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Investigation of nano structures on ta-C films made by gallium FIB lithography☆

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ABSTRACT

Focussed ion beam (FIB) writing is used as a direct lithography process on tetrahedral amorphous carbon (ta-C) layers with high sp^3 content. Ion induced conversion of sp^3 to sp^2 bonded carbon atoms by means of 30 keV Ga^+ irradiation takes place and conducting sp^2 rich sites were formed on the nano scale. Investigations of the conductivity of graphitic layers embedded in thin ta-C films were done concerning the influence of Ga^+ fluence and substrate temperature. Van-der-Pauw (VDP) structures were produced by Ga^+-FIB lithography partly in combination with optical lithography. Sheet resistance decreases with increasing Ga^+ fluence and the lowest R_S was achieved with 290 Ω sq^{-1} at 1.6×10^{17} cm^{-2} ion fluence. Conductivity of sp^2 structures could be further improved by rapid thermal annealing (RTA) without degradation of the ta-C insulation. Graphitic nano wires (NWs) were fabricated by FIB writing which dimensions and conductivity were characterised. Width and height of the NWs increase with increasing Ga^+ fluence in a width range of 50 to 150 nm and height range of 3 to 23 nm.

1. Introduction

The modification of ta-C films by ion bombardment has been studied in several works [1–5]; promising among them is the ion induced graphitisation. Vavilov et al. have shown that damage in pure diamond caused by ion bombardment and subsequent thermal treatment leads to a graphite phase in the irradiated regions [6]. In case of sp^3 rich ta-C films ion implantation causes an increase of the sp^2 bonded carbon fraction [7]. Here, we present investigations of conducting sp^2 structures embedded in thin ta-C layers fabricated by gallium FIB (Ga^+-FIB) lithography. FIB technique is suitable for material modifications such as milling, doping and film deposition on the micro and nano scale [3,4,8]. Ga^+-FIB lithography on thin ta-C films is appropriate to produce conductive nano structures in a high resistive matrix which makes the use of photo resist and film deposition dispensable. The conductivity of graphitised regions in ta-C is investigated with respect to the Ga^+ fluence and further rapid thermal annealing. Sp^2 rich NWs are produced with low ion current and the wire dimensions are characterised by scanning electron microscope (SEM) imaging and atomic force microscopy (AFM). All measurements of conductivity are performed at 4-terminal VDP and 2-terminal resistor structures converted by Ga^+-FIB into the ta-C. A combination of Ga^+-FIB and optical lithography is demonstrated for the temperature dependent conductance measurement by connecting sp^2 structures with Au contact pads produced by lift-off technique.

2. Experiment

The material of interest was hydrogen free ta-C deposited by filtered vacuum arc deposition on a 200 nm SiO_2 film grown by thermal oxidation of a single crystalline p-type silicon substrate. The new approach in this work compared to previous investigations [5] is the introduction of a SiO_2 interface layer to avoid leakage current through the bulk Si during electrical measurements. The ta-C layer thickness of 113 nm and a film density of 2.71 g cm^{-3} were determined by X-ray diffraction. Using the correlation between ta-C film density and sp^3/sp^2 ratio proposed by Atchison et al. [9] the sp^3 content was estimated to 56%.

Irradiations were done using a Zeiss NVision 40 CrossBeam® system consisting of a FIB column with a gallium liquid metal ion source oriented 54° to a Gemini electron beam column. The FIB lithography was controlled with a Raith ELPHY Plus scan processor for designing the layouts of the electrical test structures (GDSII file format) and the transfer into the ta-C layer. All irradiations were done with 30 keV Ga^+ ions at normal incidence. Fig. 1 shows examples in design and SEM images from real structures.

The test structures contain contact pads (A, B, C and D) 30×30 μm^2 in size, all irradiated with a Ga^+ fluence of 5×10^{16} cm^{-2} at 700 pA beam current yielding a low contact resistance. For the R_S measurements VDP structures (Fig. 1c) were used whereas the centred crosses between the contact pads were made by varying the Ga^+ fluence. A conductance measurement at low temperatures in a cryostate was done at the cross structure shown in Fig. 1b. The larger distance of the contact pads allows the subsequent deposition of Au bond pads and a connexion of the test chip to a sensing head by ultrasonic Au-bonding. Resistance (R_{NW}) measurements of NWs were performed using 2-

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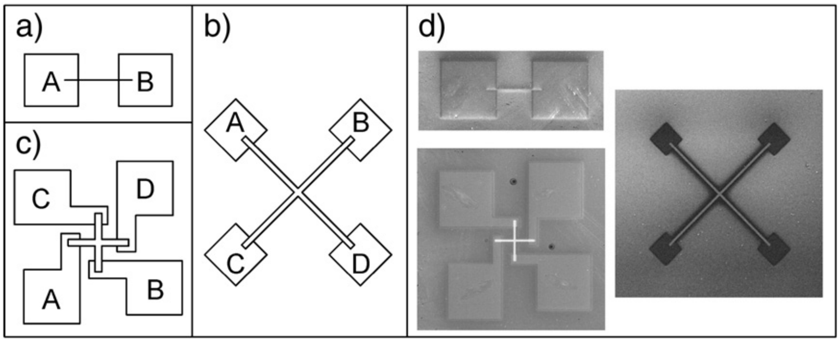

Fig. 1. Test structure designs for electrical measurements: a) 2-terminal resistor, b) cross for optical lithography, c) 4-terminal VDP [10], and d) SEM images after FIB processing.

terminal structures (Fig. 1a) taking into account that the resistance of probe tip and contact resistance R_{cont} can be neglected for wires where $R_{\mathrm{NW}} \gg R_{\mathrm{cont}}$ due to the small wire dimensions. The NWs were fabricated with 1 pA FIB current gaining small feature sizes. The width of the NWs was determined by SEM imaging and their height by AFM with respect to the Ga^+ fluence.

The measurements of R_S and R_{NW} were done for the as-implanted as well as the annealed stage. For the electrical analysis a Süss Microtech probe station PA200 combined with a Keithley 4200-SCS (Semiconductor Characterization System) was used.

3. Results and discussions

3.1. Resistance measurements

The formation of sp^2 bonded carbon by ion irradiation leads to a resistance decrease depending on the Ga^+ fluence. The centred cross of the VDP structures is irradiated with a Ga^+ fluence ranging from 5×10^{14} to $1.6 \times 10^{17}\ \mathrm{cm}^{-2}$. The sheet resistance R_S in dependence on the Ga^+ fluence for the as-implanted and annealed structures is shown in Fig. 2.

The graph can be divided into 3 sections. In section I R_S decreases with increasing fluence conform to a power function. Section II shows an exponential sheet resistance decrease at fluences above $1 \times 10^{16}\ \mathrm{cm}^{-2}$. The conductivity increases up to a Ga^+ fluence of $1 \times 10^{17}\ \mathrm{cm}^{-2}$ attributed to the sp^3 to sp^2 conversion and sp^2 clustering which attains saturation at higher fluences where the conductivity reaches a maximum. Furthermore it has to be taken into account that the influence of the implanted Ga^+ itself could lead to an increasing conductivity as well. But due to the fact that Ga cannot behave as dopant in the amorphous ta-C matrix it can be assumed that only a small conductivity increase caused by the metallic properties of Ga is efficient at very high fluences. Also in this range sputtering of the sp^2 structures occurs starting at about $1.5 \times 10^{17}\ \mathrm{cm}^{-2}$ (proven by AFM measurements). This further increase of the Ga^+ fluence does not significantly affect the layer resistivity (section III). The minimum of R_S is achieved at $1.6 \times 10^{17}\ \mathrm{cm}^{-2}$ for the as-implanted structures with 260 $\Omega\ \mathrm{sq}^{-1}$. This fluence corresponds to an amount of incorporated Ga ranging from ~20 at.% at the surface to ~40 at.% at the peak of the implantation profile [11]. Assuming an sp^2 layer thickness of approximately 40 nm according to SRIM calculations [12] a resistivity of about 1.16 mΩ cm was achieved. That is one order of magnitude lower than the value of Stanishevsky who reported a best resistivity of 20 mΩ cm at a fluence of $1.9 \times 10^{17}\ \mathrm{cm}^{-2}$ for 50 keV Ga^+ irradiation of ta-C [3]. McCulloch et al. achieved a resistivity of approximately 0.1 mΩ cm using 200 keV Xe^+ ions at a comparable lower fluence of $1 \times 10^{15}\ \mathrm{cm}^{-2}$ [13]. This indicates the dependence of the optimal achievable conductivity of ion implanted ta-C on the ion species and energy because these parameters are mainly affecting the damage profile. In contrast to ion irradiation a much poorer improvement of the resistivity down to $9.8 \times 10^3\ \Omega$ cm was achieved by Siraj et al. using 4 MeV electron beam irradiation [14].

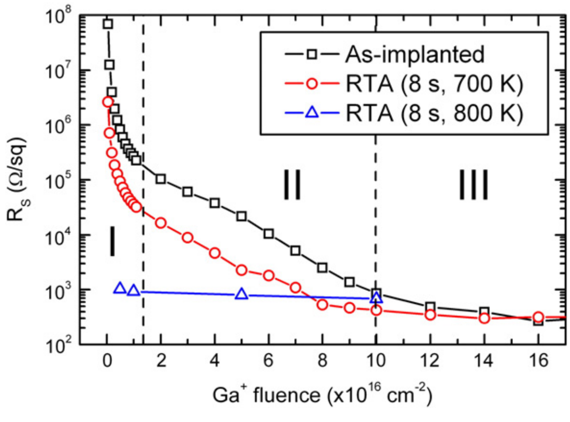

Fig. 2. Dependence of the sheet resistance R_S on the Ga^+ fluence for as-implanted and annealed structures.

The sp^3 fraction of ion implanted ta-C corresponding to various fluences was not determined so far. Recent Raman spectra obtained from irradiated areas showing a decrease of the G peak intensity as well as a shift of its position to lower wave numbers with increasing Ga^+ fluence revealed structural changes in the ta-C comparable to data from other work [4]. There are two main points inhibiting a safe sp^3 determination from visible Raman spectra in our case: this method was reported to be more sensitive to sp^2 clustering than to conversion [15] and the Raman signal of our samples is a mixed signal from the ion implanted layer as well as from the virgin part of the ta-C layer that remains unaffected due to the finite ion range in the film.

After a following RTA at 700 K for 8 s R_S drops down of about one order of magnitude shown in section I and II whilst the qualitative fluence dependence remains unaffected (Fig. 2, circles). Investigations of Kalish et al. have shown that the stability of ta-C films under thermal treatment depends on the sp^3 content and is stable up to 870–970 K for 60% sp^3 content [16]. To evaluate possible changes in the conductivity of the unirradiated ta-C a reference measurement (R_{ref}) was done between two isolated sp^2 contact pads. A reference value of $R_{\mathrm{ref}} = 1.6 \times 10^{11}\ \Omega$ was found for both the as-implanted structure and after RTA at 700 K as well, meaning the electrical insulation of the surrounding ta-C matrix remains stable. Taken into account that the sp^2 fraction in the structure is higher than in the unirradiated ta-C accompanied by a lower thermal stability the improvement of R_S after RTA can be explained by clustering of sp^2 sites and thermal induced graphitisation [16]. The RTA curve at 700 K converges to the as-implanted data in section III. From that it can be concluded that neither the maximum sp^2 fraction can be exceeded nor structural properties of the sp^2 layer which are responsible for the conductivity can be improved by thermal treatment beyond the lowest value for the as-implanted structure. The RTA-curve at 800 K, triangles in Fig. 2, shows a major change of R_S. In section I