Paved phonon transport route in graphene by vapor phase process

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ABSTRACT

Various atomistic defects ever-present in graphene have triggered unwanted phonon scattering, thereby significantly deteriorating the heat transport property of the graphene. Consequently, continuous endeavors have been made to minimize these atomistic defects. Here, we first experimentally show that defect healing based on atomic layer deposition (ALD) can significantly mitigate the degradation in the thermal conductivity of the graphene. After defect healing with Pt and Al_2O_3 ALD, the thermal conductivities of graphene synthesized by conventional chemical vapor deposition were improved by ~83% and ~64%, respectively. It is speculated that the healing atoms facilitate heat transfer across the defects, by eliminating the influence of vacancy in the graphene layer, which likely increases the phonon lifetime (leading to a noticeable improvement in thermal conductivity). This study provides an understanding of how defect engineering could affect phonon transport in 2D materials and sheds light on affordable graphene with excellent thermal conductivity.

1. Introduction

Transport of phonons (the quanta of lattice waves) in two-dimensional (2D) materials have recently attracted significant attention both from academia and industry. The unique 2D nature of graphene allows out-of-plane atomic displacements, also known as flexural phonons, which are found to be the leading heat carriers in graphene near room temperature [1]. Hence, control of the acoustic flexural modes could render many of the unique thermal properties of graphene [2,3]. Theoretical studies suggest that phonon transport in 2D systems can reveal an exotic behavior, leading to very high intrinsic thermal conductivity [4]. Several research groups have reported that thermal conductivity of suspended graphene can exceed that of the bulk graphite [5]. The high in-plane thermal conductivity of graphene is due to covalent sp^2 bonding between carbon atoms, which is stronger than the sp^3 bonds in diamond [2]. Graphene can have a higher thermal conductivity than the graphite basal planes, due to the lack of interlayer phonon scattering despite similar phonon dispersions and crystal lattice anharmonicity. Theoretical studies attribute the enhanced thermal conduction in graphene to an unusually long mean free path of long-wavelength

phonons in 2D lattices and to the low efficiency of the phonon Umklapp scattering in restoring thermal equilibrium in 2D systems compared to bulk systems [6]. The extremely high thermal conductivity results suggest graphene has applications as a thermal management material in electronics and battery cooling [7,8]. Furthermore, as opposed to their bulk counterparts, the thermal properties of 2D materials can be easily tailored, via application of external strain, introducing defects, or stacking multiple layers of the same or different 2D materials [9]. Ghosh et al. and Kim et al. documented experimental results showing that as atomic layer number increases, the phonon dispersion changes and more phase space states become available for phonon scattering, leading to a thermal conductivity decrease [10,11]. Mu et al. used molecular dynamics (MD) simulations to find that a defected region can experience large local deformation and strain, which, in turn, imposes stronger phonon scattering than simple atomic mass variation [12].

Heat flow in graphene can be tuned by introducing atomistic alterations of the honeycomb lattice [2]. Most materials have natural point defects, such as atomic vacancies, added in the process of fabrication. Given that the phonon frequency depends on the strength of the local bonds, these vacancy defects may decrease the thermal

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conductivity of materials due to bond weakening and, thus, group velocity reduction besides defect scattering [13]. The thermal conductivity of graphene can also be degraded by defects, such as polymer residue from nanofabrication, edge roughness, polycrystalline grain boundaries, and disorder from contact with a substrate or a capping layer [2,14–16]. Accordingly, the thermal conductivity of graphene synthesized by chemical vapor deposition (CVD) is typically lower than that of the mechanically exfoliated graphene from highly ordered pyrolytic graphite (HOPG) [6]. The graphene heat spreaders and graphene-based thermal fillers for thermal interface materials will likely be produced by the CVD method and the liquid phase exfoliation process, respectively. Both of these two, large-scale operations typically produce graphene with a large density of defects compared with that exfoliated from HOPG. Moreover, efforts to generate graphene at low temperature, especially below 400 °C, which would enable direct integration of graphene into a complementary metal-oxide semiconductor or flexible device, highlight the defect issue [17]. Recently, thermal conductivity reduction by defects in graphene was experimentally confirmed. Malekpour et al. used Raman spectroscopy to measure the thermal conductivity of graphene with defects induced by electron beam irradiation and noted that the thermal conductivity decreased from ∼1800 to ∼400 W/m K as the defect density changed from 2×10^{10} to 1.8×10^{11} cm^{-2} [6]. The authors explained that the additional defect sites serve as scattering centers for phonons with wavelengths shorter than the distance between vacancies. Wang et al. determined the defect-driven thermal conductivity change using a T-type sensor method and stated that the nanohole defects created by a focused ion beam decreased the thermal conductivity of graphene by about 42% [18]. The main reasons mentioned for the thermal conductivity reduction were the increase in edge roughness and stronger scattering on long-wavelength acoustic phonons, based on a lattice dynamics calculation [18].

To avoid the degradation, various defect healing methods have been proposed, such as thermal annealing, self-healing, healing by adsorption, and metal-assisted healing [19–22]. However, such processes require high-temperature conditions, which are not ideal for industrial use. Hence, selective metal deposition methods including atomic layer deposition (ALD) and electrochemical deposition, which do not need a high-temperature condition, have been recently proposed for defect healing [23–25]. The defect healing effect on electrical transport in graphene was experimentally investigated, and electrical transport was apparently enhanced by filling vacancies with hetero-materials. Graphene has metal-like properties, but acoustic phonons mainly transport heat in it because of the strong covalent sp^2 bonding, which leads to high in-plane phonon group velocities and low crystal lattice anharmonicity for in-plane vibrations [3]. Hence, the defect healing effect on the thermal conductivity of graphene cannot be estimated accurately solely from the electrical transport measurement. To the best knowledge of the authors, the defect healing effect on the thermal conductivity has not yet been experimentally confirmed.

In this study, we report that a vapor phase treatment for the defect healing could solve the thermal conductivity degradation problems caused by defects that occur during large-scale production of graphene. We perform the defect healing for CVD graphene, using the ALD process, and experimentally study the healing effect on graphene thermal conductivity by using Raman spectroscopy.

2. Materials and method

2.1. Preparation of suspended graphene

Single-layer graphene was synthesized by CVD on copper foil. Then, polymethylmethacrylate (PMMA; PMMA950 A4, MicroChem) was spin-coated on the surface of the graphene/copper at 3000 rpm for 30 s and then heated on an 80 °C hot plate for 1 min. Considering that graphene grows on both sides of the copper foil, the back side was etched by oxygen plasma at a chamber pressure of 0.3 Torr for 10 s. The sample

was floated on ammonium persulfate [(NH$_4$)$_2$S$_2$O$_8$, 0.1 M] solution until copper was sufficiently etched. Next, the PMMA/graphene film was transferred to a beaker of deionized water to rinse off the residue. The PMMA/graphene film was scooped up with the oxygen plasma-treated SiO$_2$/Si substrate, having 10-μm-diameter circular holes, to produce a suspended film. The substrate with the circular holes was prepared by photolithography and dry etching of Si substrates covered with a SiO$_2$ layer. The sample was naturally dried for 24 h and baked in an oven at 100 °C for 1 h, to improve the adhesion between the graphene and the substrate. Finally, the PMMA layer was removed, based on the previously used condition that could eliminate most of the PMMA [11]. We dipped the graphene sample in acetone at 60 °C for 15 min, followed by thermal annealing under atmospheric pressure in a furnace at 330 °C for 1 h. Afterward, we confirmed the removal of PMMA using atomic force microscopy (AFM).

2.2. Defect healing for CVD graphene using ALD

Al$_2$O$_3$ was deposited at 70 °C and ∼0.1 Torr. Trimethylaluminum (Al(CH$_3$)$_3$, TMA, Sigma–Aldrich) and H$_2$O were used as precursors. During each cycle, a 0.015 s pulse, 20 s exposure, and 30 s purge of TMA and 0.1 s pulse, 20 s exposure, and 30 s purge of H$_2$O were carried out in sequence. The ALD process was repeated eight times, for a target thickness less than 2 nm.

Pt was deposited at 200 °C and ∼0.1 Torr. Trimethyl (methylcyclopentadienyl)platinum (IV) [(MeCp)PtMe$_3$, Sigma–Aldrich] and oxygen were used as precursors. During each cycle, a 0.5 s pulse, 10 s exposure, and 15 s purge of (MeCp)PtMe$_3$ and 0.5 s pulse, 10 s exposure, and 15 s purge of O$_2$ were conducted in sequence. The ALD process was repeated 25 times, for a target thickness less than 2 nm.

2.3. Raman spectroscopy

Raman spectroscopy and mapping were performed via an inVia Raman microscope (Renishaw) at λ = 514 nm. We employed a grating (1800 gr mm^{-1}) for diffraction. The laser power was kept below 2 mW, to avoid excitation by local heating, unless specifically mentioned. The laser spot size was ∼0.32 μm with a × 50 objective lens (numerical aperture = 0.50). The pixel size of the Raman maps was 0.5 μm for both the x and y directions, respectively. The spectral resolution was 1.22 cm^{-1}, using a grating with 1800 grooves mm^{-1} and each acquisition had a 10 s accumulation time. The peak intensity ratios were obtained after subtracting the baseline.

2.4. X-ray photoelectron spectroscopy(XPS) and transmission electron microscopy(TEM)-energy dispersive X-ray spectroscopy(EDX)

XPS was carried out via an X-ray photoelectron spectrometer (Thermo Fisher Scientific K-Alpha+), in surface analysis mode. The graphene was transferred onto the TEM grid (Quantifoil, 200 meshes, 2 μm holes), as per the SiO$_2$ substrate. The TEM and EDX spectrum images were both obtained at 200 kV, using an HR-TEM instrument (JEM-ARM200F, Jeol).

3. Results and discussion

ALD is achieved based on the surface chemistry of the substrate material [23]. An inert surface without dangling bonds, such as a defect-free pristine graphene, is chemically inactive to ALD precursors. In contrast, graphene that contains many atomic defects can be naturally expected to offer preferential nucleation sites for ALD [26,27]. Namely, at the initial stage of ALD, deposition occurs selectively and primarily at the defect sites of graphene before full coverage. Consequently, the unique ALD chemistry enabled the defects to be selectively healed and distinctly visualized. The samples for this study were grown by CVD on copper foils and transferred onto an oxygen plasma-treated SiO$_2$/Si