Direct growth of few layer graphene on hexagonal boron nitride by chemical vapor deposition

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ARTICLE INFO

ABSTRACT

Few layer graphene was grown on hexagonal boron nitride single crystal flakes by chemical vapor deposition without using metal catalysts. High quality and thickness controllability of the graphene layers are confirmed by Raman spectroscopy and transmission electron microscopy. Chemical vapor deposition of graphene on this perfect-lattice-matching dielectric substrate offers many advantages including cost effectiveness, easy scalability and compatibility with standard intergraded circuit processes and promises an advance to graphene's applications in microelectronics and optoelectronics.

1. Introduction

Graphene has been an important and active research area ever since its discovery in 2004, as recognized by the Nobel Prize in physics in 2010. While graphene has shown great potential in a variety of applications, graphene-based electronics have provided the major driving force for its research. Graphene has been identified as a candidate material for both complementary metal–oxide–semiconductor (CMOS) extension technology and beyond the CMOS technology by the International Technology Roadmap for Semiconductors.

Among the many methods for graphene synthesis, thermal evaporation of SiC and chemical vapor deposition (CVD) are better positioned for electronic applications due to their potential for large scale film growth. Graphene thin films up to 4 in. in diameter can be made on SiC substrate by SiC thermal decomposition, and a radio frequency field-effect-transistor device using this film demonstrated a cutoff frequency exceeding 100 GHz [1]. The high temperature required for this process (typically 1450 °C), which presents a challenge for process control, is a disadvantage. CVD process is under rapid development and regarded as a promising approach due to its scalability, compatibility with standard integrated circuit processes and cost effectiveness. However, current CVD method needs transition metal catalysts, thus an additional step is required either to transfer the graphene film to a silicon wafer [2] or to remove the metal catalyst by insitu or exsitu high temperature treatment [3].

Direct graphene growth on dielectric materials is also possible as already demonstrated on MgO powders [4] and ZnS nano-ribbons [5]. Hexagonal boron nitride (h-BN), commonly referred to as white graphite, is an interesting dielectric material for graphene-based microelectronics and optoelectronics. This wide-band-gap (5.2–5.4 eV) material has a good lattice match with graphene (mismatch ~1.7%), thus it could serve as a dielectric substrate for graphene-based electronics. The exfoliated graphene transferred to an h-BN single crystal support demonstrated a mobility that is almost one order of magnitude higher than that of similar graphene on standard SiO$_2$/Si substrate [6]. Graphene growth

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on a single atomic h-BN buffer layer was reported [7], where the h-BN buffer layer was prepared by a metal catalyst CVD process on Ru (0 0 0 1) film. Interestingly, a significant charge donation from h-BN to graphene was observed when Ru (0 0 0 1) was used [7], but not on a similar film when Ni (1 1 1) was used, i.e., graphene/h-BN/Ni (1 1 1) [8]. Another curious observation in graphene/h-BN/Ru (0 0 0 1) was the lack of the characteristic Raman peak at ~1370 cm^{-1} for h-BN and the graphene 2D peak at ~2700 cm^{-1} [7]. Therefore, direct graphene growth on h-BN without the underlying metal catalyst layer is of interest not only for graphene-based microelectronics and optoelectronics but also for understanding the unexpected behavior when different metal layers are used beneath the atomic layer h-BN. So far, there has been no report of growing graphene on h-BN without the assistance of metal catalysts.

Herein, we will demonstrate the CVD growth, from methane, of few layer graphene on h-BN single crystal flakes without the assistance of any metal catalysts. The number of layers can be tuned by adjusting the growth time and methane flow rate. This progress may promise an advance forward towards graphene-based applications in microelectronics and optoelectronics.

2.   Experimental

The synthesis was carried out in a horizontal tube furnace inside a corundum processing tube (50 mm inner diameter). The h-BN flakes (99.99%) with sizes of 0.5–5.0 μm were placed at the center of the corundum tube as the substrates. Prior to heating, the reaction tube was evacuated, followed by the introduction of argon (Ar) as a carrier gas. The CH$_4$: Ar ratio was varied between 50:180 sccm to 90:180 sccm. The growth temperature of graphene was at 1000 °C, and the growth time ranged from 3 to 8 min. After growth, the CH$_4$ gas and the furnace were turned off, and the furnace was cooled down to room temperature under the 150 sccm Ar flowing. For graphene characterization, Raman spectroscopy (Renishaw inVia) was performed using 514.5 nm Ar$^+$ laser excitation. Scanning electron microscopy (SEM) (JEM-6510) was used for morphological study of the samples. High resolution transmission electron microscopy (HRTEM) and selected-area electron diffraction (SAED) were carried out on a JEM-2010F field emission JEOL system operated at 200 kV.

3.   Results and discussions

The single crystal flakes of h-BN have irregular shape and a broad size distribution from several hundreds of nanometers to several micrometers with a thickness of 50–300 nm. Fig. 1a shows some typical h-BN flakes after the CVD process. Detailed SEM investigations show no apparent changes in flake morphology before and after the process.

Although carbon nanotubes were occasionally observed as a byproduct in CVD growth of graphene on ZnS [5], it was not found in our investigation, indicating that graphene is more energetically favored on h-BN under the current process conditions. Fig. 1b presents a typical Raman spectrum of a graphene/h-BN sample prepared at 90 sccm CH$_4$ for 8 min. For comparison, the Raman spectrum of bare h-BN flakes was also included. As shown in Fig. 1b, the characteristic h-BN peak at 1366 cm^{-1} [9] was observed in both bare h-BN flakes and graphene/h-BN. The G band around 1580 cm^{-1} is the evidence of the sp^2 carbon in the hexagonal lattice of graphene [10]. The intensity and shape of the second-order 2D band around 2700 cm^{-1} are sensitive to the number of layers and the quality of graphene [11]: the peak intensity ratio of I_{2D}/I_G is inversely proportional to the layer number with $I_{2D}/I_G \approx 1$ for bilayer graphene (The decrease is mainly due to the interlayer electron–phonon interaction, which affects the process of the double resonance effect). The measured values of I_{2D}/I_G shown in Figs. 3b and 4b, varied from 0.56 to 0.79 for samples prepared under various process conditions, indicating that few layer graphene samples were obtained and their layer numbers increase as the growth time and methane flow rate increase. Multiple Raman measurements on large flakes indicated that the graphene is conformal coated on the entire h-BN flake. Moreover, the 2D band has single-Lorentzian line shape with a full width at half maximum of 40–52 cm^{-1}, indicative of an ordered stacking for graphene layers [2], the disorder-induced D band at 1350 cm^{-1} was not observed. These results demonstrated that few layer graphene were synthesized on the h-BN flakes.

Fig. 2a shows the HRTEM image of a typical sample prepared at 50 sccm CH$_4$ for 8 min. The as-obtained sample mainly consists of six-layer graphene (Fig. 2a). The parallel lattice planes show an ordered stacking with the interlayer spacing of 0.335 nm, compared with 0.350 nm for h-BN [12]. Different sample areas did not show any noticeable variation, suggesting that the graphene is covering the whole h-BN
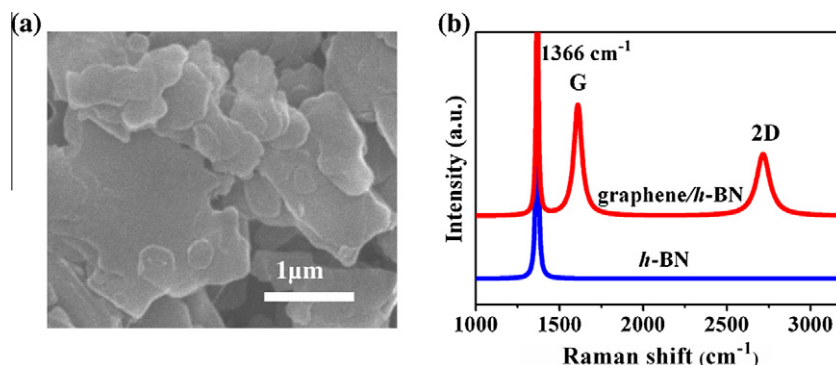

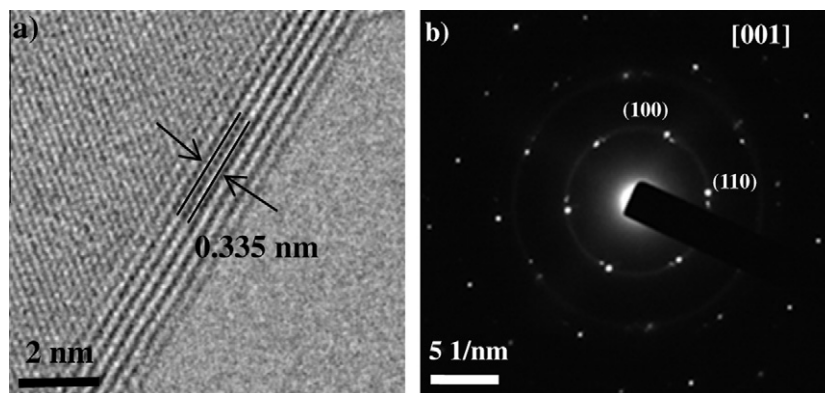**Fig. 1 – (a) SEM image of graphene on h-BN flakes. (b) Raman spectra of graphene on h-BN and bare bulk h-BN.**

Fig. 2 – (a) HRTEM image of six graphene layers on *h*-BN prepared at 1000 °C for 8 min, at CH$_4$:Ar = 50:180 sccm, and (b) SEAD of the graphene on *h*-BN.
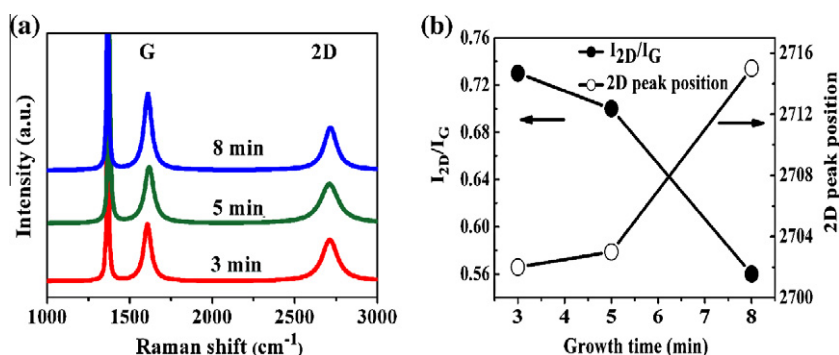

Fig. 3 – (a) Raman spectra for samples prepared for different growth times from 3 to 8 min at CH$_4$:Ar = 90:180 sccm. (b) The intensity ratio of 2D-band to G-band (I_{2D}/I_G) and the 2D peak position as a function of growth time.
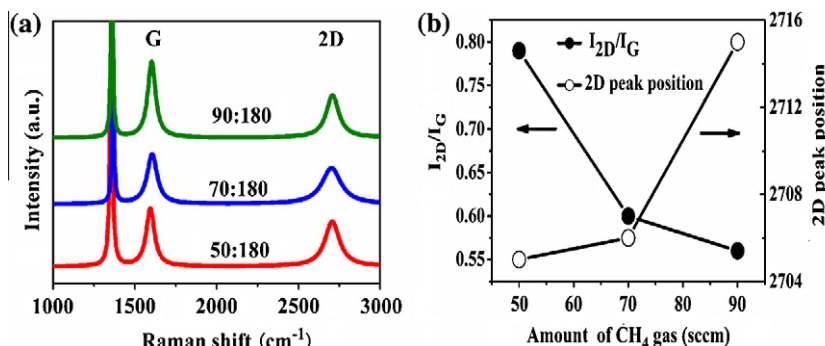

Fig. 4 – (a) Raman spectra for samples prepared at different CH$_4$:Ar ratio: 50:180, 70:180, and 90:180, (growth time: 8 min, temperature: 1000 °C). (b) The intensity ratio of 2D-band to G-band (I_{2D}/I_G) and the 2D peak position as a function of the flow ratio of CH$_4$ gas.

surface. In order to further evaluate the crystallinity of the graphene film, SAED was performed, as shown in Fig. 2b. Obviously, there are two sets of hexagonal patterns, each with a distinct hexagonal structure, one for graphene and the other for *h*-BN. The grey diffraction spots are attributed to the graphene thin film, and the bright ones come from the *h*-BN single crystal flakes. The small shift from the bright to grey spots may be due to two crystals slightly rotated from each other or the differences of in-plane lattice constants (graphene *a* = 246 pm, and *h*-BN *a* = 250.4 pm). Well-defined hexagonal diffraction spots were always observed in different regions of the graphene. These results prove that graphene grown on *h*-BN surface has good crystallinity and few defects, which are consistent with the aforementioned Raman analysis.

As already mentioned, the number of layers of graphene films can be controlled by growth time or methane flow rate. Fig. 3a presents the Raman spectra of graphene samples prepared for different growth time at CH$_4$: Ar = 90:180 sccm. With increasing growth time (from 3 to 8 min), the I_{2D}/I_G value decreases progressively (from 0.73 to 0.56). Meanwhile, the 2D peak position shifts from 2702 cm^{-1} to 2715 cm^{-1}, most likely due to stress relaxation as the layer number increases. Shorter process time were tried, preliminary results indicated that
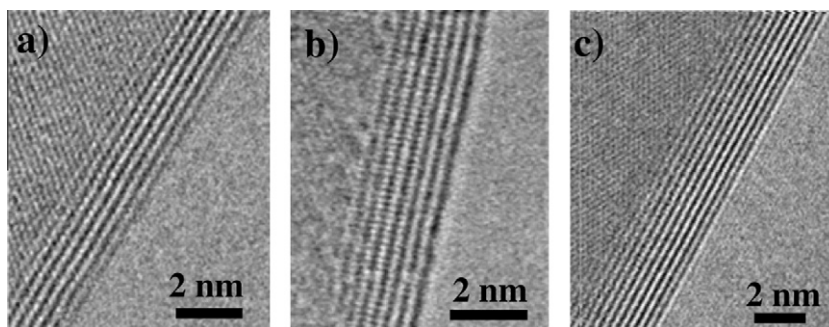
Fig. 5 – Typical HRTEM images for samples grown for 8 min in gas mixing ratio of CH₄:Ar at (a) 50:180 sccm, (b) 70:180 sccm, and (c) 90:180 sccm.

the obtained film were mainly 1–2 layer graphene with 1.5 min process time. It is evident that the layer number of graphene can be tuned by growth time.

Likewise, when increasing methane flow rates from 50 to 90 sccm (reaction time fixed at 8 min), the I_{2D}/I_G ratio decreases gradually from 0.79 to 0.56 as shown in Fig. 4. Direct measurements using HRTEM investigation, shown in Fig. 5, gave typical thicknesses of 2.0 nm (6 layers) at 50 sccm, 2.34 nm (7 layers) at 70 sccm and 3.35 nm (10 layers) at 90 sccm. Thus, the number of layers can be tuned by controlling the flow rate of CH₄.

Since the lattice mismatch between graphene and *h*-BN is only 1.7%, it is highly possible that the mechanism for graphene formation is epitaxial growth, although more detailed investigations are needed for a final confirmation.

The above results show that few layer graphene can be synthesized directly on *h*-BN single crystal flakes by CVD, and its layer number can be controlled by adjusting the growth time and methane flow rate. Recently, few layer *h*-BN film was also reported by CVD on copper foil [9].Therefore, it may be possible to combine the CVD growth of few layer *h*-BN and few layer graphene on the same substrate to obtain a graphene/*h*-BN heterostructure that may find potential applications in graphene-based electronics or optoelectronics.

4.　　Conclusions

Few layer graphene directly on single crystal *h*-BN substrate was demonstrated by CVD method without the assistance of metal catalyst. The film deposition was carried out at 1000 °C for 3–8 min at different CH₄ flow rates. Raman investigations show well defined graphene peaks at ∼1580 cm⁻¹ (G band) and ∼2700 cm⁻¹ (2D band). The peak at ∼1350 cm⁻¹ (D band) is absent indicating that the synthesized graphene is free of defect. The number of layers of graphene can be controlled between 2 and 10 by tuning the growth time and methane flow rate. Raman, HRTEM and SAED characterization confirmed that the few layer graphene grown on *h*-BN has good crystallinity, few defects and ordered layer stacking. This study identifies *h*-BN, a dielectric material with excellent dielectric properties and matched lattice constant with that of graphene, as one of the best candidates for graphene growth. Large size, defect-free and thickness controllability

promise an advance to graphene's applications in microelectronic and optoelectronic applications.

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