Epitaxial Cu contacts on semiconducting diamond

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Abstract

In this study Cu films of 30 nm and 200 nm thickness have been grown on natural type IIb semiconducting diamond C(001) substrates by electron-beam evaporation at 500 °C in UHV. As evidenced by Rutherford backscattering/channeling techniques and *in situ* low-energy electron diffraction, the as-deposited layers were shown to be epitaxial, with $\chi_{Cu}=49\%$. In addition, the technique of atomic force microscopy has demonstrated island morphology, indicative of three-dimensional growth. Moreover, the Cu films displayed excellent adhesion properties with the underlying diamond substrate. Corresponding current–voltage (I–V) measurements conducted at room temperature have shown rectifying characteristics. In addition, a Schottky barrier height of $\Phi_B \approx 1.1$ eV has been determined from ultraviolet photoemission spectroscopy.

1. Introduction

There is a significant scientific and technological interest in the fabrication of rectifying and ohmic contacts for future diamond-based electronic devices. In particular, metal, silicide and semiconductor contacts have been investigated [1–3]. Recent publications have established excellent mechanical adhesion for polycrystalline Si and SiGe contacts [2, 3]. To date, the majority of rectifying metal contacts exhibit polycrystalline morphology and appear to have poor adhesion properties [1]. In contrast, Ni is the only epitaxially grown metal contact on diamond exhibiting rectifying behavior at both room temperature and elevated temperatures [4]. In this study Cu has been selected as a suitable contact metal, since Cu has a near-lattice match to diamond similar to Ni. Furthermore, no stable Cu carbides exist in the binary Cu–C phase diagram [5]. Therefore Cu is expected to form a physically and chemically abrupt interface with diamond.

In this paper we report the first results regarding heteroepitaxially grown Cu films on C(001). The microstructure and electrical characteristics for these contacts are presented.

2. Experimental details

Several (3 × 3 and 4 × 4 mm) natural type IIb semiconducting diamond C(001) crystals (supplied by D. Drucker & ZN.N.V.) were used in this study. Two independent chemical cleaning processes were employed to remove the non-diamond carbon from the surface of the diamond substrates. The first approach was a conventional chemical clean using chromic acid ($CrO_3:H_2SO_4$) (boiling for 15 min), aqua regia ($3HCl:1HNO_3$) (boiling for 15 min) followed by deionized (DI) water (rinsing). The other procedure involved an electrochemical etch [6], for which the samples were mounted on a Teflon^{tm} holder and placed between two Pt electrodes in DI water as electrolyte. A d.c. voltage of 350 V was applied between the two electrodes. Typical etch times were 3 h. To assess and compare the effectiveness of these two cleaning processes *in situ*, low-energy diffraction (LEED) was used. A comparable unreconstructed (1 × 1) LEED pattern was observed from crystals cleaned by either approach. Following chemical cleaning the diamond crystals were blown dry with N_2, mounted on an Mo sample block and transferred into the vacuum system. In order to desorb adsorbed gas contaminants all samples were annealed to 750 °C for 15 min in ultrahigh vacuum (UHV). Prior to growth 5.0 nm of Cu was evaporated from the solid source to liberate any foreign material which may have collected on its surface between depositions. Both large area films and contacts (625 μm in diameter) were grown by electron-beam evaporation. The contact dots were fabricated by employing an Mo shadow mask.

Two independent growth chambers were employed. One system had a base pressure of about 5×10^{-9} Torr

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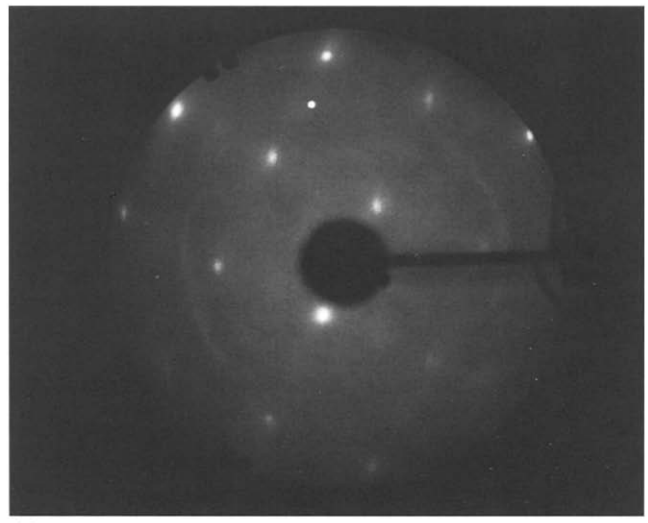
and featured a Thermionics, model 100–0010, single source evaporator. Owing to the small dimensions of this deposition chamber the pressure rose to about 2×10^{-7} Torr during growth. In this system, Cu layers of 30 nm and 200 nm thickness were deposited on substrates that were chemically cleaned by chromic acid. A deposition rate of 2.0–2.5 nm min^{-1} was used. The second chamber (base pressure ≈ 1–2×10^{-10} Torr) was equipped with a dual source, 270° HM^2 evaporator made by Thermionics. To commence the deposition a deposition rate of 1.0–1.2 nm min^{-1} was stabilized, and the shutter was removed from the front of the sample. After 20 nm was deposited, the rate was increased to 2.5–3.0 nm min^{-1} to give a final thickness of 200 nm. Electrochemically etched crystals were used here. Throughout the deposition (pressure $\approx 3 \times 10^{-8}$) the substrate was rotated to ensure uniform thickness across the sample. In both experiments a growth temperature of 500 °C was used and the thickness of the Cu layers was determined by a quartz crystal oscillator.

Several techniques were employed to analyze the samples, including *in-situ* LEED, Rutherford backscattering (RBS)/channeling, atomic force microscopy (AFM) and current–voltage (I–V) measurements.

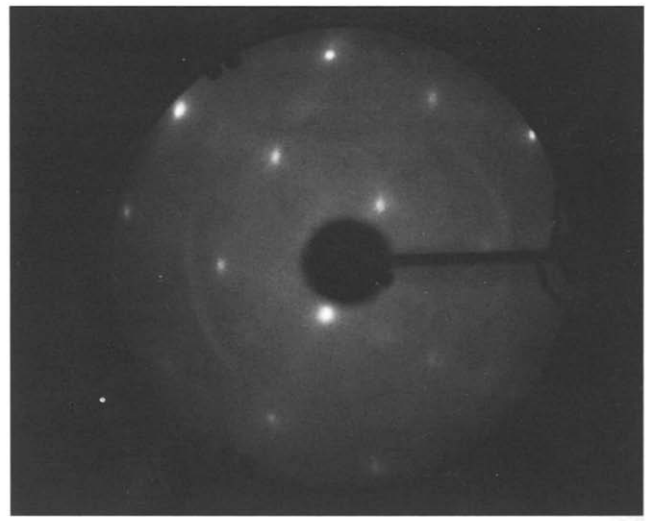
3. Results and discussion

The technique of LEED was employed to establish that the as-deposited films were epitaxial, as shown in Fig. 1(a). In particular, an unreconstructed (1 × 1) LEED pattern was seen from the as-annealed C(001) substrates (Fig. 1(b)). This (1 × 1) pattern was retained after Cu deposition. RBS/channeling has been performed using 2 MeV He^+ ions with a scattering angle of 110°. This gave a depth resolution of 6.7 nm for the Cu film. As shown in Fig. 2, the epitaxial quality of the Cu films grown under higher pressure (2×10^{-7} Torr) has been determined by channeling along the ⟨110⟩ directions of the diamond substrate. χ_{min} is the ratio of the aligned to nonaligned backscattering ion yields and gives the degree of crystallinity for the sample. Values of $\chi_{Dia} = 33\%$ and $\chi_{Cu} = 49\%$ have been established for the diamond substrate and the overgrown Cu film respectively. Furthermore, RBS analysis has shown the presence of oxygen impurities in these Cu films (peak near 950 keV). In addition, the random spectrum shows a step in the carbon signal at 760 keV, indicating a nonuniform thickness of the Cu layer. The value of χ_{Cu} appears to be fairly high but, considering χ_{Dia}, the crystalline quality of the Cu film is actually quite reasonable.

The nonuniformity in the deposited Cu layers has been attributed to island morphology for all samples, as evidenced by AFM. The samples grown in a vacuum of 2×10^{-7} Torr exhibited well separated islands. For the



(a)



(b)

Fig. 1. (a) (1 × 1) LEED pattern from type IIb C(001) substrate after chemical clean by $CrO_3 + H_2SO_4$ and $3HCl + 1HNO_3$, and following anneal at 750 °C in UHV, $E_B = 180$ eV. (b) (1 × 1) LEED pattern from 30 nm thick Cu film deposited on type IIb C(001) substrate (see (a)) at 500 °C in UHV: 3×10^{-8} Torr during growth, $E_B = 180$ eV.

Cu contacts of 30 nm thickness oriented islands of about 50 nm were observed. However, films of 200 nm thickness grew as well-defined islands of about 1000 × 500 nm in size with smooth morphologies, as shown in Fig. 3(a). These islands were found to be oriented in the ⟨110⟩ crystallographic directions. Therefore, coalescence of these islands was evident for increasing Cu coverage. However, no continuous layer was formed. Electrical measurements for these samples showed a lack of current transport across one Cu dot. This interesting phenomenon may be attributed to the observed islanding behavior of these Cu films. In comparison, AFM images of the 200 nm thick Cu films deposited under better vacuum (3×10^{-8} Torr) showed a fairly smooth and contiguous

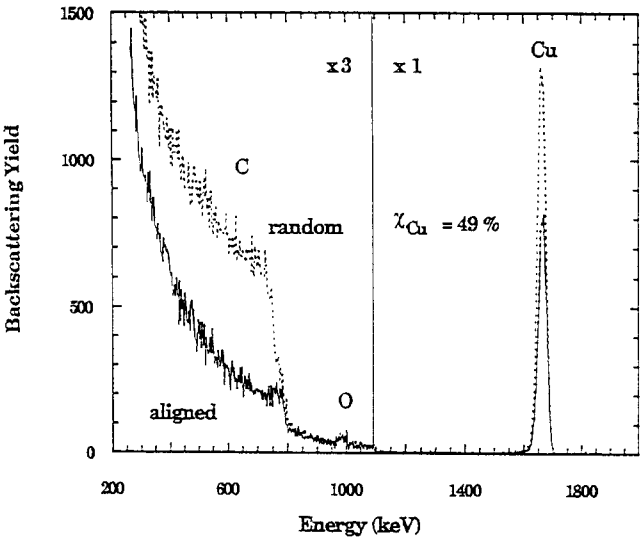


Fig. 2. RBS/channeling aligned (solid line) and random (broken line) spectrum for Cu(001) grown on C(001) substrates (cleaned by $CrO_3 + H_2SO_4$ and $3HCl + 1HNO_3$) in UHV: 2×10^{-7} Torr during growth.

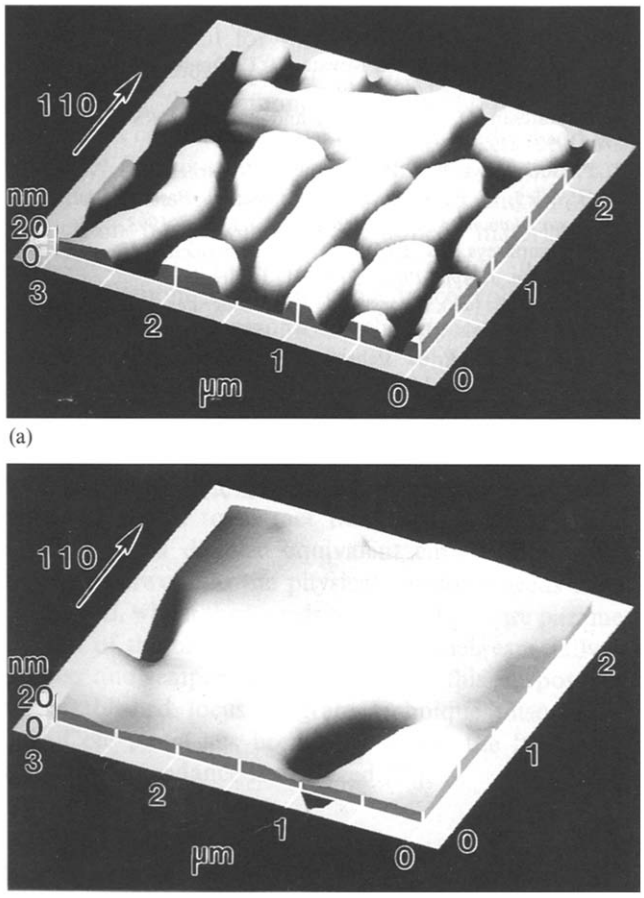


Fig. 3. AFM images of 200 nm thick epitaxial Cu film deposited on type IIb C(001) substrates in UHV: (a) cleaned by $CrO_3 + H_2SO_4$ and $3HCl + 1HNO_3$; 2×10^{-7} Torr during growth; (b) cleaned by electrochemical etch; 3×10^{-8} Torr during growth.

surface structure. However, the presence of numerous pinholes was observed (Fig. 3(b)). Corresponding *I–V* measurements between a dot and a large area back contact showed rectifying behavior. In addition, a reverse bias leakage current of about 40 nA was observed at 5 V, as shown in Fig. 4. This corresponds to a current density of 13×10^{-6} A cm^{-2}. To remove any highly conductive surface contaminants that could contribute to the reverse bias leakage current, another electrochemical etch was employed. Prior to etching the Cu dots were covered with wax while the diamond surface was kept exposed. Following the etch process the wax was readily removed with acetone. Indeed, in separate experiments investigating electrochemical etching it has been demonstrated that, besides graphite, various metals could be removed from the surface by this etching process [7, 8]. However, the *I–V* characteristics remained unchanged. Therefore it is reasonable to conclude that nondiamond carbon and possible metal contaminants have been effectively removed from the diamond surface already. Consequently, the observed turn-on voltage and corresponding leakage current are believed to be intrinsic to the Cu/C(001) interface. However, it will have to be established why Cu contacts display such a high reverse leakage current. Indeed, further studies are necessary to investigate the Cu/diamond interface structure.

Because of the nonlinearity in the semilogarithmic *I–V* plot, an independent method to measure the Schottky barrier height Φ_B had to be employed. A value of $\Phi_B \approx 1.1$ eV has been established from ultraviolet photoemission spectroscopy (UPS). Furthermore, the UPS spectra showed that deposition of Cu on diamond

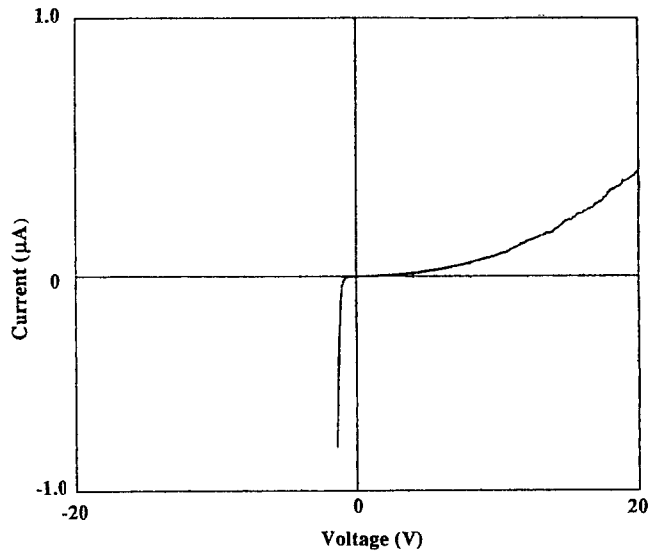


Fig. 4. Linear plot of the room temperature *I-V* characteristics of heteroepitaxial Cu contacts deposited on type IIb C(001) substrates in 3×10^{-8} Torr.

C(001) induced a negative electron affinity (NEA) on the surface [9].

It is reasonable to assume that these observations are due to a three-dimensional (3D) growth mechanism featuring a larger nucleation area and better coalescence of the islands compared with the samples deposited under higher pressure. As shown in Fig. 2, RBS/channeling clearly demonstrated the presence of oxygen impurities in the latter films. The oxygen contamination is expected to be lower for the system with better vacuum. Therefore samples deposited under lower pressure are expected to exhibit better microstructure. No significant effect on the morphology of the Cu films is expected from to the two different chemical cleaning procedures since they appear to be comparable. Therefore it is reasonable to conclude that the differences in microstructure for the epitaxial Cu layers were mainly due to a change in oxygen contamination. Further improvement pertaining to a more uniform growth, however, could be accomplished by using higher deposition rates. Also, a higher substrate temperature should increase the surface mobility of Cu on diamond and result in smoother epitaxial layers. With respect to the reports on Ni, even two-dimensional growth could be possible [4]. This needs to be the subject of future work.

Consistent results from all samples clearly indicated that various processing steps including thermal annealing, electrical probing and ultrasonic cleaning did not degrade the excellent mechanical adhesion of the Cu contacts with the underlying diamond substrates.

4. Conclusions

Epitaxial Cu films have been deposited on p-type semiconducting natural diamond C(001) substrates using electron-beam evaporation techniques. For all samples 3D growth has been observed. However, differences in the nucleation area and the degree of coalescence for the Cu islands have been correlated to the quality of vacuum in the UHV growth chamber. Excellent mechanical adhesion properties have been established for the Cu films throughout. *I–V* measurements showed rectifying behavior at room temperature. Furthermore, a Schottky barrier height of $\Phi_B \approx 1.1$ eV has been determined by means of UPS. Suggestions regarding future work to further assess and improve microstructure as well as electrical behavior have been made.

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