論文の内容の要旨

Direct Physical Exfoliation of Graphene from Graphite Using a PDMS Stamp
(PDMS スタンプを用いたグラファイトからのグラフェンの直接物理的剥離)

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This PhD research aims to study 'direct physical exfoliation of graphene' (i.e., abbreviated to 'DIPEG' in this research) on the specific site from a graphite grown on a Ni surface via chemical vapor deposition (CVD-graphite/Ni) using tunable elasticity and adhesion of a polydimethylsiloxane (PDMS) stamp for the potentially cost-effective and scalable arrays of defect-less few-layer (including mono- and bi-layers) graphene sheets, without the needs of special equipment, conditions and materials.

In chapter 1 introduces research background, and presents the objective, achievements and significance of this PhD research.

Graphene, a two-dimensional layer of carbon atoms arranged in a hexagonal lattice, provides outstanding properties, such as high electron mobility, mechanical strength, light transmittance and easily modified electrical properties by electric field or doping. Because of the potential to resolve scientific problems and improve device performance, complementary methods for suitable graphene fabrication have been competitively introduced. In particular, a physical exfoliation method is a straightforward route because it directly peels high quality graphene from bulk graphite under dry condition using only a stamp and without the use of a special apparatus or materials. However, the method suffers from not only the poor controllability due to the use of a Scotch tape, SiO_2, Au and Pd films as a stamp but also low amounts of exfoliated graphene because of the use of highly ordered pyrolytic graphite (HOPG) and epitaxial graphene as a graphene precursor.

To solve these problems, in this research firstly propose a fabrication method for direct physical exfoliation of graphene (DIPEG) on the specific site from a CVD-graphite substrate using an optimized

PDMS stamp without the use of special equipment, conditions and materials. This method is distinguished from conventional methods by the followings. First, this method firstly uses an optimized (highly flexible and adhesive) PDMS stamp, instead of the conventional SiO_2, Au and Pd films because the PDMS stamp not only allows making conformal contact with the rough CVD-graphite/Ni surface for site specific graphene exfoliation but also enables the etchant-free release from the exfoliated graphene in order to prevent the chemical damage and contamination. In addition, this method firstly employs the CVD-graphite/Ni as the graphene precursor, instead of the conventional HOPG and epitaxial graphite/SiC because the area of the CVD-graphite/Ni can easily be scaled up while maintaining its low price.

The objectives in this research are as follows. Firstly, in this research studies quantitative changes in properties (i.e., elasticity and adhesion) of PDMS versus the PDMS cross-linking time in order to determine optimal PDMS as a stamp for the conformal contact with the CVD-graphite/Ni surface. Secondly, in this research demonstrates the DIPEG method to produce the scalable array of defect-less few-layer graphene on the specific site from the CVD-graphite/Ni using the optimized PDMS stamp. Finally, this research measures properties of the exfoliated graphene sheets for various device applications.

In chapter 2 describes the preparation of a graphite substrate and optimal PDMS stamp.

Graphite grown on a Ni foil via alcohol catalytic chemical vapor deposition (ACCVD) was firstly used as a graphene precursor because the CVD-graphite/Ni offers the cheapest price (~15 USD for 10 mm^2) and scalability, compared to conventional HOPG (468 USD) and epitaxial graphene (~265 USD). After growing the graphite substrate, Raman measurements verified the formation of defect-less high quality graphite on the Ni surface. Despite these advantages, relatively rough CVD-graphite/Ni surface make it difficult to achieve conformal contact with a stamp for site specific graphene exfoliation.

Therefore, to make conformal contact to the rough CVD-graphite/Ni surface, in this research quantitatively changed properties of PDMS by varying the PDMS cross-linking time. Then, the PDMS cross-linked for 25 min was determined as an optimal stamp to make conformal contact to the CVD-graphite/Ni surface because it was revealed that the optimized PDMS stamp provides decreased elastic modulus (~52 kPa) which is approximately 28 times lower than ~1490 kPa for the typical PDMS (cross-linked for 60 min). Furthermore, the optimal PDMS surface showed the work of adhesion of ~71 mJ/m^2 which is higher than ~59 mJ/m^2 for the typical PDMS surface as well as 60 mJ/m^2 for graphene exfoliation from graphite interlayer separation.

In chapter 3 demonstrates the DIPEG method for the facile and cost-effective fabrication of defect-less few layer graphene on the specific site from CVD-graphite/Ni using the optimized PDMS stamp.

In this research considers the interlayer screening effect in the graphite under conformal contact to the optimal PDMS surface. The screening effect from the conformal contact between the PDMS and graphite surface weakens the adjacent graphite interlayer bonding to the PDMS/graphite interface, whereas other interlayers farther away from the PDMS/graphite interface remain initial bonding because the screening effect depends on van der Waals interactions which is drastically decrease with increasing mutual distance. Moreover, the screening length is known as 0.5~2 nm which corresponds to 1~6 layer graphene sheets. For these reasons, if the optimized PDMS stamp can make conformal contact to the CVD-graphite surface, the PDMS stamp can preferentially exfoliate neighboring mono- or few-layer graphene sheets from the

graphite surface, rather than thick multi-layer graphene. Therefore, it is essential not only to improve contact between the stamp and graphite surfaces.

The peel test was performed to measure the adhesion between the PDMS and graphite surfaces versus the PDMS cross-linking time. From the test, it was revealed that the optimized PDMS stamp (cross-linked for 25 min) provides enhanced adhesion (~5.1 N/m) which is approximately 17 times higher than ~0.3 N/m for the typical PDMS (cross-linked for 60 min). To exfoliate graphene by graphite interlayer separation, the adhesion between the PDMS and graphite surfaces should be greater than graphite interlayer adhesion energy (0.23 J/m^2). According to the results of the peel test, adhesion of the optimal PDMS surface (~5.1 N/m=J/m^2) is approximately 22 times higher than the graphite interlayer adhesion although the peel adhesion is not same as the work of adhesion of the graphite interlayer because the peel adhesion measured by the peel test reflects not only the adhesion between the PDMS and graphite surfaces but also the energy dissipation.

As the results of the optimization of PDMS's properties, the optimal PDMS offering high flexibility and adhesion improved contact with the rough CVD-graphite/Ni surface. Once the PDMS stamp was bonded with the graphite surface for 60 min and then debonded, imprinted patterns opposite to the graphite surface morphology was newly found on the debonded PDMS surface, which strongly verifies that the optimized PDMS stamp can make conformal contact with the CVD-graphite/Ni surface, even with Ni grain boundaries and graphite wrinkles having few nanometers in height.

In this research demonstrates the DIPEG method from the CVD-graphite/Ni using the optimized PDMS stamp. The graphite/Ni substrate was patterned by oxygen plasma for site-specific exfoliation of the defect-less few-layer (including mono- and bi-layers) graphene sheets. The optimized PDMS stamp made conformal contact over the entire graphite surface with no pressure. Then, the PDMS/graphite layer was pressed at around 0.1 MPa which is lower than the shear strength of graphite interlayer (~0.48 MPa). Then, the PDMS stamp exfoliated few-layer graphene sheets from the graphite surface during debonding the stamp. The low pressure exfoliation may have originated from the neighboring graphite interlayer bonding weakened by the screening effect under conformal contact between the optimal PDMS and graphite surfaces.

After the graphene exfoliation, the number of layers of exfoliated graphene sheets were determined by the intensity ratio between 2D at ~2700 cm^{-1} and G at ~1580 cm^{-1} bands (I_{2D}/I_G) and the full width at half maximum (FWHM) of 2D band in measured Raman spectra. As a result, it was revealed that the exfoliated graphene sheets are few layers including mono- and bi-layers. Furthermore, small or negligible D peak at ~1350 cm^{-1} proves the formation of defect-less or -free high quality graphene sheets, resulting from the physical exfoliation in dry condition without the use of acid-base etchant.

In chapter 4 measures optoelectrical properties of exfoliation graphene via the DIPEG method.

Visible light transmittances of graphene sheets exfoliated on the PDMS stamps were measured by an UV-vis-NIR absorption spectroscopy. All the exfoliation graphene samples showed the light transmittance of more than 90 % that satisfies a requirement as a transparent material.

The exfoliated graphene was bonded with a *n*-Si substrate to form Schottky junction to generate photocurrent because the graphene does rarely react with the Si surface even under high temperature as well as offers high transmittance to improve absorption rate of photon energy. Current-voltage (*I-V*)

characteristics of the fabricated graphene/Si Schottky photodiode was measured at room temperature. The formation of the Schottky barrier height was verified by the rectifying behavior of *I-V* characteristic under negative bias (-2 ~ 0 *V*). A conventional equation governed by the thermionic emission model was used to extract the reality factor (*n*= ~5.28) Schottky barrier height (ϕ_B= ~0.69 eV). The photodiode generated ~62 μA/W and ~ ~37 μA/W at -1 V_{bias} with visible (*λ*: 632) and IR (*λ*: 1465 nm) light irradiations, which is acceptable for visible and IR photodetection.

In chapter 5 gives conclusions.

In this PhD research has firstly studied the direct physical exfoliation of graphene (DIPEG) on the specific site from the CVD-graphite/Ni using the optimized PDMS stamp for the cost-effective application of the graphene sheets to the N/MEMS device arrays.

The proposed DIPEG method firstly used the CVD-graphite/Ni as a graphene precursor and the partially cross-linked PDMS as an optimal stamp because of following advantages. The CVD-graphite/Ni allowed the low cost fabrication of large area arrays of few-layer graphene sheets because it is cheap and easily enlargeable, compared to the conventional HOPG and epitaxial graphite/SiC. Furthermore, the optimized PDMS stamp enabled not only to improve the contact even with the nano scale graphite/Ni wrinkles but also to eliminate the chemical etching process with an acid-based etchant for the transfer of the exfoliated graphene sheets from the stamp into a substrate.

In pursuing these objectives, followings have been achieved. Firstly, when the PDMS stamp was optimized by the quantitative changes in the elasticity and adhesion, the optimal PDMS stamp cross-linked for 25 min (i.e., shorter than 60 min for typical PDMS) provided approximately 28 times lower elasticity (opposite to flexibility) and 17 times higher adhesion than those of typical PDMS. Secondly, once few-layer (including mono- and bi-layers) graphene sheets were exfoliated from the CVD-graphite/Ni via the DIPEG method in dry condition, and the small amounts of defects in the graphene was verified by the high G/D band intensity ratio of ~20 in Raman spectrum, compared to ~4 obtained from chemically exfoliated graphene. Then, graphene-Si Schottky photodiode generated photocurrent of ~62 μA/W with visible light irradiation (*λ*: 632 nm) and ~37 μA/W with IR light irradiation (*λ*: 1465 nm), which are acceptable for visible/IR light detection.

In this PhD research newly obtained significant information which can give the following contributions. Firstly, information about quantitative changes in elasticity and adhesion of PDMS versus cross-linking time can give the contribution to the preparation of an optimal PDMS stamp not only for the DIPEG process but also for the potential contact printing of nano structures, devices and cells. Secondly, information about the required adhesion between the PDMS and CVD-graphite/Ni surfaces for the DIPEG can provide the contribution to the realization of the cost-effective fabrication of scalable arrays of defect-less few-layer graphene sheets on the specific site. Thirdly, information about the photocurrent of the graphene-Si Schottky photodiode under visible and IR light irradiation can offer the contribution to the application of the photodiode for visible and IR light detection. Finally, the DIPEG method firstly proposed in this research can provide opportunities to straightforwardly apply the arrays of the defect-less few-layer graphene sheets to N/MEMS devices, especially optoelectronic device because the PDMS stamp underneath the exfoliated graphene sheets after the DIPEG process can be directly used as a transparent and stretchable substrate.