DEVELOPMENT OF GRAPHENE DRUM RESONATOR WITH NANOCAVITY BY LOW-PRESSURE DRY TRANSFER TECHNIQUE

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ABSTRACT

We developed cavity-sealed single-layer graphene drum resonator by using low-pressure dry transfer technique, without using sacrificial layer etching process. Maximum diameter of 45 μm with gap length of 810 nm was obtained. Raman spectra of suspended graphene was found to be 2D/G ratio of 1.73 and few D peak. A dry transfer technique provides the flat device surface with sealed nanocavity, which can be used up to 6 μm in diameter for standard photolithography to pattern graphene and Ti/Au electrodes. We demonstrated fundamental resonance frequency ranges of 0.74-1.36 MHz with a quality factor of about 300 with 30-45 μm in diameter.

INTRODUCTION

Graphene is a well-known ideal 2D semiconductor material with excellent mechanical and electrical properties. From a mechanical point of view, single-layer graphene has high Young's modulus of 1TPa while the silicon well-known as general 3D semiconductor material indicate that of about 190 GPa, and it can sustain strain up to 25% without breaking [1]. Graphene with carbon atomic single layer has the extremely light in-plane mass density of 7.4×10^{-16} g/μm^2 [2]. Moreover, graphene indicate impermeability to standard gases including helium, and it has thermal and chemical stabilities with no dangling bonds on its surface [3, 4]. From an electrical point of view, the electron mobility of 2000000 cm^2/Vs of graphene has been predicted in an ideal situation without impurity charge and ripples, while silicon shows that of most about 1500 cm^2/Vs today [5]. At experimental level, electron mobility 10,000 to 15,000 cm^2/Vs is routinely observed for exfoliated graphene on SiO_2 on Si [6, 7].

As mentioned above, graphene with various attractive physical properties attracts the attention of researchers in electronics field all over the world. For example, graphene-based high-electron-mobility-transistors (HEMTs) offer a possibility to extend operational frequency to THz range compared with InP- and GaAs-based HEMTs of GHz range [4]. Also, graphene has essentially only the surface and all of it is exposed to surroundings, therefore the amount of change in electrical resistance due to the adsorbed molecules is very high. A lot of graphene-based chemical sensors which detects individual gas molecules or IgE protein have been reported, which detect a change in electric resistance caused by molecular adsorption [8, 9, 10, 11]. Furthermore, suspended graphene structures released from the substrate are also promising for sensor applications. For instance, the sensitivity per unit area of graphene piezoresistive pressure sensor indicates 20-100 times higher than that of other conventional sensors [12]. In addition, the small mass density and robust mechanical stiffness are ideal properties for a nano electromechanical systems (NEMS) resonator for an ultra-high sensitivity mass sensor or a radio frequency filter with tunable frequency [13, 14].

C. Chen et al. successfully demonstrated the electrically readout of mechanical resonance in MHz range for an exfoliated graphene doubly-clamped by metal electrodes at both ends [15]. High quality factor of ~10^4 was also achieved in high vacuum and cryogenic environment. The oscillators with tunable frequency which can operate at room temperature utilizing the circular drumhead of chemical vaper deposited (CVD) graphene have also been reported [14]. However, these suspended graphene resonated with high quality factor above 1000 in vacuum range of 10^{-3} Pa. It is very challenging to observe the resonance with high quality factor in atmospheric environment because energy loss of resonator increases due to air damping.

For deposition of graphene, mechanical exfoliation, CVD on nickel or copper foils, and epitaxial growth on silicon carbide were reported. CVD graphene is desirable for device application compared to mechanical exfoliation due to mass production. In order to use CVD graphene grown on a metal catalyst in combination with semiconductor devices, transfer process of graphene from the metal catalyst to an arbitrary substrate is required. Most transferred graphene used wet transfer technique which conducts transfer on an arbitrary substrate in liquid [16, 17]. However, for wet transfer to a substrate with the cavity, the liquid is trapped into the cavity and break the graphene. Therefore, in recent years, dry transfer technique have been studied, which utilizes thermal release tape or poly methyl methacrylate (PMMA) for mechanical support to transfer graphene, among them a method using PMMA is promising for maintaining the quality due to less-invasive attach and detach [18].

For mass detection using the NEMS resonator, in-plane strain control for graphene resonator is also very important. Sensing characteristic of graphene resonator can drastically improve by applying tensile strain to the suspended graphene. Minimum detection limit of adsorbed mass Δm can be expressed by the following relationship [19] :

$$\Delta m \approx 2m_0\left(\frac{b}{Q\omega_0}\right)^{1/2} 10^{-DR/20}$$

where DR is the dynamic range of the resonator and b is the bandwidth. The equation indicates that the improvement of fQ product of resonator is important for mass sensing. A tensile strain induced graphene resonator increased fQ product which was addressed both experimentally and theoretically [20, 21].

The characteristics of NEMS devices is dependent on its geometries. Suspended graphene structures employed with doubly clamped geometry or drum geometry, which means that membrane is clamped both ends of graphene and fully clamped on all edges, respectively [22, 23]. Drum graphene resonator has higher quality factor than doubly clamped one because the free edges of the doubly clamped graphene resonators is supposed to cause energy dissipation [24]. Therefore, the drum structure is an ideal geometry for the NEMS resonator with high fQ product.

In this work, we develop a graphene drum resonator with a low-pressure-sealed cavity of -1.0 atm by conducting dry transfer of graphene in vacuum condition. There are several advantages of the low-pressure-sealed drum structure. First, a low-pressure-sealed cavity provides a high quality factor of graphene NEMS resonator because air damping would be reduced. Second, in-plane strain in suspended graphene can be controlled by the cavity pressure, which means that it is induced by the pressure difference between the vacuum cavity and outside. We successfully observed mechanical resonance of the graphene drum in diameter of 30-45 μm.

DESIGN OF GRAPHENE RESONATOR

We estimated a fundamental resonant frequency of a graphene drum resonator by using finite element analysis (FEA) software COMSOL. It is difficult to predict the resonant frequency of the graphene resonator because resonant frequency of graphene membrane is very sensitive to the initial tension. This reason is that the bending rigidity of ultrathin membrane such as graphene or MoS2 drastically decreases while the contribution of the initial tension increases [25]. In this study, we estimated the resonant frequency of the graphene resonator by predicting the initial tension from experimental value reported by ref. [26]. Figure 1 shows the analysis conditions of the graphene drum. The mass density, Young's modulus and Poisson's ratio of graphene were set to 2200 kg/cm^3, 1 TPa, and 0.16, respectively. An initial tension was applied to in-plane direction from the upper edge of the graphene drum and the lower circumference was fixed constraint. First, the initial tension induced by the substrate to suspended graphene drum was calculated based on the relationship between the diameter and fundamental frequency in single layer graphene drum investigated by Barton et al. [26].

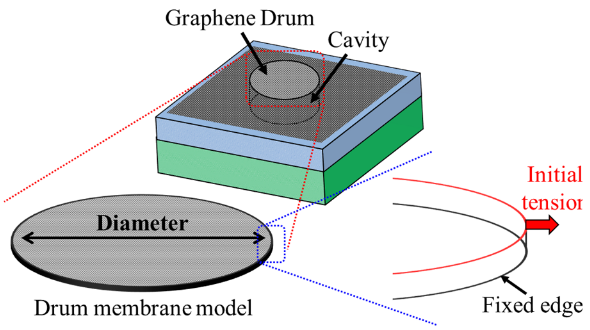

Figure 1: Schematic image of an analysis condition of graphene drum.

Figure 2 shows a graph plotting the initial tension calculated for each diameter. The initial tension was found to be about 31.5 mN/m in the diameter range of 6-16 μm. This result indicates the possibility to predict the resonant frequency of the graphene drum beforehand by considering the initial tension of 31.5 mN/m. Figure 3 shows the analytical results of the resonance frequency for each diameter of the graphene drum when an initial tension of 31.5 mN/m is applied. From this prediction, the resonant frequencies of 2.65, 2.23 and 1.68 MHz were obtained in a diameter of 30, 35 and 45 μm, respectively.

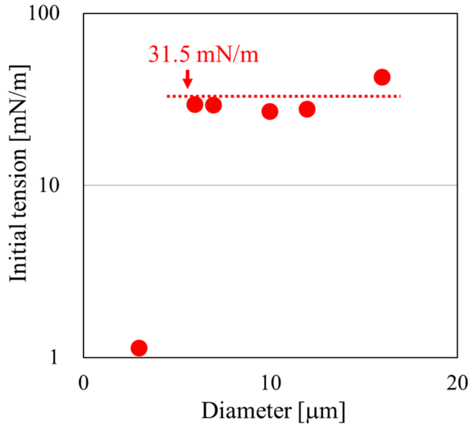

Figure 2: Analytical initial tension value for graphene drums using experimentally obtained resonant frequencies reported by ref [26].

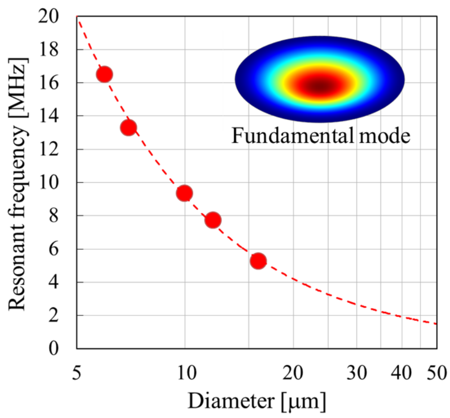

Figure 3: Prediction of fundamental resonant frequency of graphene drum resonator for each diameter at an initial tension of 31.5 mN/m.

FABRICATION PROCESS

Figure 4 shows a low-pressure dry transfer process of CVD graphene to a Si substrate with pre-patterned cavities. PMMA solution was spin-coated with a thickness of 3.0 μm on graphene/Cu foil, and Cu was etched in solution supported with polydimethylsiloxane (PDMS) block. After Cu-etch process, PDMS/PMMA/graphene was cleanly dried in air. PDMS/PMMA/graphene was transferred on a thermal-SiO_2/Si substrate with holes created by reactive ion etching (RIE) and baked on hotplate over transition temperature of PMMA in a vacuum chamber evacuated about -1.0 atm. This thermal process made softening of PMMA and adhesion improvement between graphene and substrate [18]. Also, real contact area between graphene and substrate increased, and transition temperature of PMMA decreased by evacuating air. As a result, stronger adhesion was obtained than that of atmospheric pressure process. Finally, PMMA was removed by a warm NMP-based solvent at 60 ℃. The chip was dried by CO_2

supercritical drying because wet process broke the suspended graphene by the surface tension generated during liquid drying without supercritical drying. We successfully obtained suspended graphene by using CO_2 supercritical drying.

Subsequently, the graphene and the top electrodes were patterned by standard photolithography in order to make electrical contact with graphene. Although spin coat of photoresist broke large-size graphene drums above 8 µm in diameter, it was confirmed that the drum structures with a diameter up to 6 µm were successfully maintained. We note that a supercritical drying was always used for drying the chip after resist removal.

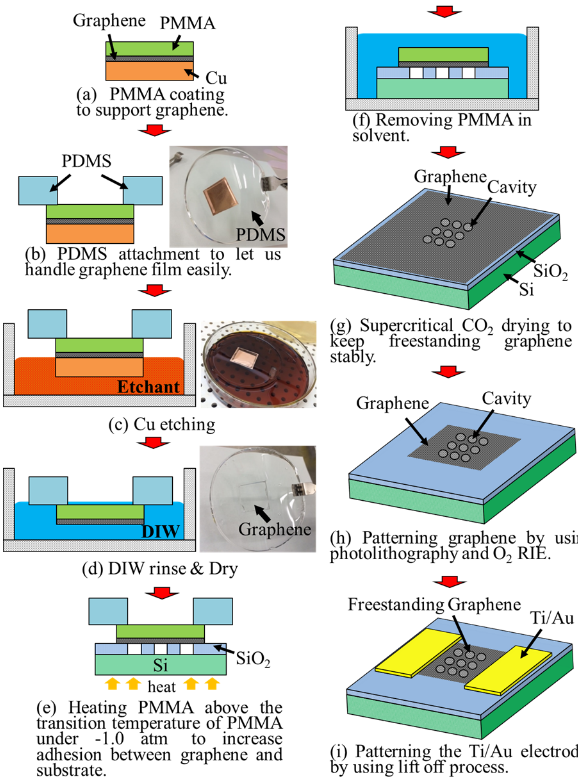

Figure 4: Fabrication process for proposed graphene resonator array by using low-pressure dry transfer technique.

RESULT AND DISCUSSION

Figure 5 shows SEM images of the sealed cavity graphene resonators developed by dry transfer technique. Maximum resonator size of 45 µm in diameter with gap length of 810 nm was obtained. Although the defect of the graphene was seen in a part of the field, the freestanding graphene drum can be observed on the cavity. This aspect ratio defined as drum diameter per gap depth was 55.5, which is 2.28 times higher than previously reported drum structure by dry transfer technique from Ji Won Suk [18]. The aspect ratio of the structure is important for NEMS devices because the electromechanical transduction factor meaning conversion efficiency at converting the electrical energy into mechanical motion is inversely proportional to the square of gap depth while proportional to the surface area [27]. Figure 6(a) shows Raman spectra of freestanding graphene to estimate a quality of graphene. Raman

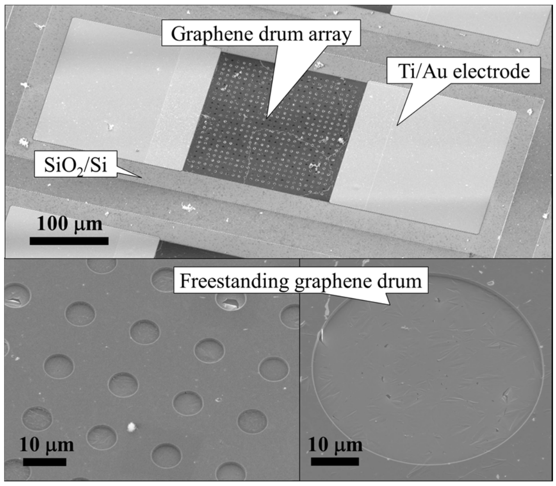

Figure 5: SEM images of developed graphene drum resonators. Maximum diameter of 45 µm with gap length of 810 nm was obtained.

spectroscopic measurement is commonly used for evaluation of a quality of graphene, such as number of layers, defects, lattice distortion. The spectral peak peculiar to graphene is a G peak near 1590 cm^{-1} and a 2D peak near 2700 cm^{-1}, and a D peak around 1350 cm^{-1}. The number of layers of graphene can be estimated from the 2D/G ratio and the defect amount can be estimated from the G/D ratio. The 2D/G ratio of 1.73 and few D peaks were shown in figure 6, which indicate that a high quality single layer

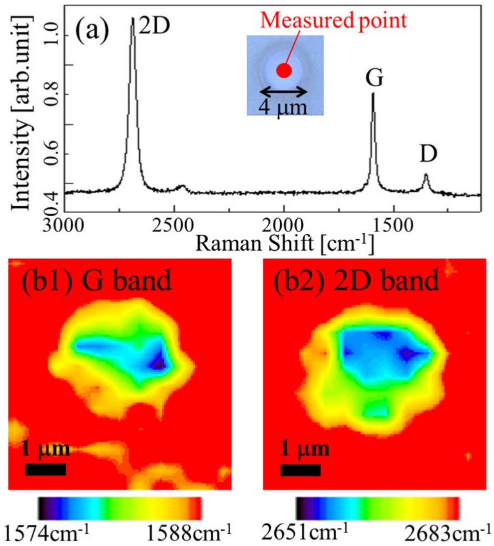

Figure 6: (a) Raman spectrum of freestanding graphene and (b) Raman maps of G- and 2D-band peak positions in the cavity with 4 µm diameter.

graphene drum was successfully developed in this work.

Figure 6(b) shows Raman maps of the G- and 2D-band peak positions of graphene transferred on to circular cavity with a diameter of 4 µm. Biaxial strain was developed in only cavity area. On the basis of previously measured shift rates [28], a maximum G-band shift of 12cm^{-1} indicates about 0.16 % strain and 2D shift of 38 cm^{-1} indicates about 0.19 % strain. Also, pressure difference develops strain in graphene with a rate of 0.19 %/bar from previous study [29]. Therefore, this strain indicated that the cavity kept vacuum condition and pressure difference applied the strain into graphene drum.

Figure 7 characterizes the resonance frequency by using a laser Doppler vibrometer in a vacuum chamber evacuated to pressure of about 6.0×10^{-2} Pa. We obtained fundamental resonance frequencies range of 0.74-1.36 MHz with the quality factor of about 300 with 30-45 μm in diameter. We confirmed that the resonance frequency was increased in accordance with decreasing the cavity diameter.

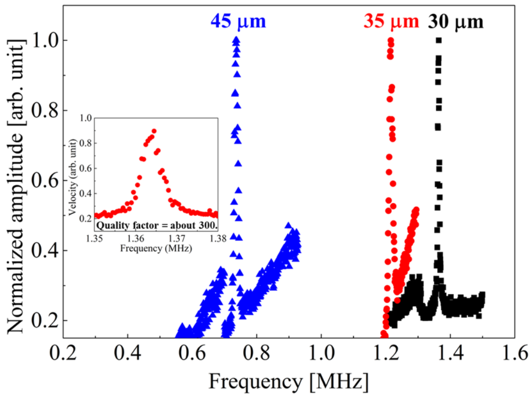

Figure 7: Resonance frequency of graphene drum in each diameter measured by using a laser Doppler vibrometer in a vacuum chamber at room temperature. Inset shows the highest quality factor peak observed with 30 μm in diameter graphene drum.

These results almost agree with analytically predicted resonant frequency range of 1.68-2.65 MHz by finite element analysis as shown in Figure 8. Therefore, we successfully developed a large-area graphene drum resonator by low-pressure dry transfer technique and demonstrated the prediction method of fundamental resonant frequency for graphene resonator by conventional FEA.

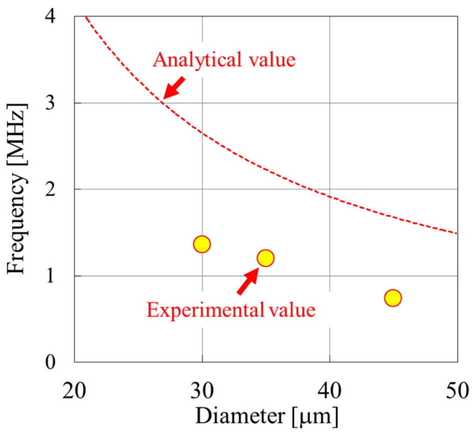

Figure 8: The comparison of analytical resonant frequency by FEA and obtained experimental value.

CONCLUSION

We developed cavity-sealed single-layer graphene drum resonator by using low-pressure dry transfer technique. Maximum diameter of 45 μm with gap length of 810 nm was obtained. We demonstrated fundamental resonance frequency ranges of 0.74-1.36 MHz with a quality factor of about 300 with 30-45 μm in diameter. The observed fundamental resonant frequency almost agree with analytically predicted resonant frequency range of 1.68-2.65 MHz by finite element analysis considering the initial tension of 31.5 mN/m.

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