700 °C when Mo was deposited on polycrystalline diamond. Moreover, when the homoepitaxial diamond layer is doped with boron, oxygen remains in the carbide, even after annealing at 900 °C. Despite the presence of oxygen, ohmic contacts are obtained on homoepitaxial diamond films, with a low contact resistivity of about $10^{-3} \Omega \cdot \text{cm}^2$ for boron concentrations of $1.6 \times 10^{21} \text{ cm}^{-3}$. Erbium begins to react with lightly doped homoepitaxial diamond films at 700 °C. This gives a Schottky contact with the highest reported potential barrier of 1.9 eV and with a high rectification ratio larger than 10^3 up to at least 500 °C.

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