Comparative study of electrical properties of nano to polycrystalline diamond films

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Abstract. Low-resistance ohmic or Schottky contacts between diamond and metal is primary goal of electronic devices and microsystems based on diamond. The contact resistance depends not only on the choice of metals but also on annealing, layer thickness and other parameters. Combination of titanium, platinum and gold (with co-deposited gold on top to prevent oxidation) is most widely used and yields to good conductivity after being annealed. Diamond films were grown by Microwave Plasma (MP) and Hot Filament Chemical Vapor Deposition (HF CVD) on Si substrates. The dependence of electrical properties on the film morphology was studied. The surface morphology of grown layers was analyzed by scanning electron microscopy (SEM). The different crystallographic character of diamond layers, i.e. either polycrystalline or nanocrystalline, was achieved by using different deposition conditions. Lower-quality diamond films were less sensitive to variation in the operating conditions. The film break-down voltage and other electrical parameters strongly depend on the morphological character, the grain size and defects in layers.

1. Introduction
Options and advantages of diamond layers used in electronics are well known. Parameters better by order of magnitude could be achieved when diamond is used as a semiconductor instead of conventional ones like Si, GaAs, GaN, etc. - table 1 [1, 2]. Unfortunately, not all difficulties connected with technology of diamond layer implementation are mastered to their perfection. The main problem is the reproducibility of diamond layer parameters (p or n conductivity and compatibility with Si
technology – high temperature processes during diamond growth). Next important task is to provide suitable contacts to diamond layers (ohmic, rectifying) and their good adhesion.

Ohmic contacts can be produced by different technology – by ion implantation, by sputtering, by CVD or by combination of these methods in connection with annealing [3]. At present refractory metals like Ti, Ta, Ni, Mo are used. They could form carbides [4]. The carbide interlayer is reducing the resistivity between metal and diamond and is also increasing the contact adhesion. As a typical example the 100 – 150 nm thick Ti layer covered with Au layer of 150 nm thickness can be considered. Very interesting combination is the Ti/Pt/Au structure (100 nm/40 nm/100 nm). The role of individual layers is following: Ti is forming carbide with diamond, Au is preventing oxidation and Pt is stopping diffusion between Au and Ti layers [5].

In this contribution we investigate the influence of the diamond morphology on the final electrical properties. The proper processing of metal contact is pointed out.

| Property               | Diamond | Si   | GaAs |
|------------------------|---------|------|------|
| Barrier height [eV]    | 5.45    | 1.124| 1.43 |
| Permittivity           | 5.5     | 11.7 | 11.7 |
| Electron mobility [cm²/Vs]| 1900   | 1350 | 8800 |
| Hole mobility [cm²/Vs] | 1600    | 480  | 400  |
| Resistance [Ωcm]       | 10⁶     | 10⁷  | 10⁷  |
| Break down voltage [V/cm] | 1 x 10⁷ | 3 x 10³ | 3.5 x 10³ |
| Max. working temperature [°C] | 1000  | 225  | 470  |

2. Experiment

In this study we compare two types of diamond layers, nanocrystalline and polycrystalline, grown by two techniques. Nanocrystalline diamond films were grown on p type Si(100) substrates (15 mm in diameter) by microwave plasma enhanced CVD in the ellipsoidal cavity reactor [6]. Prior to deposition process, the substrates were mechanically seeded in ultrasonic bath using a 5 nm diamond powder for 40 minutes. The growth step was performed at constant methane concentration (1 % CH₄ in H₂) and at the total gas pressure of 30 mbar. The total microwave power was 900 W and substrate temperature was 860 °C, measured by the two-color pyrometer working at the wavelengths of 1.35 and 1.55 μm (CHINO type). The layer thicknesses after 2 hour and 3 hour growth were 497 nm (Sample A) and 520 nm (Sample B), respectively. Before electrical contact formation, the diamond layers were cleaned for 1 hour in solution of H₂SO₄ + KNO₃ with 10:1 ratio at temperature of 200°C. Ohmic contacts were formed by standard lithographic process by lift-off technique using the combination of (Sample B)-Ti/Pt/Au (with thicknesses of 100 nm/50 nm – a diode structure) and (Sample A) NCD070417-Ti/Au (100 nm/100 nm with 300x300 μm²) materials deposited by rf reactive sputtering.

Polycrystalline diamond was produced in double bias enhanced HF CVD reactor described previously [7]. The used gas phase was a mixture of 2 % CH₄ in H₂ with Ar, the total pressure in reactor was 3 000 Pa and flow rates were 6:300:50 sccm. Gasses were activated by 5 pieces of 0.7 mm thick and 120 mm long tungsten filaments heated to 2 100 °C ± 50 °C. The substrate temperature was maintained at 550 °C. The Ti ohmic contact (with thickness of 100 nm and diameter of 500 μm) was sputtered by a glow discharge.

3. Results and discussion

In Fig. 1 a-c characteristic SEM images of diamond thin films grown by MWP CVD and HF CVD are shown. In Fig. 1a) the not fully closed layer was deposited and microcrystalline structure (with individual grains of 500 – 1 μm) exhibit film non-homogeneity which can be caused by either low nucleation density or by failure during deposition or by technological process parameter adjustment. However, Sample B (Fig. 1 b)) exhibits the nanocrystalline character with grain sizes below 100 nm.
and in this case, the whole substrate surface is homogeneously covered. Finally, Fig. 1 c) reveals a standard surface of microcrystalline diamond layer with grain sizes larger than 500 nm, growth by HF CVD technology.

Fig. 2) – 4) compare electrical characteristics for deposited diamond layers with different morphological structures (micro to nanocrystalline) and co deposition process such as annealing in Ar atmosphere.

From I-V break down characteristics we can see a pronounced difference between Sample B (Fig. 2) and Sample A (Fig. 3). First, based on measured I-V characteristics we can conclude that the formed contacts on microcrystalline diamond layer exhibit rectifying junction character, which is in contradiction to our assumption of ohmic contact formation. We assume the presence of hydrogen doped interlayer between contacts and diamond layer, which was created during diamond growth final stage [8].

Repeated break down measurement on Sample A shows a constant I-V characteristic without observable structural damage. The break down here occurs due to „holes“ in the diamond structure. In other words it is not a break down in reality, but it is just a bridging between contact and SiC/SiO₂ interlayer on silicon substrate. The average break down intensity was about 1.5 MV/cm (at 25 to 30 V). For Sample B, no break down voltage was measurable due to the limitations of the measuring set up. Based on the mathematical approximation we estimate the break down voltage to be approx. 2.2 MV/cm. For Sample 3 produced by HF CVD technology, we investigated the influence of annealing on the I-V characteristics. The contacts were either as deposited or annealed for 2 min in Ar atmosphere at 420 ºC. Due to that we have achieved a current increase flowing through the structure at unchanged voltages. It is assumed that this change was induced by TiC interlayer formation which resulted in decreasing of the contact resistance.
4. Conclusion
Study of I –V characteristics of the diamond films reveals different behavior, following the different morphological characteristics of the diamond films. The extension of this study to different sets of films, both MPCVD and HFCVD, and to different properties, like film surface roughness, diamond grain size and secondary nucleation which improve the nanodiamond layers growth, may provide useful information on layer quality. In particular, a study of the electrical measurements is simple, fast and non-destructive technique to evaluate the “basic” film properties.

Acknowledgement
The authors would like to thank J. Kováč and L. Harmatha for fruitful discussions and Mr. J. Král for technical assistance. This work was financially supported by grant of Science and Technology Assistance Agency no. APVT-20-034404 and Scientific Grant Agency of the Ministry of Education of Slovak Republic and the Slovak Academy of Sciences No. VEGA-1/2061/05, and AV 4/0124/06.

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