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Growth and Investigation of Graphen Films on Surface of 6H-SIC Substrates

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Abstract: Influence of High vacuum annealing on 6H-SiC(0001) wafers surfaces is studied. Annealing is carried out at the temperature range of 1300-1400°C and at residual pressure of ~10^{-6} Torr. Auger spectroscopy and RHEED data shows that the used annealing conditions did not lead to any surface reconstruction of the processed wafers. Atomic force microscopy reviles atomically flat surface terraces separated by steps of unit cell height (h=1.5nm). Than multigraphene films grown by sublimation on the surface of 6H-SiC (000-1) C face substrate. It is shown that a pregrowth annealing of the substrate in a quasi-closed growth cell improves the structural perfection of a multigraphene film. Ohmic contacts to the film were fabricated and the Hall effect was studied at low temperatures. It was found that a 2D holes gas exists in the films. A conclusion was made that the conductivity of the film is determined by defects existing within the graphene layer or at the interface between the graphene film and a SiC substrate.

Key words: Multigraphene · SiC sublimation · Hall effect · Weak localization

INTRODUCTION

Graphene (GR) is presently considered to be a real candidate for the microelectronics of the future [1-4]. Also of interest in this regard are films composed of several graphene layers (multigraphene) or ultrathin graphite films on various substrates, which may be more stable and easily obtainable than graphene itself.

One of ways to form GR is by thermal decomposition of the surface (thermal destruction) of single-crystal silicon carbide SiC in a vacuum or in the atmosphere of argon. The method is based on nonstoichiometric evaporation of silicon from the surface of single-crystal SiC under a high-temperature heating and a hexagonal lattice is form from residual carbon atoms on its surface [5]. The main problem of the thermal destruction method is the quality of the silicon carbide wafers it uses, because all surface defects and irregularities of a SiC crystal will be inherited by the graphene film. It is known that, upon a mechanical treatment of a crystal, nanoscratches with depths of 5 to 15 nm, produced by abrasive grains during polishing, are observed on its surface.

The pre-growth treatment is an important step in preparing the wafer to epitaxial growth. This is particularly an actual problem for silicon carbide, a material having high chemical and thermal stability, which hinders removal of the surface layer distorted by mechanical polishing by means of liquid etching methods. As a result of mechanical treatments the surface of the SiC wafers is saturated with various kinds of defects, which adversely affects the quality of the layers grown on them.

There exist several methods for treatment of SiC wafers to remove the distorted surface layer. In the most widely used technique, silicon carbide wafers are etched in the atmosphere of hydrogen at a temperature of 1400-1500°C [6]. However, this technique is inapplicable in a vacuum technology, because permanent use of gases in the vacuum chamber adversely affects the evacuation rate and residual pressure. As an alternative to the above method can serve annealing of SiC substrates in a vacuum in a quasi-closed growth cell, which can also remove the distorted surface layer without using any gases.

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In this study, we examined the effect of a high-vacuum annealing in pregrowth processing on the quality and transport properties of multigraphene layers.

RESULTS AND DISCUSSION

Pre-Growth Sic Substrate Treatment: We used semi-insulating 6H-SiC (0001) CREE wafers. Prior to experiments, a standard procedure of substrate cleaning with deionized water and organic solvents was performed. Wafers were annealed in a high-vacuum chamber at 1300-1400°C and a residual pressure of $\sim 10^{-6}$ Torr. The annealing time ranged from 5 to 30 minutes. To avoid graphitization of the SiC surface under high-temperature heating, the wafers were covered by graphite or tantalum cup. This precludes the surface of the wafers from sublimation and non desirable graphitization.

A surface stoichiometry change of the annealed samples was studied by Auger spectroscopy. Figure 1 shows an Auger spectrum of SiC substrate before (a) and after (b) annealing. It is obvious that these spectra have a similar character; there are no stoichiometry changes after high temperature annealing. Thus the Auger investigation shows, that the graphite (tantalum) cap allows avoiding a surface graphitization process by heating of SiC substrate.

Atomic force microscopy (AFM) studies were used to determinate a surface morphology changes by thermal annealing of SiC wafers. Surface morphology of SiC substrate after mechanical polishing is shown on the Figure 2a. Mechanical treatment leaves scratches all over the surface with breadth in the nanometer range. Such surface imperfections have dramatic effect on the quality of epilayer or grapheme films.

High vacuum annealing removes the scratches and forms atomically flat terraces separated by steps (Fig. 2b). The lateral distance between the steps (terrace width) is 300-600nm depending on unintentional miscut of the on-axis surface. Compared with the starting wafer, the root mean square (RMS) roughness of the surface is four times smaller for the annealed sample. On the Figure 3b is shown a profile of the annealed surface. The measured step heights were about 1.5 nm, i.e. close to the unit cell of 6H-SiC.

Fig. 3. (a) A typical AFM image of silicon carbide substrate (scan field 1x1 μm) after annealing in vacuum by 1300-1400°C, (b) surface profile (step height is 1.5 nm).

The surface of the samples annealed in a vacuum was also studied by means of reflection high-energy electron diffraction (RHEED). Figure 4 shows electron diffraction

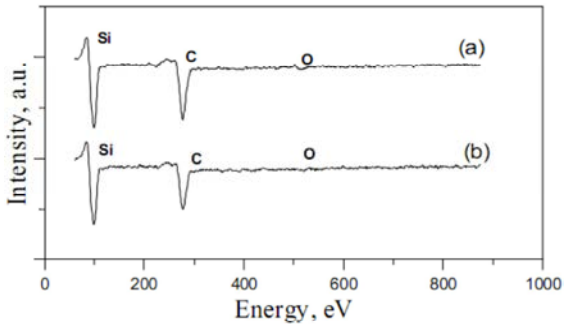

Fig. 1: Auger spectrum of SiC substrate before (a) and after (b) annealing

patterns of a sample before (Fig. 4a) and after the treatment (Fig. 4b). In both cases, the electron diffraction patterns shows vertical rod-like reflections and Kikuchi lines, which points to a high surface perfection of the samples under study. The position of the reflections indicates that annealing does not lead to a surface reconstruction of the single crystal, because no additional structural reflections appear in the diffraction pattern.

Graphen Growth and Characterization: Multigraphene was synthesized both on mechanically polished substrates and on those subjected to a pregrowth thermal treatment at 1300-1400 °C. To obtain multigraphene layers, samples were again annealed, now in a open growth cell in a high-vacuum chamber at temperatures of 1400-1500°C. The presence of a multigraphene film upon a high-vacuum annealing in an open growth cell was confirmed by Auger electron spectroscopy and Raman spectroscopy. In both cases (multigraphene film on the surface upon a mechanical polishing or pretreatment) only the peak of carbon was present in the Auger spectra (in details [7,8]). Thickness of obtained multigraphene films is about 3-5 moholayers. As was shown early, in case of growing on C-face, multigraphene films has approximately the same behavior as one monolayer film [9].

To perform electrical measurements with multigraphene films, we formed test structures with a Hall-bar configuration by photolithography and etching with an argon beam through a photoresist mask.The measurements were made on multigraphene films with dimensions of 37 x 10 to 114 x 10 μm. A double-layer Ti/Au composite serves as the metallization of the contact pads of the Hall-bar structures. A Ti sublayer with a thickness of 20 Å was deposited to improve the adhesion of the main metallic coating (Au) whose thickness was 300 nm.

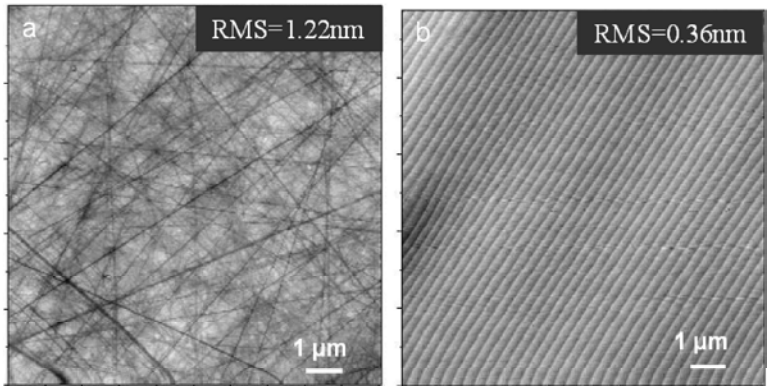

Fig. 2: A typical AFM image of a silicon carbide substrate (scan field 10x10 μm) (a) after mechanical polishing, (b) after annealing in vacuum by 1300-1400°C.

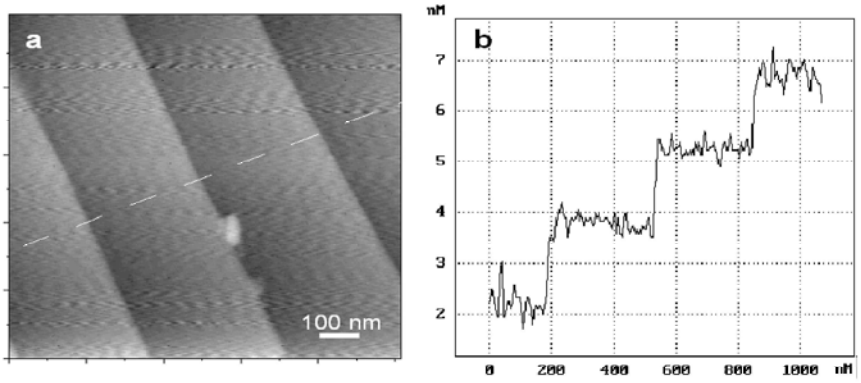

Fig. 3: (a) A typical AFM image of silicon carbide substrate (scan field 1x1 μm) after annealing in vacuum by 1300-1400°C, (b) surface profile (step height is 1.5 nm).

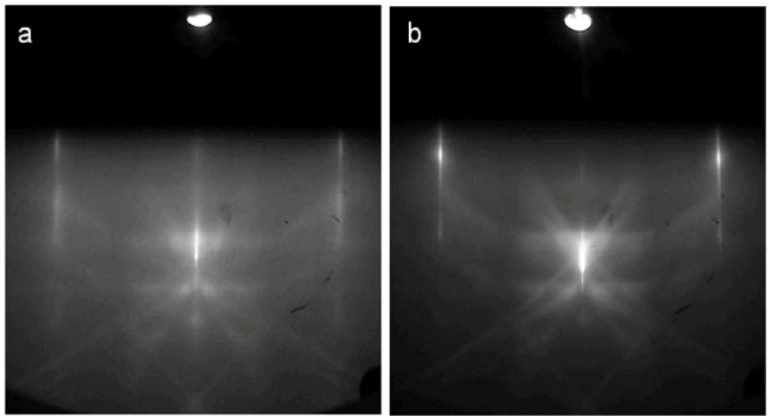

Fig. 4: (a) RHEED image of a silicon carbide substrate (b) RHEED image of a silicon carbide substrate after annealing in vacuum by 1300-1400°C

Current-voltage (I-V) characteristics and the Hall effect were measured in the temperature range 1.4-300 K. At room temperature the I-V characteristics of the contacts were linear and the resistance of the multigraphene film was 0.3-12 MΩ for different samples and increased in proportion to the strip length.

Figure 5 shows the temperature dependence of the resistance of a graphene film grown on a substrate not subjected to a preliminary annealing. The film shows a typically insulating behavior (resistance increases by seven orders of magnitude as the temperature is lowered from 100 to 1.4 K).

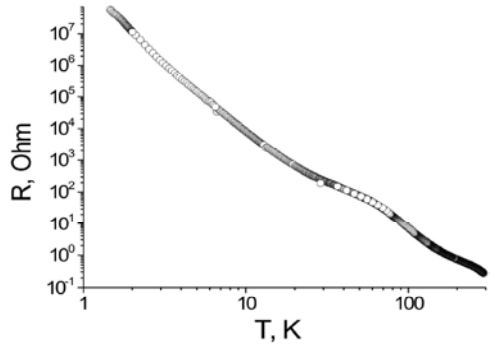

Fig. 5: Temperature dependence of the conductivity of the structures under study after mechanical treatment.

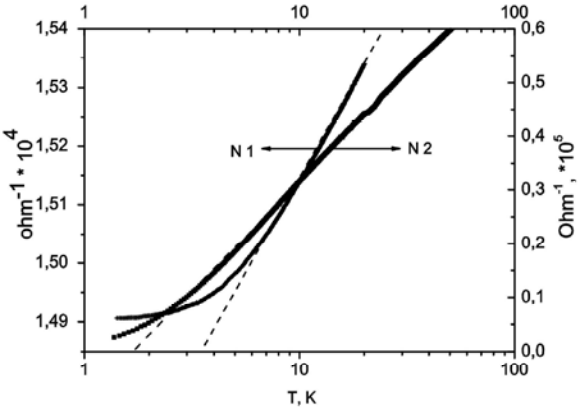

Fig. 6: Temperature dependence of the conductivity of the structures under study after annealing in a quasi-closed growth cell.

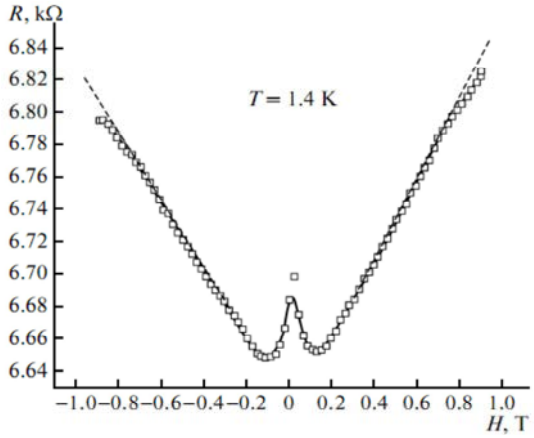

Fig. 7: Magnetoresistance of sample at a temperature of 1.4 K

Figure 6 shows the temperature dependence of the conductivity of two samples, *1* (GR-56) and *2* (GR-53), obtained upon pregrowth annealing. It can be seen that the conductivity weakly varies with temperature (by less than a factor of 5 on changing the temperature by two orders of magnitude). The low-temperature conductivity of sample *1* is an order of magnitude higher than that of sample *2*, which is presumably due to the morphology of the samples. At T < 40 K, the conductivity weakly depends on temperature and, as the temperature is lowered, decreases by a logarithmic law characteristic of 2D dirty metals (weak localization mode). According to the theory (see, e.g. [10]), the slope of the logarithmic dependence for 2D systems is a universal quantity given by $e^2/h \sim 4 \times 10^{-5}\Omega^{-1}$. For our samples, this slope is almost the same: $3 \times 10^{-6}\Omega^{-1}$ for sample *1* and $2 \times 10^{-6}\ \Omega^{-1}$ for sample *2*, which is an order of magnitude smaller than the universal value. However, the conductivity calculations disregarded that samples are rectangular, rather than square. Then the resistance per square should be reduced by a factor of 5 - 10. Accordingly, the slope of the temperature dependence should be raised (at a length of a sample 10 times its width, this slope ratio will be $2 \times 10^{-5}\Omega^{-1}$, which almost agrees with the theoretical estimate). In the low-temperature limit (1.4 K), the conductivity tends to a constant value for both samples. The observed leveling-off of the low-temperature conductivity may be due, on the one hand, to the finiteness of the size of the conducting sample (~10 μm), compared with the phase coherence length L_δ, which may become equal to the sample size at sufficiently low temperatures, with the logarithmic dependence disappearing. For multigraphene, values $L_\delta \sim 1$ - 10 μm at low T have been reported [11]. On the other hand, the mechanism leading to a low-temperature leveling-off of the temperature dependence of the conductivity may be associated with the leveling-off of the $\tau_\delta(T)$ dependence [12]. (τ_δ is time of the phase relaxation)

The Hall effect measured at 4.2 and 1.4 K gives the same carrier concentrations ($R_H = 1/ne$) $n \sim 5 \times 10^{12}$ cm^{-2}. The Hall mobility calculated from the conductivity, $\mu = \sigma/ne$ was found to be low, about 100 cm^2 V^{-1} s^{-1}.

Sample (1) GR-56, Sample (2) GR -53: Figure 7 shows the low-temperature run of the magnetoresistance (MR) (decreasing of sample resistance with increasing of magnetic field in weak field region). A negative-magnetoresistance peak can be seen, associated with the weak localization (it is also manifested at 4.2 K, so that it cannot be due to superconductivity of the contacts). In stronger fields, we have a linear-in-field positive MR frequently observed in inhomogeneous metals and associated with the so-called parallel conductivity effect

in which the electric current is redistributed with increasing magnetic field, being concentrated in layers with low mobility [10].

Summary: From the results above, we infer that high vacuum annealing indeed improves the quality of SiC surfaces, with polish damage being replaced by uniform arrays of large terraces. The auger spectroscopy and RHEED confirms that there are not surface reconstructions of SiC substrate. Thus, annealing of silicon carbide substrates in a vacuum can be used to perform an *in situ* pre-growth treatment to produce graphene on the SiC surface as well as before epitaxial growth.

Thus, the pregrowth annealing of SiC substrates in a quasi-closed growth cell made it possible to synthesize homogeneous multigraphene films with increased area on the surface of a SiC single crystal. Raman studies demonstrated that, under the same growth conditions, a pregrowth temperature treatment of the substrate surface leads to a decrease in the number of surface defects in a multigraphene film being obtained, compared with the case in which only mechanically polished substrates are used. AFM studies directly confirmed the better homogeneity and smaller number of defects in a multigraphene film in the first case. Thus, annealing of SiC substrates in a quasi-closed growth cell can be used for in situ processing prior to growth of graphene films.

RESULTS

The results of a study of the low-temperature transport properties of the samples we obtained are indicative of the existence of a 2D hole gas. The comparatively high carrier concentration (10^{12} cm^{-2}) and low mobility (100 cm^2 /V s) suggest that the carriers are related to defects at the SiC-multigraphene interface or to residual defects of the multigraphene itself, rather than being intrinsic.

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