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Epitaxial graphene resonators obtained by electrochemical etching

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1. Introduction

Graphene is an ideal material for use in nano-electromechanical systems (NEMS) owing to its very high stiffness and low mass density. Recently, the fundamental vibrational properties of NEMS resonators made from graphene have been intensively studied with systems fabricated from exfoliated graphene flakes [1-3]. This is because this simple production method, exfoliation, helps us to easily create high-quality graphene flakes. However, this method has no ability to arbitrarily control the shape, thickness, and homogeneity of graphene. On the other hand, epitaxial growth on a silicon carbide (SiC) substrate allows us to create large uniform graphene sheets. Furthermore, by combining this method with an electrochemical wet etching process for SiC, we can design the resonator structure at will. In fact, doubly clamped beams and its array structures have been successfully created on SiC substrate [4]. However, it has been reported that these processes induce disorder in graphene, which may degrade resonator performance.

In this study, we investigate vibrational properties of graphene resonators fabricated using the combination of epitaxial growth and wet etching. To create graphene resonators without disorder, we try to establish a fabrication method by further adding a hydrogen intercalation scheme for decoupling the Si-C bonds [5]. Note that in a buffer layer some carbon atoms are bound to silicon atoms of the substrate, which is a possible cause of the disorder induced via the wet etching of SiC. Using a transmission electron microscope (TEM), we directly observe the layer structure of graphene resonators created with the above method. We further examine the quality of our graphene layer using Raman spectroscopy. Finally, we discuss the vibrational properties, such as the fundamental frequency and quality factor, of our graphene resonators.

2. Experimental

Figures 1(a)-(d) schematically illustrate our samples in the following fabrication processes: Graphene was grown epitaxially on the silicon face of n-type 4H-SiC substrates by heating the substrate in ultra-high vacuum [Fig. 1(a)]. Double-clamped beam structures were then patterned on the epitaxial graphene by photolithography and reactive-ion etching using CF_4 [Fig. 1(b)]. Next, hydrogen was intercalated to decouple the epitaxial graphene from its substrate, as illustrated in Fig. 1(f), and Au/Cr (200 nm/5 nm) film was deposited as a mask for the wet etching [Fig. 1(c) and (d)]. Note that as shown in Fig. 1(g) our graphene was patterned to a bow-tie-shaped beam. The electrochemical wet etching was performed using the patterned graphene on SiC and a Pt wire as the anode and cathode, respectively. Here, voltage was applied between them with a constant current density of 1 mA/cm^2 and monitored by using Ag/AgCl reference electrode. The Xe-UV light was irradiated on the sample to generate electron-hole pairs for the enhancement of the etching reaction. The electrolyte was 1wt% aqueous KOH solutions. We performed the etching for 6 hours.

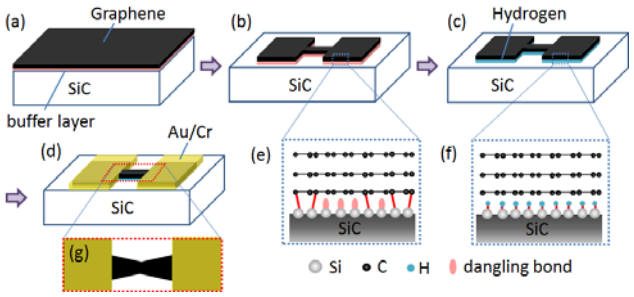

Fig. 1. (a)-(d) Schematic drawing of the sample in each fabrication process. (e)-(f) Side-view models of the epitaxial graphene before (e) and after (f) the hydrogen intercalation. (g) Magnified image of the sample schematically shown in Fig. 1(d).

3. Results and Discussion

We first characterized the etched structure with a scanning electron microscope (SEM) and TEM. Figure 2(a) shows an SEM image (tilted at 55 degrees) of an etched epitaxial graphene. We can here see that the double-clamped graphene beam 7.6 μm in length and 3.7 μm in maximum width is successfully suspended between Au/Cr pads. White flakes observed on the graphene are photoresist residues. Figure 2(b) shows a cross-sectional TEM image of the suspended graphene. Trilayer graphene is clearly observed in the TEM image, where each black line represents a graphene layer. Low-energy electron microscopy revealed that before the wet etching bilayer graphene and a buffer layer had been formed on the SiC substrate as shown in Fig. 1(e). This result and the TEM image in Fig. 2(b) indicate that the number of layers before and after the etching process was unchanged. We thus conclude that the buffer layer served as the suspended graphene.

Next, based on Raman spectroscopy, we discuss the property of the graphene layer in each fabrication process. We compare the spectra of the unstrained trilayer graphene and both the epitaxial and suspended graphene. For the unstrained graphene, G peak at 1587 cm^{-1} and 2D peak at

2698 cm^{-1} were observed [6]. We found that the epitaxial graphene showed a blue-shift of G (2D) peak at 1599 (2736) cm^{-1}. From this result, we estimate the compressive strain to be about 0.5 %. The finite magnitude of this quantity can be attributed to the large difference in the thermal expansion coefficients between graphene and SiC. In contrast, for the suspended graphene, red-shifts of the G and 2D peaks were found at 1585 and 2701 cm^{-1}, respectively. The estimated compressive strain decreases to about 0.04 %, indicating that stress is released as a result of the successful wet etching. Regarding disorder of graphene that results in a D peak in the spectra, the D peak was observed after the etching process but not before it. This suggests that the wet etching process induces disorder. We thus suspect that our intercalation was not sufficient for removing all Si-C bonds. The imperfect intercalation was also suggested by the Raman spectra of the intercalated graphene before the etching, where a small red-shift of the G (2D) peak at 1597 (2727) cm^{-1} was observed. Hence, we need to optimize the intercalation conditions. .

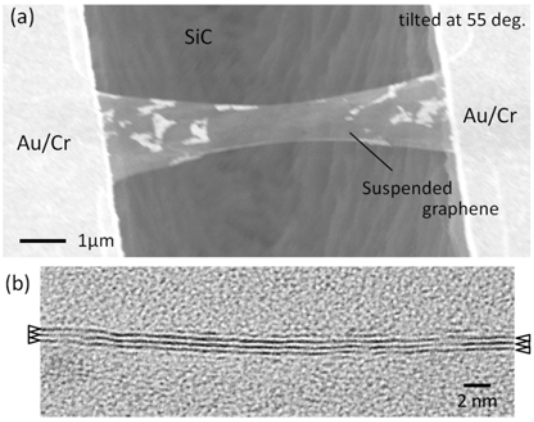

Fig. 2. SEM image tilted at 55 degrees (a) and cross-sectional TEM image of the suspended graphene (b). White triangles indicate graphene layers.

Finally, we discuss vibrational properties of the graphene resonator. We induced the vibration of the resonators by using piezo-actuator and then detected it by monitoring the reflected light intensity. Figure 3 shows the amplitude versus frequency of the induced vibration at room temperatures (RT) under a vacuum of $\sim 10^{-5}$ Pa. From a fit to a Lorentzian, we evaluated the quality factor Q to be about 600 and a resonant frequency f_o = 7.52 MHz. The obtained Q factor is as high as those measured at RT in previous studies [1-4]. Higher Q factors will be obtained if photoresist residues can be removed. The fundamental resonance mode f_o for mechanical resonators under no tension is given by [7]

$$f_o = At/L^2 (E/\rho)^{1/2}, \qquad (1)$$

where the length L and thickness t of our graphene beam are 7.6 μm and 1.0 nm, respectively. The clamping coefficient A is 1.03 for doubly clamped beams. Using Young's modulus E = 1 TPa and mass density ρ = 2200 kg/m^3 of bulk graphite as parameters [8], we calculated f_o to be 0.37 MHz. Considering precisely the bow-tie shape of beams, we performed a finite element analysis, and then obtained almost the same f_o value of 0.43 MHz. However, the observed f_o value of 7.52 MHz is over ten times higher than these calculated values. Although mechanical resonators under tension show higher f_o values [1], our graphene on SiC is under compressive strain as mentioned above. Shivaraman *et al.* have observed resonators with a buckled shape and side-flanges and concluded that these deformations lead to an increase in the stiffness of the beams [4]. We also found bends in graphene along its width in close-up SEM images of our resonators, suggesting that the high f_o value is due to deformation of the suspended graphene.

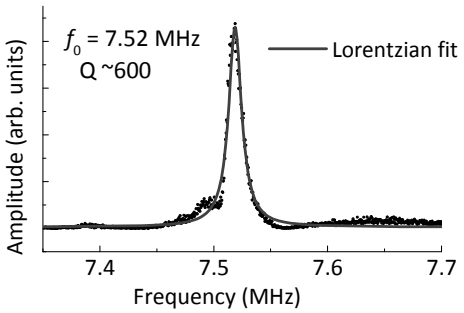

Fig. 3. Amplitude versus frequency for a suspended graphene.

4. Conclusion

We investigated vibration properties of resonators fabricated from epitaxial graphene by using electrochemical etching and hydrogen intercalation. We directly measured the layer structure of the graphene resonator using TEM and clarified that the buffer layer worked as the suspended graphene after the wet etching process. We found that the resonant frequency of the fundamental resonance mode is much higher than expected from the standard beam theory, which is attributed to the deformation of the beam. Raman spectra indicated that our intercalation scheme did not perfectly suppress the introduction of disorder in graphene due to the wet etching. In the future, we will optimize the conditions of the hydrogen intercalation to create higher quality graphene resonators.

Acknowledgement

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