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学位論文題目　Strain-induced Change of Electronic Properties of Graphene Nano-Ribbon (グラフェンナノリボン電子物性のひずみ依存性解明)
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論文内容要旨

Population aging has become a global demographic trend which will further intensify during the latter half of the twenty-first century. The number of the older persons is expected to be increased to more than 2 billion all over the world in 2050. The chronic disease are more common at the older ages, especially some non-communicable and disabling diseases including memory loss, urinary incontinence and immobility. These older sick people require 24-hour and high-quality nursing care, which brings about severe care burden for the caregivers. One solution to reduce such care burden is the introduction of the sensor network, which is not only capable to monitor the activity of the older people in the nursing room continuously, but also timely notifies the caregivers support when accidents or accident-prone activities of the old people are detected. The construction of this kind of sensor network requires various sensors which can detect the human motions accurately. Based on the human motion behaviors, these sensors should at least have the capability to detect the human motions including elongation, shrinkage, bending and folding.

Strain sensors have been considered as an effective approach for monitoring human motions. However, the traditional rigid strain sensors including metallic strain sensors and capacitive strain gauges possess poor deformability and strain sensitivity. In comparison with these rigid sensing materials, carbon nanotubes (CNTs) have exhibited distinct characteristics in strain sensors application, such as excellent strain sensitivity, light weight, superior physical robustness and high transparency. However, strain sensitivity of CNT-based sensors varies drastically depending on the structural parameters of CNTs including diameter, number of walls and chirality. Fine control of these structural parameters has remained a large challenge. Therefore, the fabricated CNTs-based strain sensors showed poor repeatability. In addition, the vertical structure of the CNTs exhibits poor compatibility with the existing device fabrication process, which caused great difficulties in sensor fabrication.

Compared to CNTs, the two-dimensional (2D) graphene is considered as the most promising strain sensing material due to its controllable geometric structure and good compatibility with the existing top-down device fabrication process. With the miniaturization of electronic devices, graphene sheets have to be cut into narrow strips with a width of several tens of nanometers for the application. The strips of graphene are named graphene nano-ribbons (GNRs). When the width of graphene is narrowed to nanometer scale, both side edges of the ribbon structure significantly modify its electronic band structure, resulting in the opening of the band gap of the GNRs. The previous theoretical studies have demonstrated that electronic properties of graphene nano-ribbons (GNRs) change significantly under the application of tensile strain. Based on this characteristic, it can be said that GNRs have the potential to be applied to highly sensitive strain sensors. So far, some graphene-based strain sensors with different structures have been proposed. However, due to the lack of theoretical framework, the fabricated graphene-based stain sensors showed low strain sensitivity. In addition, although the fabricated grapahene-based strain sensors exhibited the performance to detect three-dimensional deformational, the underlying mechanism has not been fully clarified. Therefore, to realize the highly sensitive grapahene-based strain sensors, theoretical optimization of the structure of graphene-based strain sensors is necessary. Especially, the effect of 3D deformation on the electronic properties of graphene should be investigated.

In order to fabricate graphene-based strain sensors, large single-crystal monolayer is required. Thermal chemical vapor deposition (CVD) growth of graphene on a Cu substrate is a promising method to synthesize high-quality large-area graphene with controllable layer number. In the commonly previously CVD process, methane is used as the precursor. However, owing to the high dissociation energy of methane, the growth rate of graphene is very low, resulting in the high production cost. Therefore, hydrocarbon gas with high reactivity such as acetylene should be considered as the precursor for the growth of graphene. In addition, the previous theoretical studies have also demonstrated that the healing of divacancy defects was realized in the presence of acetylene, implying that acetylene-based CVD process has great potential for the synthesis of high-quality monolayer graphene. However, so far, CVD growth of high-quality monolayer graphene using acetylene as the precursor remains a large challenge due to its extremely high reactivity. Therefore, to develop an acetylene-based CVD process for graphene growth, it is necessary to limit the acetylene supply.

In order to fabricate graphene-based strain sensors, the development of a stable and low-cost fabrication process is necessary. Because monolayer graphene is very fragile, it is easily damaged in the conventional device fabrication process due to the thermal stress induced in the photolithography process. In addition, the remover used in the resist peeling process may also cause the peeling of graphene from the substrate. In addition, transfer of graphene onto a flexible substrate without damage remains a large challenge.

The purpose of this study, therefore, is to clarify the structural factors which dominate the strain sensitive of graphene nano-ribbon and develop an appropriate fabrication process for low-cost and high-reliability graphene-based strain sensors.

First, the structural factors for the development of highly sensitive graphene-based strain sensors were investigated systematically based on theoretical calculations. The effect of 3D deformation (bending and folding) on the electronic structure of armchair GNRs (AGNRs) was systematically investigated using density functional theory (DFT) calculation. In addition, a non-equilibrium Green's function approach based on tight-binding approximation was employed to analyze the change in the electronic conductivity of AGNRs under uniaxial tensile load. Also, the dependence of the ribbon width on its electronic band structure was analyzed in detail. It is found that the bending and folding deformation will induce the orbital hybridization, resulting in the change in the band gap of AGNRs. On the other hand, the tensile strain can induce the drastic change in the band gap of AGNRs, and the inverse evolution between the band gap and uniaxial tensile strain was observed. DFT calculations suggest that for the application of strain sensors the width of GNR should be smaller than 70 nm.

In order to synthesize graphene sheets which are used for strain sensors, a novel stable and low-cost fabrication process of graphene has been developed by applying low-pressure CVD (LPCVD) method using acetylene gas as precursor. Cu pockets were employed to limit the acetylene supply to the substrates. Then graphene was grown on its inner surface. Before CVD growth, the Cu pockets were treated with the pre-annealing and oxidation process in air. By applying these techniques, it is possible to precisely control the chemical reactions in the CVD process including the absorption/decomposition of acetylene precursor on the Cu surface, surface diffusion of carbon species, the nucleation of graphene domains and so on. The synthesized graphene was transferred onto the 300 nm SiO_2/Si substrate and characterized by Raman spectroscopy. It is found that large-area and high-quality monolayer graphene was successfully synthesized on the lightly oxidized Cu (111) surface under very low partial pressure of acetylene within 20 min. Selected area electron diffraction (SAED) measurement further confirmed that the synthesized graphene shows high crystallinity with a grain size up to 400 μm.

A stable and low-cost fabrication process of graphene devices on a SiO_2/Si substrate was established. The substrates was carefully cleaned before and after the thermal oxidation process. Then, the fabricated SiO_2/Si substrate was treated by using oxygen plasma before the transfer of graphene. By employing this process, hydroxide radicals were formed on the SiO_2/Si surface, resulting in a hydrophilic surface. Thus, the contact strength between the grown graphene and the SiO_2/Si substrate was further improved, resulting in a smooth interface and surface. In the photolithography process, an isolating layer formed by LOR5A resist was employed to protect graphene from being damaged by the positive resist OFPR800 (34 cp) both in the metal evaporation process and in the reactive ion etching process. Finally, a back-gate FET structure was successfully fabricated by using this process on the SiO_2/Si substrate, and the FET showed PMOS characteristics as was expected. The measured mobility of holes was 1130 $cm^2/(V \cdot s)$. This result clearly indicates that the high-quality graphene was successfully deposited on the SiO_2/Si substrate suing acetylene-based CVD process and the proposed process was easily adaptable with the conventional fabrication processes for thin-film devices. Next, a graphene-base strain gauge was formed on a soft PDMS substrate. Because the adhesion energy of graphene on Cu was higher than that of the SiO_2/Si substrate, the graphene strain sensor was directly fabricated using the graphene/Cu sample which was fixed onto the Si substrate using a double sided tape. Then, the sensor shape was finely patterned using the graphene/Cu sample. After the device was fabricated, PDMS was molded on its surface. By etching the Cu layer, the device was transferred onto the PDMS substrate. In this study, the length of the gauge was 5 mm, and its width was 10 μm. Based on the theoretical analysis, this gauge should have shown metallic conductivity. The resistance of the graphene-based strain gauge increased almost linearly with the applied both uniaxial and bending tensile loads, and the measured gauge factor was about 3. This value agreed well with the conventional metallic strain gauge. These results clearly indicate that the graphene-based strain gauge was successfully fabricated on a soft PDMS substrate.

Therefore, it was concluded that stable and low-cost fabrication process for the development of graphene-based transistors and strain gauges has been successfully developed by using the CVD process with acetylene gas. In addition, the developed transparent and flexible graphene-based strain sensors exhibited many advantages including light weight, high physical robustness, simple fabrication process and low cost. Utilizing these features, graphene-based strain sensors also exhibit wide potential applications in the fields of the displays, fatigue detection and electronic skin. This study also has paved the way to develop ultrahigh-sensitive GNRs-based strain sensors in near future.

論文審査結果の要旨

21世紀の少子高齢化社会の安全・安心を支える手術支援あるいは介護支援用ヒューマンインターフェース基盤技術として，生体の局所変形を実時間計測できる大規模変形対応超高感度，小型軽量ひずみセンサの開発が望まれている。生体内部や表皮での使用を可能とするため，カーボンナノマテリアル特にグラフェンナノリボンの応用が期待されているが，その電子物性の支配因子の理論的解明，大規模変形対応可能なフレキシブル基板上へのセンサ製造技術の開発など課題が多く実用化には至っていない。そこで本研究は，三次元変形を呈するグラフェンナノリボン電子物性の支配因子を解析的に解明するとともに，大変形追従可能なフレキシブル基板上へのグラフェンナノリボン応用ひずみセンサの製造技術開発を目的としたもので，全編5章からなる。

第1章は緒論であり，本研究の背景と課題を述べるとともに，本研究の目的である，三次元大規模変形負荷環境におけるグラフェンナノリボン電子物性変動支配因子解明の必要性と，ヒューマンインターフェースとしてフレキシブル基板上に大量生産可能なグラフェンナノリボン応用ひずみセンサ製造プロセス開発の必要性を述べている。

第2章では，第一原理解析および分子動力学解析を応用し，グラフェンナノリボン電子物性の変動支配構造因子を解析している。特に隣接した炭素原子のπ軌道のなす角（二面角）を用いることで，三次元変形を呈するグラフェンナノリボンのバンドギャップ変化をその寸法に依存せず統一的に評価できることを明らかにするとともに，この二面角は伝導帯におけるσ－π軌道の混成状態の強さを表していること，などを明らかにしている。また，グラフェンナノリボンの半導体的電子物性は幅約70nm以下で発現し，そのひずみ依存性もリボン幅寸法に依存して大きく変動することを定量的に明らかにしている。さらにtight-bindingグリーン関数法を応用したグラフェンナノリボン電子輸送特性解析手法を開発し，一軸引張負荷環境における単層グラフェンナノリボンの電子バンド構造と電気抵抗変化を解析し，ひずみゲージとしてゲージ率最大約50, 000を実現できる可能性も示している。これらの知見は安定した超高感度小型ひずみセンサを実現する上で不可欠かつ重要な知見である。

第3章では，化学気相蒸着（CVD）法を応用し，高品質な単層グラフェンを高速かつ安定に成膜するプロセスを開発している。特に従来品質制御が困難と考えられてきたアセチレンガスを応用し，1）気相熱分解で安定した高速供給可能なアセチレンガスの超低分圧制御手法と，2）グラフェンと格子整合性が高い超清浄(111)強配向Cu基板の製造方法および3）結晶粒界近傍の平坦化により結晶核発生密度を抑制する表面極薄酸化手法，などを確立することで，従来最高品質を実現できていると考えられてきたメタンガスを応用して製造したものと同等以上の品質の単層グラフェン膜を従来比5倍以上の速度で実現している。これは超高感度ひずみセンサの実現に向けて重要な知見である。

第4章では，第3章で構築した高速・高品質単層グラフェン膜形成プロセスと既存の微細加工，薄膜配線プロセスを統合したグラフェンナノリボン応用薄膜デバイス製造プロセスを開発している。 銅基板上に形成したグラフェン膜を既存薄膜プロセスに移行可能なSiO_2/Si基板に転写する技術，低熱応力制御微細加工技術，などを確立し，グラフェン膜応用トランジスタ構造の試作と動作確認を通し，開発した統合プロセスの有効性を実証している。さらに，微細加工した単層グラフェンナノリボンを大規模変形対応可能なフレキシブル基板（polydimedlylsiloxane）上に低損傷で転写するプロセスを確立し，ひずみゲージの試作に成功するとともに，試作ひずみゲージが最大4%の一軸引張負荷，曲げ負荷に追従応答することも実証し，当初目標であるヒューマンインターフェース適用可能性も示している。これらは超高感度ひずみセンサの実現可能性を明確に示す重要な知見である。

第5章は本論文の結論である。

以上本論文は，大規模変形に対応可能な超高感度ひずみセンサの実現に不可欠な，グラフェンナノリボンの電子物性のひずみ依存性支配因子を原子レベル解析により定量的に解明するとともに， ヒューマンインターフェースに適用可能な高速・高品質単層グラフェン成膜プロセス，フレキシブル基板上へのグラフェンナノリボン応用ひずみセンサ製造プロセスを確立したもので，ナノメカニクスおよびナノスケールでのセンサ・実装工学の発展に寄与するところが少なくない。

よって、本論文は博士（工学）の学位論文として合格と認める。