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ELECTRONIC PROPERTIES OF GRAPHITE-LIKE ION TRACKS IN INSULATING TETRAHEDRAL AMORPHOUS CARBON

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Abstract. We investigated the formation of quasi one-dimensional conducting filaments in tetrahedral amorphous carbon (ta-C) films created by swift heavy ion irradiation. Various ta-C films with thicknesses of about 100 nm were grown using mass-separated ion beam deposition on highly conducting Si and Ni substrates. After deposition, the films were irradiated with 1GeV ^{238}U ions at fluences between 10^9 and 10^{11} ions/cm^2. Due to their high electronic energy loss of about 40 keV/nm, the swift heavy ions graphitize the predominantly (70%) sp^3-bound tertahedral amorphous carbon film (ta-C) along their trajectories, yielding conducting nanowires embedded in an insulating matrix. Using atomic force microscopy (AFM) with conducting cantilevers and an applied bias voltage the presence of conducting tracks was confirmed and their conductivities were determined to be several orders of magnitude higher than that of the host matrix. Temperature-dependent electrical measurements were performed on the irradiated samples at 300K - 15K with fields of up to 5V/µm.

1. INTRODUCTION

The swift heavy ion irradiation of highly resistive diamond like carbon films with a high sp^3-bond fraction, in the following referred to as ta-C (tetrahedral amorphous carbon), results in graphite-like conductive ion tracks with a diameter of about 10 nm [1], a review of ta-C is given in [2]. Due to the high electronic stopping power of the ions, the electronic system of the sample is excitated. The interaction between electrons and phonons leads to a local heating of the material, and a transformation from mainly sp^3-bond to sp^2-bond carbon occurs. Each impinging ion induces a graphite-like ion track, all of them have similar diameters. Track formation occurs when a certain threshold value, depending on the ion species, is exceeded [3]. In this work, the ta-C films were irradiated with uranium-ions at 1 GeV. The extremely high electronic energy loss of about 40 keV/nm remains constant over the whole film thickness, the resulting ion tracks are continuous, as the material is transformed into a sp^2-bond structure along the whole film thickness. With the procedure of swift heavy ion irradiation, a reproducible ensemble of comparable nanowires is generated. Due to their potentially high aspect ratio, ten nanometers in diameter with length of up to 1 mm depending on the film thickness, studies of field emission properties have been done [4]. This work focuses on the conduction mechanism of the tracks. The conduction process is expected to differ from that of bulk sp^2-bonded amorphous

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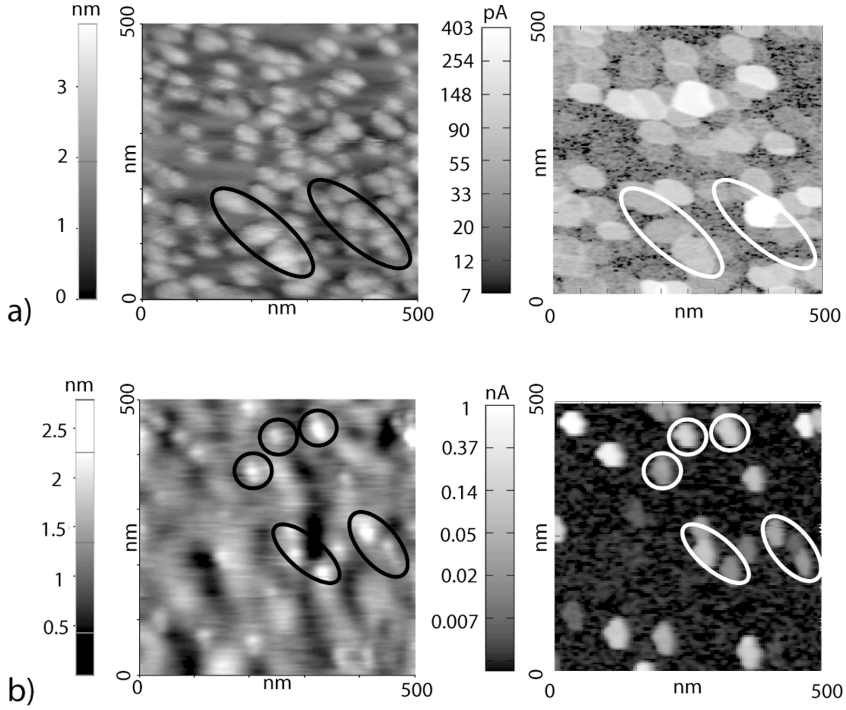

Fig. 1. AFM-images of irradiated ta-C samples. (a) Ta-C on silicon was irradiated with 10^{11} ions/cm^2. The current image (right) with applied voltage of 1 V was recorded simultaneously with the topography image (left). (b) The irradiation fluence of ta-C on nickel was 10^{10} ions/cm^2. The positions of conducting spots in the current image (right) with 0.15 V corresponds to the hillocks in the topography image (left), few spots are marked as a guide to the eye. The number of hillocks per area agrees with the irradiation fluence. Note the logarithmic colour scale at the current images.

carbon due to the small track diameter, for a detailed study of amorphous carbon films see for example [5]. The conductivity of the ion tracks has been examined at room temperature as a function of hydrogen-content [1] and sp^3-content of the DLC-films [6]. Here, we present an investigation of the temperature dependence of the conduction mechanism.

2. EXPERIMENTAL DETAILS

The ta-C-films were deposited at room temperature using a mass-separated ion beam consisting of $^{12}C^+$. Details of the method are described elsewhere [7]. The energy of the deposited carbon atoms was 100 eV to obtain the maximum sp^3-bond fraction of 80% [8]. Highly doped silicon wafers with (111)-orientation and nickel single crystals with (100)-orientation were used as substrates. The native oxide layer of the silicon was removed and the nickel substrates were cleaned by sputtering with Ar-ions.

The irradiation of the samples was done using 1 GeV U-ions at the UNILAC at GSI (Gesellschaft für Schwerionenforschung in Darmstadt). An Al-degrader foil (0.01269 g/cm^2) was used to reach equlibrium charge state and maximun energy loss of 40 keV/nm at 1 GeV, and track formation commences at the film surface. The irradiation fluences were varied between 10^9 and 10^{11} ions/cm^2.

The electrical measurements using a Keithley 237 high voltage source measure unit (SMU) were two-point measurements with one contact on the ta-C films and the substrate as back contact. To establish a contact on the ta-C surface, gold was thermally evapourated onto the film, forming circular contact pads with diameters of 0.5 to 1 mm. The samples were mounted onto a cryostat for cooling; the measurement was performed under high vacuum conditions and in a temperature range

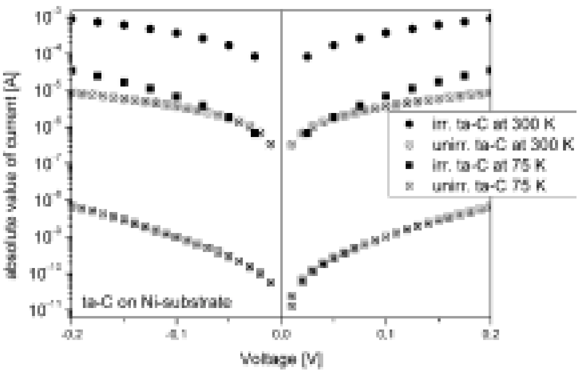

Fig. 2. Comparison of the current through an irradiated (10^{10} ions/cm²) and unirradiated ta-C sample on nickel. The difference is two orders of magnitudes at 300K and four orders of magnitude at 75K. The contacs have similar diameters.

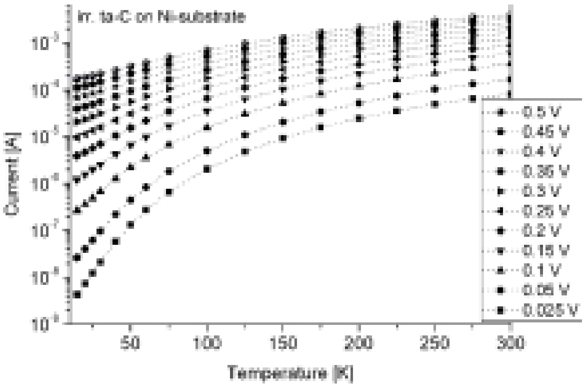

Fig. 3. *I-T*-characteristics of irradiated (10^{10} ions/cm^2) ta-C on nickel. At 0.5 V less temperature dependence is observed at lower temperatures compared to 0.025 V. The dotted line is to guide the eye.

of 300K down to 15K. The typical working pressure was $6 \cdot 10^{-4}$ Pa. The AFM-images were recorded with an XE-100 atomic force microscope by PSIA at Hochschule Harz in Wernigerode. All images were recorded in contact mode. AFM-cantilevers covered with a conductive Pt/Ir-film were used to obtain current images.

3. RESULTS AND DISCUSSION

The presence of conducting ion tracks was confirmed by means of AFM-measurements. Fig. 1 shows a set of AFM-images of the examined samples. Fig. 1a, left side, is a topography image of irradiated ta-C on silicon. The irradiation fluence was 10^{11} ions/cm². At the surface of the sample, material is transported outward and the density is reduced inside the tracks [1] because of the transformation from sp^3-bound to sp^2-bound structure. This material forms a small hillock of a height of about 3 nm. The right side of Fig. 1a is a current image, recorded simultaneously with the topography image by applying a voltage of 1 V between the sample and the cantilever. The positions of the more conducting spots correspond to the hillocks, some spots are marked as a guide to the eye. In Fig. 1b the topography image of irradiated ta-C deposited on Ni can bee seen on the left. The irradiation fluence is 10^{10} ions/cm². The right side of Fig. 1b shows the current image taken after applying a voltage of 0.15 V. There is also a visible link between conducting spots and hillocks. The number of ion tracks per area corresponds to the irradiation fluence. The ion tracks in ta-C on Ni seem to be more conductive than those in ta-C on Si, because a lower voltage results into a higher current. This can be confirmed by electrical measurements on macroscopic contacts.

Some results of these measurements are shown in Fig. 2. The ta-C was deposited on nickel and irradiated with 10^{10} ions/cm². The current flowing through this sample is compared with the one flowing through an unirradiated sample of the same thickness and the same diameter of contacts. Although only 0.78% of the surface are irradiated, assuming the ion tracks have a diameter of 10 nanometer [1], the current is two orders of magnitude larger than the one through the unirradiated sample at 300K. The difference becomes larger at lower temperatures, for example at 75K. Considering the contact area, the conductivity of ion tracks is about five orders of magnitude larger than the conductivity of unirradiated ta-C. This conductivity contrast visible in Fig. 2 is in good agreement with irradiated and unirradiated ta-C on silicon in Ref [6]. In the following discussion we assume that the current through the unirradiated surrounding material in irradiated samples is negligible.

To analyse the current mechanism, temperature-current characteristics have been examined. Fig. 3 shows the temperature-dependent current

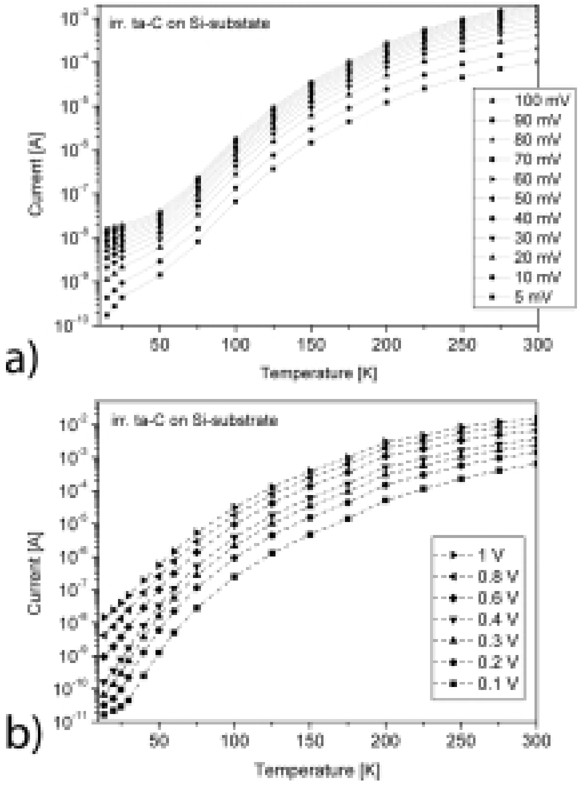

Fig. 4. *I*-*T*-characteristics of irradiated (10^{11} ions/cm²) ta-C on silicon. At low voltages, a kink appears at about 50K (a). This kink dissapears at higher voltages (b). Dotted lines in a) and b) are to guide the eye.

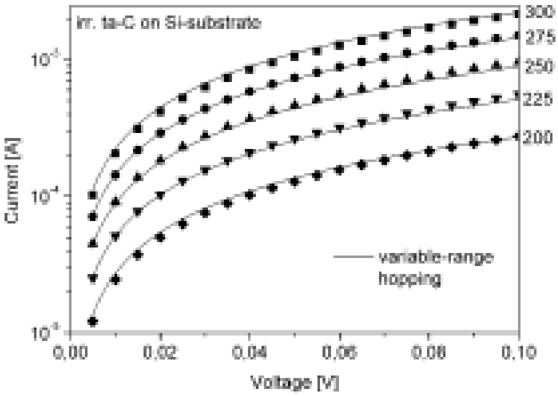

Fig. 5. *I*-*U*-characteristics of irradiated (10^{11} ions/cm²) ta-C on silicon with a fit after variable-range hopping with moderate field (solid lines). The measured data is described.

with constant voltage for irradiated ta-C on nickel. At applied voltages of 0.5 V, which for a film thickness of about 80 nm corresponds to an applied field of 6 V/µm, the temperature dependence of the current at lower temperatures decreases with increasing voltage. The analogous diagram for irradiated ta-C on silicon is shown in Fig. 4. The most conspicuous difference is a kink in Fig. 4a at lower temperatures and low voltages. A measurement at higher voltages shows that the kink disappears (Fig. 4b). The sample on the silicon substrate becomes less conductive at higher temperatures than the sample on the nickel substate, which is indicated by the slope of the *I*-*T*-characteristics in the range of 50K to 150K. This may be a hint that the current transport mechanism is affected by the substrate or the interface between substrate and ta-C.

In Refs. [5,9], hopping conduction such as variable-range hopping [10] is said to be the main transport mechanism at lower electrical fields, resulting in linear current voltage characteristics. The conductivity is described as follows: $\sigma = q\nu_{Ph}N(E_F)R^2\exp(B/T^{1/4})$ [10]. The expression for B is $B = B_0(\alpha^3/k_BN(E_F))^{1/4}$. Here, B_0 is a constant with the value $2(3/2\pi)^{1/4}$=1.66; α is the inverse radius of the defect states near the Fermi level; q is the carrier charge, ν_{Ph} the phonon frequency, and $N(E_F)$ the density of the defect states at the Fermi level. The hopping distance R is $R = 3^{5/4}/4(2\pi\alpha N(E_F)k_BT)^{1/4}$. In Fig. 5, current-voltage characteristics have been fitted with this hopping model. Using a density of the defect states of $1\cdot10^{19}$ /eV/cm² or $1\cdot10^{22}$ /eV/cm² [5], the radius of the defect states is calculated to be 3 nm or 0.3 nm, respectively. These values are in the order of magnitude of Ref. [5], in which hopping conduction with small sp^2-clusters is proposed. Computer simulations show that irradiation leads to formation of a disturbed sp^2-network [11] with possibly isolated sp^2 sites, the presence of small sp^2-clusters inside the tracks can be assumed. No experiments have been performed yet to analyse the contact resistance, thus the coefficient to the exponential function could not be taken into account, although the parameters in the fit are not independent.

As the measured current-voltage characterisics become non-linear at lower temperatures, this model should be extended. As an approach we apply the model of variable-range hopping with moderate field [12]. The conductivity has to be

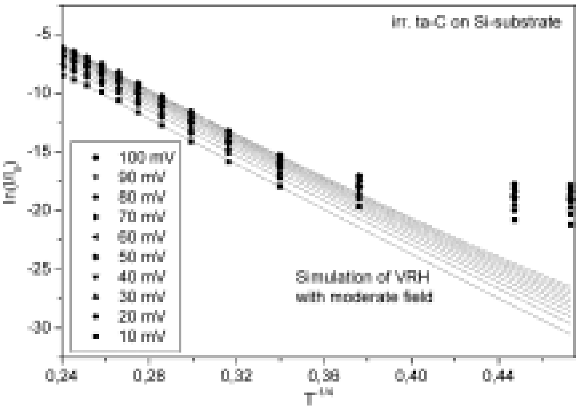

Fig. 6. Ln(I/I_0)-$T^{-1/4}$-characterisics of irradiated (10^{11} ions/cm^2) ta-C on silicon, I_0 equals 1 A. The solid lines are fitted from 300K to 75K after the variable-range hopping with moderate field model and extrapolated to 15K. The measured data is almost linearised as expected for variable-range hopping conduction at higher temperatures. No kink is predicted.

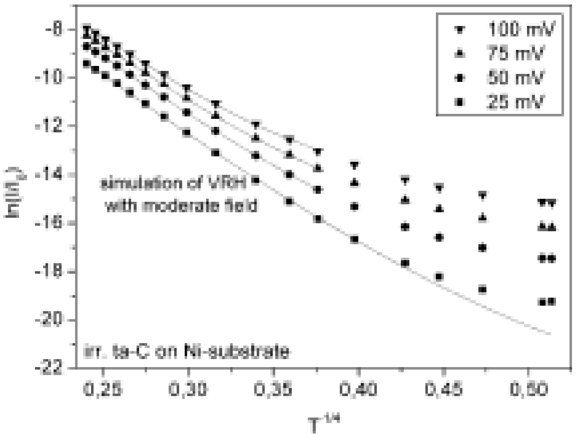

Fig. 7. Ln(I/I_0)-$T^{-1/4}$-characterisics of irradiated (10^{10} ions/cm^2) ta-C on nickel, I_0 equals 1 A. The solid lines are fitted from 300K to 50K after the variable-range hopping with moderate field model and extrapolated to 15K for 0.025 V (see Fig.7). The measured data also is linearised as expected for variable-range hopping conduction at higher temperatures. The range to 100 mV was chosen for reasons of comparability with Fig. 7. The fit was not extrapolated for higher voltages, due to lacking validity of the conduction model in this voltage range.

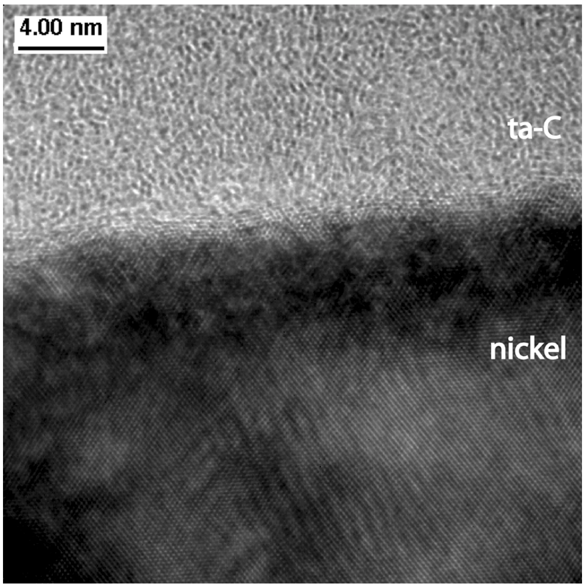

Fig. 8. TEM-image of ta-C on nickel. The crystal structure of the substrate is visible up to the interface.

multiplied by ($qE\gamma R/k_BT$). Here, E is the applied electrical field, γ a constant of value 0.17 and R the hopping distance. The limit of validity is given by $qE/2k_B\alpha T<1$ [12]. In Fig. 6, the model of variable-range hopping (VRH) with moderate field is fitted to the data of irradiated (10^{11} ions/cm^2) ta-C on silicon to a temperature range from 300K to 75K and extrapolated to the entire temperature range. The measured data is almost linearised by an ln(I/I_0)-$T^{-1/4}$-plot at higher temperatures, as expected for hopping conduction. The kink at lower temperatures is not described by the model.

As shown in Fig. 7, the process described above was also applied to irradiated (10^{10} ions/cm^2) ta-C on nickel to a temperature range of 300K to 50K. To compare the curves with those in Fig. 6, values up to 100 mV have been chosen. The fitting curves (solid lines) for 100 mV, 75 mV, and 50 mV have not been extrapolated to the whole temperature range because of lacking validity of the hopping model in this voltage range. This means, compared to ta-C on silicon, that either the radius of the defect states is larger or the density of the defect states is lower. Values for these quantities can be discussed after measurement of contact resistances.

One difference between these samples is the interface (substrate – ta-C). The interface of silicon and ta-C has been examined elsewhere [13,14]. TEM-images in Ref. [13] show a highly strained region at the surface of the substrate. SIMS investigations reveal a concentration gradient of carbon in the substrate with a reach of about 140 nm, forming a non-stoichiometric SiC-interlayer. This is also described in Ref. [14]. Both publications describe the formation of the SiC-interlayer with strain induced diffusion. A TEM image of the nickel – ta-C interface is shown in Fig. 8. The crystal structure of the substrate is visible up to the interface. An EDX linescan (not shown here) shows no measurable content of nickel inside the sample, an amorphous semiconductor-metal junction is expected. For the sample on silicon, a ta-C-SiC-Si junction is likely, the non-stoichiometric SiC forms an electrical barrier.

4. CONCLUSIONS

An ensemble of individual conducting ion tracks has been formed by irradiation of ta-C. The conductivity contrast of about four to five orders of magnitude is similar between unirradiated and irradiated ta-C on silicon and nickel substrates. The change in the slope of the current-temperature characteristics of irradiated ta-C on silicon and nickel indicates an influence of the substrate or interface on the conduction process. This influence may be due to the semiconducting silicon even if it is highly doped, or to the strained region. The SiC-layer at the interface might be an electrical barrier between the ion track and the substrate.

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