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Transfer-free synthesis of graphene-like atomically thin carbon films on SiC by ion beam mixing technique

Rui Zhang[a,*], Fenghua Chen[a], Jinbin Wang[a], Dejun Fu[b]

[a] Department of Physics, Taiyuan University of Science and Technology, 030024 Taiyuan, China
[b] Key Laboratory of Artificial Micro- and Nano-Materials of Ministry of Education and Hubei Nuclear Solid Physics Key Laboratory, Wuhan University, 430072 Wuhan, China

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ABSTRACT

Here we demonstrate the synthesis of graphene directly on SiC substrates at 900 °C using ion beam mixing technique with energetic carbon cluster ions on Ni/SiC structures. The thickness of 7–8 nm Ni films was evaporated on the SiC substrates, followed by C cluster ion bombarding. Carbon cluster ions C_4 were bombarded at 16 keV with the dosage of 4×10^{16} atoms/cm^2. After thermal annealing process Ni silicides were formed, whereas C atoms either from the decomposition of the SiC substrates or the implanted contributes to the graphene synthesis by segregating and precipitating process. The limited solubility of carbon atoms in silicides, involving SiC, Ni_2Si, Ni_5Si_2, Ni_3Si, resulted in diffusion and precipitation of carbon atoms to form graphene on top of Ni and the interface of Ni/SiC. The ion beam mixing technique provides an attractive production method of a transfer-free graphene growth on SiC and be compatible with current device fabrication.

1. Introduction

Graphene, a one-atom-thick nano-material with the honeycomb structure, has a wide range of applications for its promising properties in optical, electrical and mechanical devices production [1–4]. Since its discovery, numerous methods have been explored in an effort to achieve the goals of the high-efficiency and high-quality synthesis of graphene, such as mechanical exfoliation of graphite [1], chemical vapor deposition (CVD) [5–6], thermal decomposition of SiC [7–8], ion implantation [9–15]. The mechanical exfoliation is time-consuming and labor-costing. Although CVD as a productive growth technique is broadly applied for the synthesis of graphene, it requires surface segregation of the absorbed carbon into metals, like Ni or Cu. The thermal decomposition of SiC for epitaxial graphene synthesis has also been carefully investigated due to its unique superiority, such as wafer-scale growth. Herein, few layers of Si atoms are sublimated from the surface of the monocrystalline SiC in high vacuum, leaving a C-rich face to form the epitaxial wafer-scale graphene layers. However, the ultra-high decomposition temperature of SiC is always required for graphene synthesis, which has become another big obstacle to limit the application of the method for large-scale industry production of graphene-based electronic devices, besides the high substrate cost, relatively small size (150 mm) and integration difficulty in standard CMOS technics.[16] Ion implantation, as a compatible technique with the existing Si electronic industry, is recently used to synthesize the graphene on various substrates and shows several advantages. It is characterized by a non-equilibrium processing, which removes the solid solubility limitation in the host materials, and can accurately control the atoms amount and depth distribution of the introduced impurities by the implantation dosage and energy, respectively. Previously, we reported that the graphitization temperature of SiC for graphene synthesis could be reduced at least 200 °C by ion implantation direct into SiC due to the radiation damage induced to the substrates [14]. In this work, we present a method of graphene synthesis direct on SiC by ion-beam mixing technique with carbon cluster ions bombarding into Ni/SiC structures. It has been found that an annealing process of Ni/SiC system by ion beam mixing technique of carbon clusters resulted in the formation of multi-layer graphene on the top of Ni films and at the interface of Ni/SiC. Our work is devoted to exploring the carbon source for graphene synthesis and the catalysis effect of the transition metal Ni films and the properties of Ni/SiC interface. This will provide an approach for improving the quality of graphene by ion implantation method after further parameters optimization.

2. Experimental details

The commercial single crystalline C-polished 6H-SiC () wafers are available with the cleaved dimension 5×5 mm^2. 7–8 nm Ni films as

* Corresponding author.
E-mail address: zrzx_0921@tyust.edu.cn (R. Zhang).

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the capping layers were deposited on the polished side of the 6H-SiC wafers by magnetron sputtering. The carbon cluster ions C_4 were extracted from a source of negative ions by cesium sputtering (SNICS). The ion beam mixing process was conducted by C_4 with the energy of 16 keV, which provided nominal effective energy per atom of 4 keV. The solubility of the carbon in SiC is lower than in Ni layer, the high dosage up to 4×10^{16} atoms/cm^2 is necessary. During the implantation process the pressure in the chamber was kept in 10^{-3}–10^{-4} Pa in order to diminish the contamination. Subsequently, ex-situ thermal annealing was performed at 900 °C in a static Ar gas atmosphere for 1 h, followed by cooling down to room temperature at a rate of 20 °C/min. Afterwards, the Ni films and the reaction product of Ni silicides were etched by immersing the substrates into 5 wt% HCl aqueous solution for 5 min. After etching, the substrate was rinsed by deionized water.

The implantation condition was calculated using the program of SRIM 2013 (the Stropping and Range of Ions in Matter) which simulates the ions depth profile and damage distribution [17]. The carbon distribution profile shows the projected range of 4 keV energy per atom is about 8.6 nm with the longitudinal straggling about 6 nm.

The ion beam analysis technique Rutherford Backscattering Spectrometry (RBS), based on elastic collision between the incident charged particles and nucleus of target atoms, is used to obtain the information about atomic transport across the interface, due to its sensitive elemental identification and depth resolution. RBS measurements were implemented using 3.0 MeV Li^{2+} particles from 2×1.7 MV tandetron accelerators on as-prepared and annealed samples under normal incidence. The backscattered particles were detected using a surface barrier solid-state detector with scattering angle 170° relative to the incident beam and the final accumulated charge was 10 μC. The obtained RBS spectra were analyzed by using a computer program SIMNRA 6.06. The SIMNRA program is aimed at simulating RBS spectra and accessing the thickness and the composition of each layer of analyzed samples by comparing the experimental and simulated data [18].

To characterize the surface morphology of graphene growth on the SiC substrate, the scanning electron microscopy (SEM) observation were performed at the energy of 10 kV in the secondary electron image mode and the atomic force microscopy (AFM) measurements were carried out by working in tapping mode. The Raman measurements were conducted using a confocal Raman microscopy (LabRAM HR800) with the 488 nm laser excitation length at a power of 10 mW. X-ray photoelectron spectroscopy (XPS) spectra were acquired to investigate the elemental species and chemical state of the graphene layer grown on the surface. XPS analysis was recorded by Thermo Scientific Escalab 250 Xi spectrometer with Mg Kα radiation of 1253.6 eV as the excitation source in an ultra-high vacuum system.

3. Results and discussion

Ion beam mixing by C cluster ions irradiated at room temperature has resulted in Ni and C atoms mixture across the interface and heavy damage to the substrates. Ion implantation with high dosage may induce very heavy damage to the substrates. The appropriate energy of the cluster ions was chosen to accomplish the ion beam mixing process. Some incident C ions mixing with Ni ions were implanted into SiC substrates. Besides, some another amount of C ions were implanted in the Ni/SiC interface region through the buffer layer of Ni films. The two parts of carbon atoms provide the carbon source for graphene synthesis. Fig. 1(a) illustrates the process of graphene growth on Ni/SiC and SiC surface, which involves the following three steps: i) the Ni layer as a catalyst and capping layer was deposited on the SiC substrate, as the Ni/SiC structure; ii) the implantation process from the ion beam mixing technique with energetic C cluster ions injecting into Ni/SiC structure; iii) the Ni/SiC structure was annealed in a furnace in Ar gas atmosphere. Fig. 1(b) shows the depth profile and the damage distribution of the C ions implanted into the Ni/SiC structure by SRIM stimulated program. The cascade of energetic Ni, Si and C recoils created from the primary collisions produced a few displacements per atoms (dpa) in the Ni/SiC region. At the interface between the Ni layer and the SiC substrate, as shown in Fig. 1(c), both the C atoms and Ni atoms were injected into the near-surface of SiC, according to the SRIM program simulations.

Fig. 2(a) shows the typical RBS spectra of the as-prepared (black cure) and the annealed ion-irradiated Ni/SiC (red curve) samples, respectively. The experimental data were perfectly fitted with the simulated data by SIMNRA program. The expected Ni and Si atoms are detected as the arrows marked in the fitted RBS spectra. The peak of the deposited Ni film is rather sharp with a narrow energy range corresponding to the thickness of the Ni films about 8 nm. This reveals good adherence of the Ni films to the SiC substrates and negligible surface sputtering effect of Ni films during the ion beam mixing process by carbon clusters. It can be seen that the Ni peak of the irradiated samples has a substantial broadening after annealing process. The rear edge of the Ni peak extended to lower channel number is centered at about 314 and a slight downshift of Si signal is observed because of the inelastic energy losses in the Ni overlayer. Moreover, we note that the height of the Ni peak of the irradiated sample has reduced after annealing process. Those are the conclusive evidence that the intermixing has occurred across the Ni/SiC interface. And the top Ni atoms migrate toward SiC substrates after C ion beam bombardment and annealing process. A faint C peak has developed in the RBS spectrum of the annealed ion-irradiated sample, indicating that the C atoms have released and accumulated at the surface. The Ni frontier peak with a subtle downshift and less steep after annealing process relative to the as-prepared sample is concluded that Ni atoms are no longer present at the very surface anymore, i.e., the formation of the ultra-thin carbon films has covered over the surface of Ni/SiC.

The thickness and composition of the as-prepared and the annealed ion-irradiated Ni/SiC samples was quantitatively estimated from the spectra using SIMNRA software to obtain the elemental depth profiles, i.e. atomic concentration of elements versus areal density (atomics/cm^2), as shown in Fig. 2 (b) and (c). To obtain the information of the spectra, the target is described as a succession of specifying layers, for each layer designed its thickness and relative atomic concentration of elements. The value of the thickness is given in the thin film unit (TFU) of 10^{15} atoms·cm^{-2}. As for Ni 1×10^{15} atoms·cm^{-2} corresponding to 0.1095 nm, the thickness of a given atomic concentration Ni layer (c_{Ni}) in metric system is expressed as [19]:

$$h_{nm} = h_{TFU} \times 0.1095 \times c_{Ni} \quad (1)$$

So the thickness of the Ni film of the as-prepared sample was calculated to be 8.59 nm, which was roughly consistent with the expected results. While the as-deposited Ni films are presumably unstable and they will agglomerate to form islands when subjected to sufficient high temperature, the Ni film of the annealed ion-irradiated sample shows a reduced thickness of 6.16 nm [20]. However, here it is impossible to estimate the stoichiometric composition from the atomic concentration as a function of depth (Fig. 2(b) and (c)) on account of the signal incorporation of Si and C atoms from the SiC substrate. It is reported that the Ni silicides mixing with C were formed at the SiC surface after thermal annealing process [21].

Raman scattering spectroscopy was conducted to identify graphene and its quality, as shown in Fig. 3(a). The obtained result of the graphene growth on the Ni surface after annealing the C_4-ion beam bombarding sample is shown as the black curve. Three characteristic phonon peaks are clearly observed by Raman scattering spectroscopy at D band ($\sim$1350 cm^{-1}), G band ($\sim$1585 cm^{-1}), and 2D band ($\sim$2710 cm^{-1}). The measured 2D peak position and the intensity ratio of 2D to G band (I_{2D}/I_G) depend strongly on the thickness of the graphene and usually can identify the thickness variations of graphene under appropriate conditions. Based on this point, it confirms the synthesis of multi-layer graphene on top of the Ni films. It is well known that the ratio of intensity of the D to G band can be used to estimate the