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Full Length Article

A new direct growth method of graphene on Si-face of 6H-SiC by synergy of the inner and external carbon sources

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ABSTRACT

Graphene is a promising two-dimensional material that has possible application in various disciplines, due to its super properties, including high carrier mobility, chemical stability, and optical transparency etc. In this paper, we report an inner and external carbon synergy (IECS) method to grow graphene on Si-face of 6H-SiC. This method combined the advantages of chemical vapor deposition (CVD) and traditional epitaxial growth (EG) based on silicon carbide, which providing a feasible approach for growing graphene on the SiC substrates. The graphene was synthesized within just 3 min, which was more than one order of magnitude faster than the graphene grown on 6H-SiC substrates by the traditional EG method. The growth temperature was ~200 °C lower than the EG process. The directly grown graphene maintained the compatibility with the semiconductor technique, which is benefit for use in graphene-based microelectronic devices.

1. Introduction

Graphene is a single layer of sp^2 hybridized carbon atoms arranged in a two-dimensional (2D) honeycomb pattern crystal lattice that has gained attention for its excellent electrical and mechanical properties [1–6]. Graphene boasts super properties, such as high carrier mobility, chemical stability, optical transparency, and low density. High quality graphene has been predicted to be applicable in tetra-hertz range medical imaging, conductive composites, liquid crystal displays, field effect transistors, batteries, solar cells, energy storage devices, microprocessors, and solid-state gas sensors [2–4].

There have been various methods developed for synthesizing graphene, including the graphite mechanical exfoliation [1], chemical vapor deposition (CVD) [7,8], epitaxial growth (EG) [9–11], and chemical routes [5]. The chemical vapor deposition and the epitaxial growth on silicon carbide (SiC) methods have been the most successful for use in large size and high quality graphene growth. They offer the advantage of providing large (several tens of microns) coherent graphene domains [7–14].

The CVD method is a relatively simple and low cost technique for graphene growth, where the carbon is simultaneously provided by the methane gas flow (commonplace) [15–19]. This method has been used to produce graphene that has reached impressive sizes (for example 30 in., the largest graphene ever made by any method) [7,8]. However, the CVD method is only able to grow graphene on metallic substrates. The grown graphene has to be stripped off and then transferred onto the insulating substrates for practical use. During this process, the breakages, the metal etching residues, and the organic contaminations become introduced, causing damage and contamination to the graphene. This greatly decreases the crystal quality [12–14].

Therefore, searching for an insulated substrate to avoid of stripping off is essential and necessary. SiC substrates have the ability to integrate with the present semiconductor technology. This has led to them becoming the choice for high quality graphene growth. The EG method retains the carbon from SiC substrates while the silicon atoms are sublimated at temperatures over 1300 °C [20–22]. The graphene could be grown directly on the SiC substrates and could integrate with the present semiconductor technology [9,10]. This would allow the strip and transfer step to be omitted. The SiC substrate acts as an insulator, so the intrinsic properties of graphene are preserved. Moreover, epitaxial graphene on SiC is suitable for optics, because the substrate is transparent over a very broad frequency spectrum. It is also suitable for use in high-frequency

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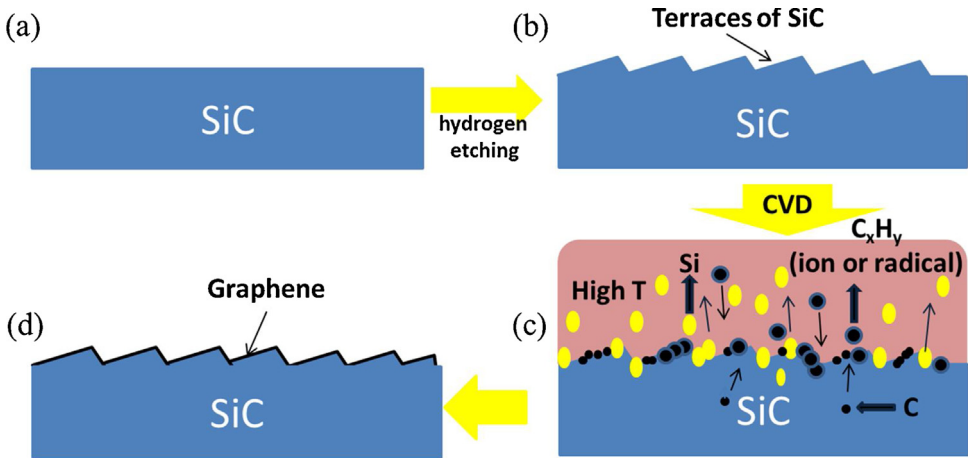

Fig. 1. Schematic of the basic proposed approach for the direct growth of high quality graphene on the 6H-SiC substrate. (a) Cleaning of the 6H-SiC substrate. (b) Well-ordered atomic terraces on the 6H-SiC substrate surface after hydrogen etching. (c) Formation process of graphene preferentially-grown on the 6H-SiC Si-face layers. (d) Full graphene layer on a 6H-SiC Si-face substrate surface.

devices, where losses due to residual conductivity of the substrate need to be minimized by using high-quality insulating materials [11]. Similar to the CVD method, some disadvantages also can be found for the EG method. There is obvious buffer layer between the as-grown graphene and the SiC substrate frequently found, which resulted in a decrease of carrier mobility for the graphene prepared on the SiC substrate [23,24]. The growth temperature for this method was relatively high, usually above 1600°C [25–27]. Thus, a new method is required to obtain a monolayer graphene growth based on the SiC substrate.

For this motivation, we here demonstrated a novel and feasible method for directly growing graphene on the Si-face of 6H-SiC. This new method, denoted as inner and external carbon synergy (IECS) method, involves the inner carbon source (C atoms that provide the nucleation sites at the initial stage of graphene growth) stemming from SiC substrates during silicon atoms sublimating at temperatures over 1300 °C. The external carbon source is provided by the gas flow of methane, which would decompose into C or CH_x at high temperatures and support the graphene growth. This new method would obtain the monolayer graphene growth. The graphene was successfully prepared at a much lower temperature (1450 °C) and within a shorter period (3 min) than the traditional EG method. The improved graphene growth technique would be beneficial for applications within graphene-based microelectronic devices.

2. Experimental

2.1. Synthesis of graphene

A homemade rapid-heating chemical vapor deposition (RH-CVD) system was used to grow the monolayer graphene films. Two types of carbon sources, originating from SiC substrate (inner carbon) and alkanes gases (external carbon), were utilized synergistically. The inner carbon was obtained from the SiC, where it provided nucleation sites. The external carbon supplied the active elements, which precipitated on the Si-face of the 6H-SiC substrate during the RH-CVD process. This stable and continuous external carbon source promoted the graphene growth.

Fig. 1 shows the designed synthesis routine for the direct growth of graphene on the Si-face of the 6H-SiC substrates. The 6H-SiC substrate underwent the cleaning treatment and the hydrogen etching (50% H_2 in Ar) at 1550 °C under a 100–800 mbar pressure to produce well-ordered atomic terraces of SiC on the substrate surface (Fig. 1(a) and (b)). The SiC substrate was covered completely with terraces (the tested sample was about 1 cm^2).

The substrate was heated to 1600 °C for 3 min under a 100 mbar pressure to lift the silicon off of the SiC surface, exposing the inner carbon (nucleation process). The exposed inner carbon became the spontaneous nucleation site. The growth temperature of the substrate sharply decreased to 1250–1550 °C for the different period (1–6 min) during graphene growth. The total pressure was controlled around 100–800 mbar with a gas mixture of Ar (10–50 sccm), H_2 (4–32 sccm), and CH_4 (0.5–8 sccm). The CH_4 gas was selected as the external carbon source. During the growth process, the external carbon source (CH_4 gas) decomposed simultaneously. The decomposed products were equably deposited on the surface of the 6H-SiC (0001) substrates (Fig. 1(c)).

After the planned growth period, the power supply was switched off and the substrate was rapidly cooled at a rate of 16–100 °C/s to an ambient temperature in cold-wall reactor (Fig. 1(d)). The large-area graphene was obtained on the SiC substrate directly.

2.2. Characterizations

The morphologies of the samples were investigated via atomic force microscope (AFM, DI 3000, Digital Instruments, US). The tapping mode was performed under ambient conditions, during the AFM measurement. The Raman scattering spectra were measured with an excitation source of a 532 nm laser (40 mW) with a HR 800 system from Horiba Jobin Yvon. A 100X objective, with a numerical aperture 0.50, was used. The focused spot was about 0.5 μm in diameter. X-ray photoelectron spectra (XPS) measurements of C1s were recorded with a Thermo fisher ESCALAB 250 X-ray photoelectron spectrometer that was monochromatized with Al K_α X-ray radiation in an ultrahigh vacuum (<10^{-7} Pa). A low voltage electron flood gun was used for the charge compensation. The binding energy was calibrated with the C1s peak (284.6 eV) of carbon as a reference.

3. Results and discussion

3.1. Synthesis of graphene by IECS method

Fig. 2(a) showed the surface morphology of the 6H-SiC substrate after hydrogen etching (50% H_2 in Ar) at 1550 °C for 30 min under a pressure of 200 mbar. The terraces covered the entire wafer (about 100 μm^2) with a typical step height of 0.4–0.8 nm and a step width of 300–400 μm. The well-ordered atomic terraces on the surface of