Titanium Nitride Grown by Sputtering for Contacts on Boron-Doped Diamond

Vincent Mortet,* Omar Elmazria, Wim Deferme, Michael Daenen, Jan D'Haen, Andrada Lazea, Anne Morel, Ken Haenen, Marc D'Olieslaeger

Due to its exceptional properties, semiconducting diamond is expected to be used for electrically active devices which can be operated in harsh environments. Such devices need reliable ohmic contacts that can also stand hostile environments. Titanium nitride (TiN) is a chemically stable material with good electrical conductivity. In this work, TiN contacts on boron-doped diamond have been made and characterised. TiN films were deposited by reactive magnetron sputtering. Boron-doped diamond layers were deposited by plasma enhanced chemical vapour deposition. Optimal deposition conditions have been determined to obtain TiN films with low resistivity ($\sim$100 $\mu\Omega \cdot$ cm), high reflectance in the IR region and low stress. TiN contacts show ohmic behaviour after annealing at 750 °C.

Introduction

The exceptional properties of diamond and the possibility to obtain diamond films at low pressure on different types of substrates, make this material a good candidate for a large number of novel applications. Diamond also offers the possibility to fabricate electrically active devices which can be operated at elevated temperatures, in hostile environments. Diamond can also be used in biomedical applications and it fulfils the main requisites for use in human implants due to its biocompatibility and its chemical stability.

V. Mortet, W. Deferme, M. Daenen, J. D'Haen, A. Lazea, K. Haenen, M. D'Olieslaeger
Institute for Materials Research, Hasselt University, Wetenschapspark 1, 3590, Diepenbeek, Belgium
Fax. +32 (0)11 26 88 99; E-mail: vincent.mortet@uhasselt.be
V. Mortet, K. Haenen, J. D'Haen, A. Lazea, M. D'Olieslaeger
IMEC, Division IMOMEC, Wetenschapspark 1, 3590, Diepenbeek, Belgium
O. Elmazria
LPMIA, Université H. Poincaré, Nancy I, F-54506, Vandoeuvre-les-Nancy Cedex, France
A. Morel
ENSAM, boulevard du Ronceray, B.P. 3525, F-49035 Angers Cedex , France

Titanium nitride (TiN) is a hard, dense, refractory material with high electrical conductivity. TiN has good optical properties, including an attractive gold-tinged appearance when pure, and it has a high reflectance in the IR range. TiN is thermodynamically stable in air upto 600 °C and it is inert to corrosive media. Like diamond, TiN is a non-toxic and biocompatible material. TiN meets the food and drug administration (FDA) guidelines and it has been approved for use in numerous medical/surgical devices, including implants. TiN is also widely employed in semiconductor manufacturing as a 'diffusion barrier' layer and it has already been used as ohmic contact on GaN and SiC.[1,2]

The use of TiN in combination with diamond is attractive for the construction of ohmic contacts, operating either at elevated temperatures, in hostile chemical and radiation environments or in biological environment.

In this paper, an optimisation of TiN thin films grown by reactive DC-pulsed magnetron sputtering is reported. Structural, mechanical, optical and electrical properties of TiN films have been measured. Homoepitaxial boron-doped diamond layers were grown by plasma enhanced chemical vapor deposition and they were characterised by Fourier transform photocurrent spectroscopy (FTPS).[3] Finally, TiN contacts on boron-doped diamond have been made and characterised.

Experimental Part

The TiN layers were deposited on silicon (100) and fused-silica substrates. The substrates were ultrasonically cleaned in trichloroethylene, acetone and alcohol and they were dried with pure nitrogen. The titanium target (10 cm in diameter, 99.99% purity), which is held on the water-cooled magnetron cathode, was sputtered in a mixture of argon and nitrogen. The argon and nitrogen flow rates (Φ_{Ar} and Φ_N, respectively) were controlled by two mass flow meters and the total gas flow rate was kept constant (50 sccm). The total pressure was controlled with a throttling valve situated in front of the turbo-molecular drag pump. The target power supply was driven in constant-power mode at 250 kHz pulse frequency and 1 600 ns pulse width. The distance between the target and the substrate holder can be adjusted. The substrates were not heated and their temperature was only dependent on the plasma heating.

Before deposition, the sputtering chamber was evacuated to a pressure below 2×10^{-6} mbar. The target was cleaned in an argon discharge for 10 min and it was pre-sputtered in the same conditions as the film deposition conditions for additional 10 min. During these steps, the substrates are shielded from deposition by a shutter. TiN films were deposited under various target power (P), total pressure (P_t), target to substrate distance (d) and nitrogen ratio ($R_N = \Phi_N/(\Phi_{Ar}+\Phi_N)$). The investigated deposition conditions are summarised in Table 1.

TiN films were characterised by X-ray diffraction in θ–2θ scan mode with Cu $K_{\alpha 1}$ radiation and scanning electron microscopy (SEM). The films thicknesses were measured by SEM cross-section observation. The mechanical stress was calculated from substrate curvature measurements using the Stoney formula.[4] The substrates curvatures were measured by a Dektak^{3}ST profilometer. Electrical characterisations of the films were performed using a four-points probe. Finally, optical reflectance of TiN films was also measured in near IR, visible and ultraviolet range (NIR-Vis-UV).

Boron-doped diamond layers were grown on (100) Ib $2.5 \times 2.5 \times 0.5$ mm^3 single crystal diamond samples by plasma enhanced chemical vapour deposition (PECVD) in a homemade NIRIM type reactor.[5] Before deposition, the vacuum chamber is evacuated to a base pressure lower than 10^{-6} mbar with a turbo-molecular pump. Boron doping is achieved using trimethylboron (TMB) diluted in hydrogen (200 ppm). The thickness of the boron-doped layers was calculated from the mass measurement assuming that the density of the epilayer is 3.52. Resistivity of the p-type layers was measured using the Van der Pauw resistivity measurement method. The incorporation of substitutional boron in the diamond layer was confirmed using FTPS at liquid nitrogen temperature. Ohmic titanium/aluminum inter-digitated electrodes with a spacial period of 400 mm were obtained by lift-off. Electrical characterisation of the diamond layer and TiN contacts were made using circular transmission line model measurements (c-TLM).[6]

Results and Discussion

TiN Growth

First, TiN films were deposited at different nitrogen concentrations at low pressure (with $d = 5$ cm, $P =$ 450 W). Films deposited at $R_N = 100\%$ are grey, films deposited at lower nitrogen concentration have a copper-like colour, whereas films deposited at $R_N = 5\%$ are golden which is a particularity of stoichiometric TiN. X-ray diffraction patterns of these films are reported in Figure 1. All films deposited at a nitrogen concentration higher than 30% do not exhibit any diffraction peak. At lower nitrogen concentration, X-ray diffraction patterns show a peak at 2θ $\sim$36.6° related to the (111) TiN peak. The most intense peak was obtained at $R_N = 5\%$ and it is shifted to lower 2θ. This is probably due to a high stress in the layer as one can see from the inset of Figure 1 where the variation of the films stress as a function of the nitrogen concentration is represented. The stress is compressive and maximum ($\sim$1.3 GPa) at $R_N = 5\%$.

Second, TiN films were deposited at different target's powers and different total pressures at $R_N = 5\%$. All these films show the X-ray diffraction peak of (111) TiN. The optimal target power has been found to be 450 W. As one can see on Figure 2(a), the stress of the layer is high ($\sim$2 Gpa) at low pressure whatever the target power is, and it decreases to nearly no stress for pressures higher than $(20–30) \times 10^{-3}$ mbar. We have observed that films deposited at higher pressure and without stress, are slightly less shiny than the films deposited at lower pressure. Figure 2(b) shows the resistivity of the TiN films as a function of the total pressure and the target power. The resistivity of the films is low ($\sim$100 $\mu\Omega \cdot$ cm) at low pressure and rises at the threshold pressure of $\sim(20–30) \times 10^{-3}$ mbar. Figure 3 shows the reflectivity spectra of TiN films deposited

Table 1. Summary of the investigated deposition conditions and the optimal deposition conditions.

	Studied range	Optimal conditions
Base pressure	2×10^{-6} mbar	–
Target	Ti (99.99% pure),Ø 10 cm	–
Gases	Argon - Nitrogen	5% nitrogen in Argon
Target-to-substrate distance	5–13 cm	5 cm
Target power	375–750 W	375–450 W
Total pressure	$(4.7–49) \times 10^{-3}$ mbar	$(20–30) \times 10^{-3}$ mbar

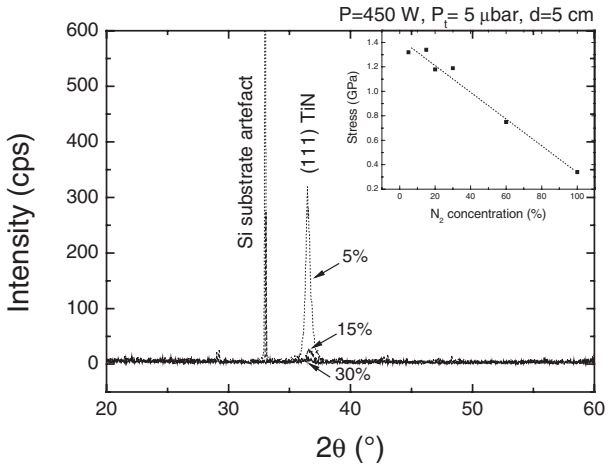

Figure 1. X-ray diffraction pattern of TiN films obtained at different nitrogen concentrations. Inset: variation of the mechanical stress of TiN as a function of the nitrogen concentration in the discharge gas.

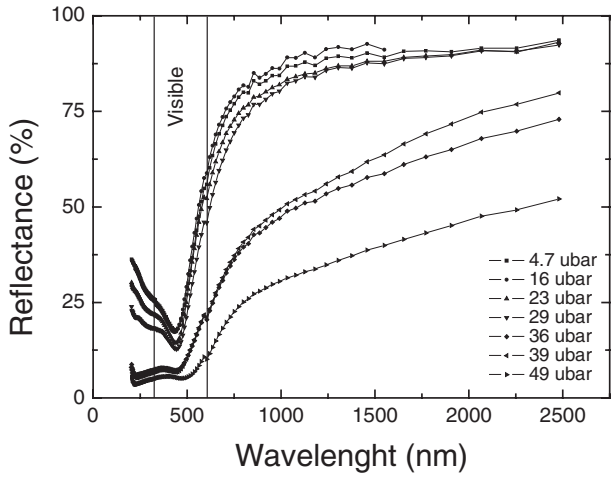

Figure 3. Variation of the reflectance in UV-visible-NIR range of TiN films grown at different total pressures of the deposition chamber.

at different pressures. The reflectivity spectra are characteristic of a free-electron system in a metal with a reflectivity edge at ~400 nm, due to a screened plasma resonance.[7] One can see that the reflectivity in the IR region of TiN films deposited at low pressure is higher than those deposited at high pressure whatever the target power. The lower reflectivity might be due to either surface scattering due to the films roughness or different electrical properties of the films. TiN films with the lowest resistivity are obtained at target powers between 375 and 450 W. Figure 4 show the typical SEM pictures of a film deposited at low pressure and a film deposited at high pressure. Films deposited at low pressure are smooth with very fine grains, whereas films deposited at high pressure are rough with large grains.

Properties of films deposited at low pressure and different target-to-substrate distances (from 5 to 13 cm) have been investigated. No significant effects of the target-to-substrate distance on the stress, the morphology and the reflectivity of the layers have been observed, however the distance increase does decrease the crystalline quality and the deposition rate.

In the optimal deposition conditions ($P = 375$–450 W, $P_t = 20$ mbar, $R_N = 5\%$, $d = 5$ cm), low stress and high reflectivity in the IR range, low resistivity TiN films with a (111) crystalline orientation are obtained. The chemical stability of TiN films has been tested. TiN films were let in Aqua Regia and in an Al etchant solution ($H_3PO_4/HNO_3/H_2O$ at 60:7:10). TiN films are slowly etched in Aqua Regia

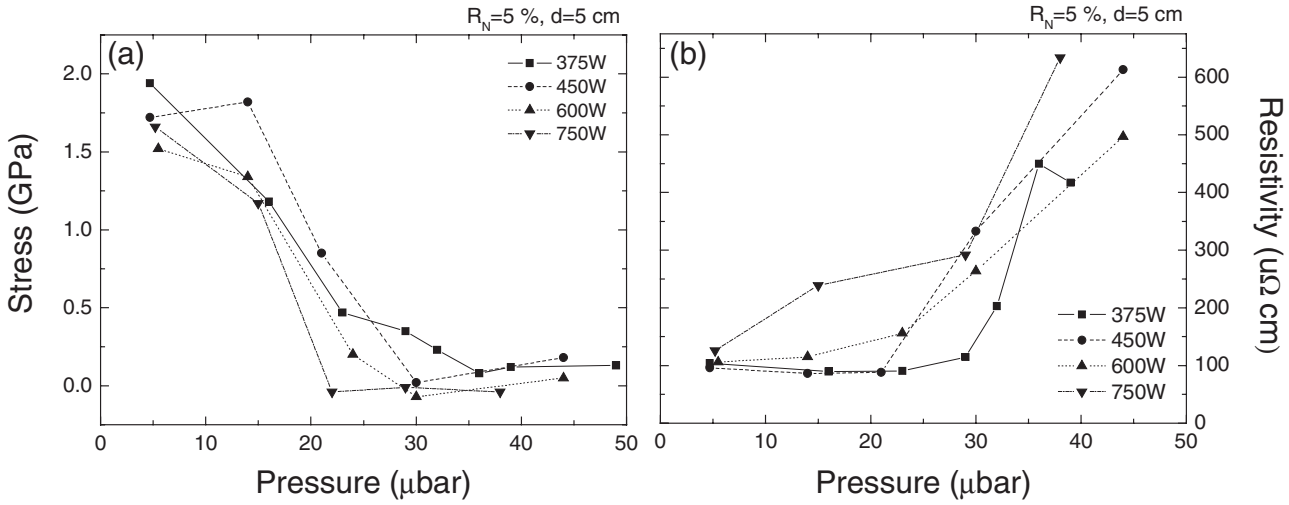

Figure 2. Variation of the mechanical stress (a) and the resistivity (b) as a function of the total pressure in the deposition chamber.

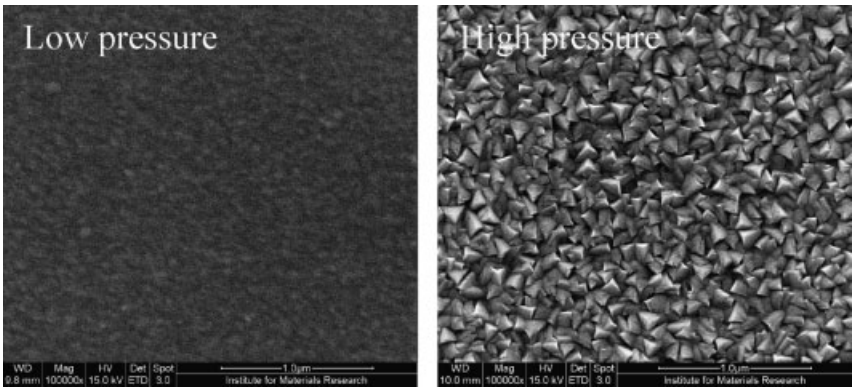

Figure 4. SEM images of TiN films' surface deposited at low and high pressure ($P = 450$ W, $R_N = 5\%$ and $d = 5$ cm).

(10 nm/h) and they are not etched in the Al etching solution while they are etched in hot H_2O_2.

Homoepitaxial Boron-Doped Diamond Growth and Electrical Characterisation

Doped diamond layers were grown in a mixture of 1% of methane diluted in hydrogen at a total pressure of 110 mbar, a microwave power of 500 W and a substrate temperature of ~1 100 °C. The B/C ratio in the plasma was adjusted from 4 to 32 ppm. During deposition, the total gases mass flow rate was kept constant at 500 sccm. The layers morphology has been observed by optical microscopy. The diamond layers show pits and non-epitaxial crystallites on their surfaces. The number of those defects varies a lot from one sample to another. Those defects can come from the quality of the samples surface before deposition and/or the cleaning process before deposition. Figure 5 shows the FTPS spectra of a boron-doped diamond layer obtained using a B/C ratio of 4 ppm. The spectrum exhibits a clear photoionisation threshold at 0.37 eV and a peak at 0.347 eV. The photocurrent signal shows two series of equidistant minima starting at 0.30 and 0.35 eV with a period of ~165 meV. All these results are a clear signature of boron incorporation in the diamond layer.[8] The resistivity of the diamond layer decreases from 14 to 0.8 $\Omega \cdot$cm as the TMB concentration increases.

Electrical characterisation of TiN contacts on boron-doped diamond layer were made using circular transmission line model measurements. The circular contacts were obtained by lift-off. Prior to TiN deposition, the surface of the doped diamond layers were oxidised in hot H_2SO_4 and KNO_3 solution to remove non-diamond carbon. Figure 6 shows the I–V curves of a boron-doped diamond layer (18 ppm) with as deposited and annealed (at 450 and 750 °C) TiN contacts. As deposited and 450 °C annealed contacts are highly resistive, while contacts annealed at 750 °C show ohmic contact behaviour. The specific contact resistance (ρ_c) could only be determined for the diamond layers grown with a B/C $\geq$ 26 ppm: $\rho_c \sim 10^{-2}\ \Omega \cdot \text{cm}^2$. This result is one order of magnitude higher than Ti/Pt/Au contacts.[9] This might be due to a low dopant concentration[9] or/and a different reactivity of TiN and Ti to form ohmic contact.

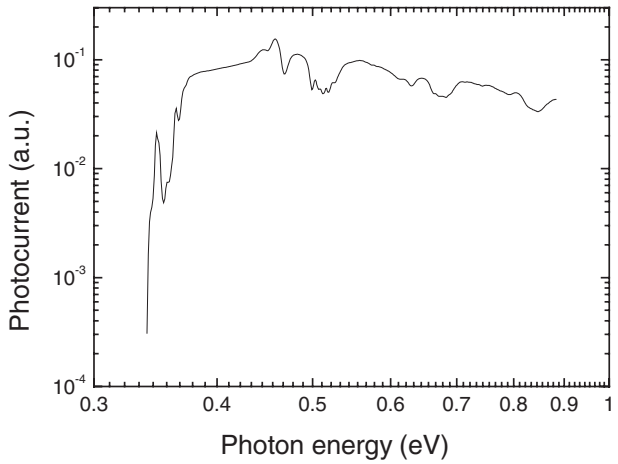

Figure 5. FTPS spectra of boron-doped diamond layer (B/C = 4 ppm).

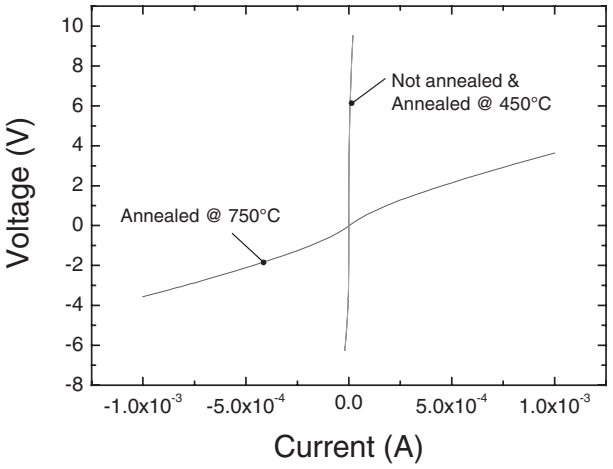

Figure 6. *I–V* characteristics of TiN contacts on boron-doped diamond layer (B/C = 18 ppm) after different annealing treatments.

Conclusion

TiN films deposited by reactive magnetron sputtering have been studied and characterised. Smooth and conductive TiN films with low stress were obtained in optimal deposition conditions. It has been observed that the properties of the TiN films are strongly dependent on the nitrogen concentration and the total pressure. TiN contacts were deposited using photolithography and lift-off techniques onto boron-doped diamond obtained by PECVD. Experimental results show that ohmic contacts can be formed after annealing at temperatures $\geq$750 °C. The first results show that TiN conctacts can be formed on boron-doped diamond and they can be used for electronic applications in harsh environments or in biological environments on a p-type diamond semiconductor.

Acknowledgements: This work was supported by the *IWT-SBO*-project no. 030219 'CVD Diamond, a novel multifunctional material for high temperature electronics, high power/high frequency electronics and bioelectronics' and the EU FP6 Marie Curie RTN "DRIVE", MRTN-CT-2004-512224. K.H. is a Postdoctoral Fellow of the Research Foundation – Flanders (FWO-Vlaanderen).

Received: September 19, 2006; Revised: November 8, 2006; Accepted: November 23, 2006; DOI: 10.1002/ppap.200730506

Keywords: films; titanium nitride; characterization; sputtering; X-ray

[1] C. A. Dimitriadis, Th. Karakostas, S. Logothetidis, G. Kamarinos, J. Brini, G. Nouet, *Solid-State Electron.* **1999**, *43,* 1969.
[2] B. Pécz, *Appl. Surf. Sci.* **2001**, *184,* 287.
[3] M. Vanecek, A. Poruba, *Appl. Phys. Lett.* **2002**, *80,* 719.
[4] G. G. Stoney, *Proc. R. Soc.* **1909**, *A82,* 172.
[5] Koji Kobasi, "*Diamond Films – Chemical Vapor Deposition for Oriented and Heteroepitaxial Growth*", Elsevier, Amsterdam 2005,p. 17.
[6] G. K. Reeves, *Solid-State Electron.* **1980**, *23,* 487.
[7] A. Tarniowy, R. Mania, M. Rekas, *Thin solid Films* **1997**, *311,* 93.
[8] R. Kravets, Ph.D. Thesis, Czech Technical University, Prague, 2005.
[9] Y. G. Chen, M. Ogura, S. Yamasaki, H. Okushi, *Diamond Relat. Mater.* **2004**, *13,* 2121.