

Development of atomically thin optical devices with graphene for astronomical applications

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ABSTRACT

High-speed atomic oxygen (AO) irradiation tests were performed for free-standing graphene membranes to investigate the degradation in terms of mechanical intensity for astronomical applications. The high-speed AO was irradiated with a typical velocity of 5 km/s and fluence values of 3×10^{15} , 1×10^{16} , 3×10^{16} , and 1×10^{17} atoms/cm². Two kinds of samples were prepared using single- and bi-layer graphene sheets with through-hole patterns with diameters of 10 μm and 10-200 μm , respectively. Consequently, the yield rate is found to be approximately 90% and 100% for the single- and bi-layer free-standing graphene samples, respectively. Almost all ruptured events occurred after the minimum fluence of 3×10^{15} atoms/cm². The results suggest that the lifetime of the free-standing graphene structure can be longer by increasing the number of layers or any other causes such as accelerated metal outgassing contaminants remaining the vacuum chamber and detonation waves are not negligible and almost no damages are seen through the high-speed AO irradiation up to the fluence value of 1×10^{17} atoms/cm². To improve the sensitivity, our original transfer method was introduced and we fabricated 300 / 900 μm diameter free-standing single- / bi-layer graphene structures successfully. Additionally, we confirmed that our technique can be applied to ground-based applications such as high-sensitivity graphene Transmission Electron Microscopy (TEM) support films.

Keywords: graphene, X-ray astronomy, high-speed atomic oxygen, thin-film devices

1. INTRODUCTION

Thin-film optical devices have been widely used in a variety of fields including astronomy and actually on board, for example, X-ray satellites^{1,2} as passive temperature control systems and optical blocking filters. For such mission payload instruments, not only tolerance for severe space environments such as thermal cycles, UV, high-speed atomic oxygen (AO), and high-energy particles, but also higher performance is needed at the same time. In the case of X-ray astronomy, the transmission of filters especially in a soft X-ray energy band below 1 keV sometimes limits the instrument sensitivity and thus new approaches have been desired because interesting astronomical objects such as stars³, supernova remnants⁴, and galaxies^{5,6} mainly emit soft X-rays.

Recently, as a new approach, ideas to replace conventional polymeric materials with new materials have been proposed. Barbera et al. (2022)⁷ proposed to utilize carbon nanotube (CNT), which shows low-energy X-ray transparency, high mechanical strength, and excellent thermal conductivity, and succeeded in fabricating a small, aluminum-coated, free-standing pellicle membrane and quantitatively demonstrating the effectiveness of X-ray transparency.

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Kashiwakura et al. (2024)⁸ proposed to utilize atomically thin graphene to realize ultimately high X-ray transparency. In this study, they explored the potential of atomically thin graphene to achieve ultimately high X-ray transparency. As a first step, they focused on the tolerance of high-speed AO which can be exposed directly during the launch and in orbit because AO is a major component of the atmosphere at altitudes of 200 to 600 km. In such a situation, the AO flow velocity is expected to be very fast, specifically about 8 km/s, which corresponds to about 5 eV at an altitude of 500 km, and AO is known to induce various complex chemical and physical reactions with polymer materials.⁹ Kashiwakura et al. (2024)⁸ reported that they quantitatively evaluated the degradation of graphene using Raman spectroscopy and demonstrated that the degradation occurs significantly between 2×10^{17} and 1×10^{18} atoms/cm². However, the study was performed only for the single-layer graphene sheets on the SiO₂/Si substrates. Therefore, in this study, we prepared not only single- but also bi-layer free-standing graphene samples with a various diameter and conducted high-speed AO irradiation tests for the first time.

2. EXPERIMENTAL METHOD

2.1 Sample

The samples we used in this study consisted of a single- or bi-layer graphene sheets and a quartz substrate. The single-layer graphene sample was fabricated in the following manner: firstly formed on a Cu/sapphire substrate through chemical vapor deposition¹⁰, followed by the coating and baking of a polymethyl methacrylate (PMMA) protective film at a temperature of 180°C for 1 min. Thereafter, the Cu/sapphire substrate was then etched with ammonium persulfate, followed by pure water rinsing, transfer to a quartz substrate, and finally removal of the PMMA protective cover with acetone. The bi-layer graphene sheet was fabricated by transferring a single-layer graphene sheet with the PMMA protective cover to another single-layer graphene sheet on the Cu/sapphire substrate and then the same process described above was conducted. The quartz substrate is 10 mm × 10 mm in size and 0.2 mm thick. Figure 1(a) shows a schematic diagram of the quartz substrate, and (b) shows an optical microscope image of the bi-layer graphene sample on the quartz substrate. The quartz substrate is perforated with through holes, which makes it possible to realize free-standing graphene structures. We prepared two kinds of quartz substrates with different patterns of 25 holes with a diameter of 10 μm and 5 holes with diameters of 10, 20, 30, 40, 50, 75, 100, 200, 250 and 300 μm for the single- and bi-layer graphene samples, respectively as shown in Figure 1(c). The large-size free-standing graphene structure was fabricated using the bi-layer graphene sheets.

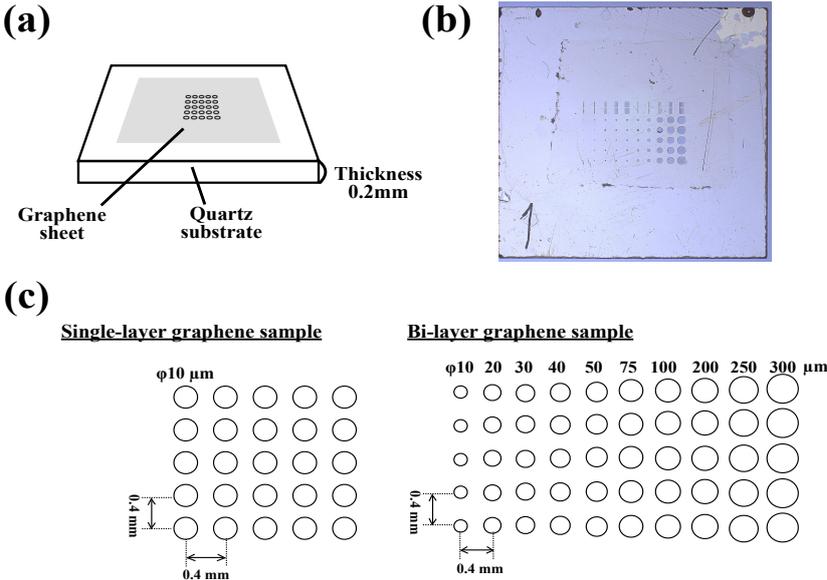


Figure 1. (a) Schematic diagram of the single-layer graphene sample transferred to the quartz substrate. (b) Example of an optical microscope image of the bi-layer graphene sample transferred to the quartz substrate. (c) Schematic diagrams of through-hole patterns on the quartz substrates with single- (left) and bi-layer (right) graphene sheets.

The fabricated graphene samples were observed by Scanning Electron Microscopy (SEM) and the SEM images of the single- and bi-layer free-standing graphene structure are shown in Figure 2. The SEM observations were performed with a voltage of 1.00 kV. It is found that some of the samples had small cracks and were heavily fractured.

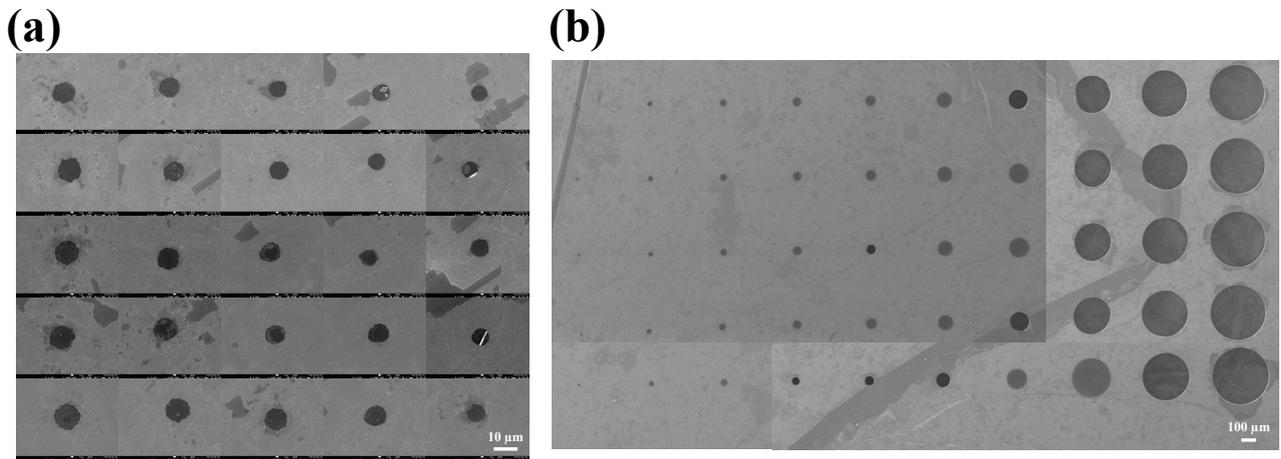


Figure 2. SEM images of the single- (left) and bi-layer (right) graphene samples.

Next, to prevent erosion from the edges of the graphene sheets and limit an irradiation area, the sample was mounted in an aluminum jig as shown in Figure 3.

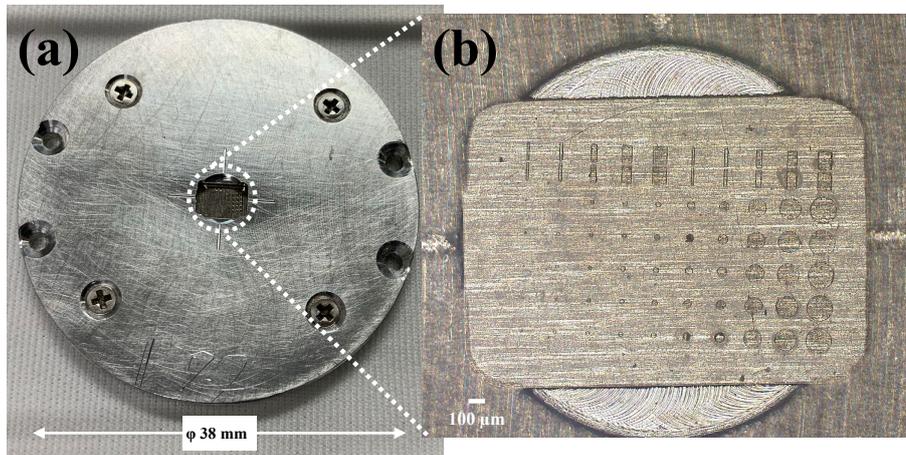


Figure 3. (a) Overview of the graphene sample covered by the aluminum jig. (b) A close-up view of a central part of (a).

2.2 High-Speed Atomic Oxygen Irradiation Tests For Free-Standing Graphene Structures

In the upper atmosphere, UV radiation from the sun dissociates oxygen molecules and produces AO. At altitudes from about 200 km to 600 km, the AO is the dominant component of the atmosphere, accounting for more than 80 % of the air at an altitude of about 400 km.¹¹ The AO with an energy of 4 - 5 eV is expected to give rise to numerous chemical and physical interactions on the graphene sheet known as erosion for polymeric material, resulting in degradation of physical properties such as mechanical intensity.^{8,9,11}

Here, we investigated the impacts of high-speed AO for the free-standing graphene structure assuming a low orbit case at an altitude of ~ 500 km corresponding to a relative velocity of ~ 8 km/s and a kinetic energy of ~ 5 eV. We utilized a laser detonation AO beam source at Kobe University¹² as is the case with the previous work⁸. In this paper, the single- and bi-layer free-standing graphene samples were exposed to high-speed AO and their yields after the irradiation tests were evaluated for the first time. Considering the previous study, high-speed AO was irradiated with fluence values of 3×10^{15} , 1×10^{16} , 3×10^{16} , and 1×10^{17} atoms/cm². Note that the irradiation fluence of 3×10^{15} atoms/cm² corresponds to the minimum value in our experimental setup. To determine the energy distribution under irradiation, the time of flight (TOF) of ionized high-speed AO was measured using a quadrupole mass spectrometer positioned downstream of the high-speed AO beamline. The velocity was derived from the TOF, and the average velocity was calculated to be approximately 5 km/s.

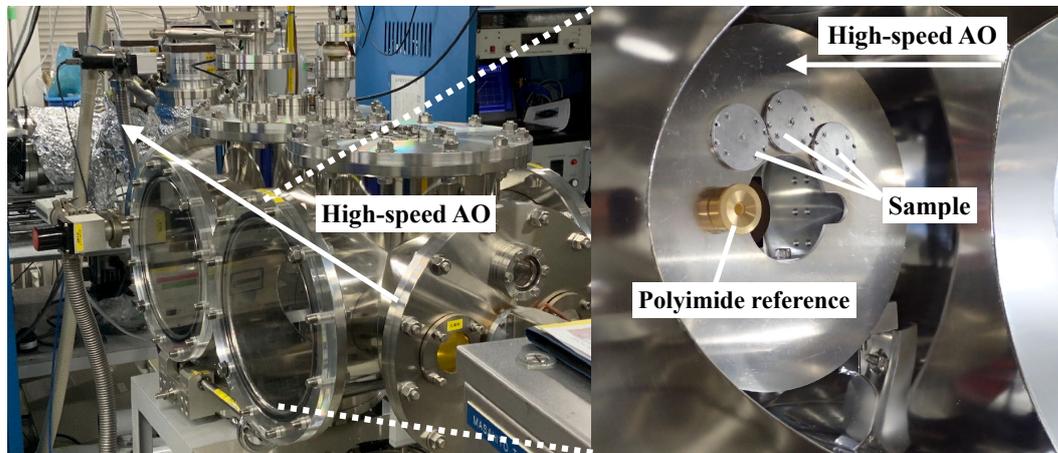


Figure 4. Left: overview of the high-speed AO irradiation test facility.⁷ Right: single- and bi-layer graphene samples covered by the aluminum jigs and a polyimide reference sample in the sample chamber.

3. RESULTS & DISCUSSION

After the high-speed AO irradiation experiments, we investigated surface conditions and measured yield of intact free-standing structures based on SEM images. The observed yield of the free-standing graphene structures for each high-speed AO irradiation fluence is shown in Table 1. Consequently, the yield rate for the single-layer graphene sample with $\phi 10$ μm holes was about 90% at a high-speed AO fluence of 1×10^{17} atoms/cm², and no significant changes were found for the bi-layer graphene sample up to the fluence value of 1×10^{17} atoms/cm². The results are consistent with our previous study that the significant degradation was seen in their Raman spectra of the single-layer graphene sample between 2×10^{17} and 2×10^{18} atoms/cm². Figures 5 and 6 show some examples of SEM images for intact and ruptured structures, respectively.

Table 1. Yields of the free-standing graphene structures for each high-speed AO irradiation fluence.

Layer	Hole size	# of holes ¹	Total fluences [atoms/cm ²]			
			3×10 ¹⁵	1×10 ¹⁶	3×10 ¹⁶	1×10 ¹⁷
Single-layer	φ10 μm	48 (50)	44	44	44	43
Bi-layer	φ10 μm	4 (5)	4	4	4	4
	φ20 μm	5 (5)	5	5	5	5
	φ30 μm	5 (5)	5	5	5	5
	φ40 μm	4 (5)	4	4	4	4
	φ50 μm	3 (5)	3	3	3	3
	φ75 μm	4 (5)	4	4	4	4
	φ100 μm	3 (5)	3	3	3	3
	φ200 μm	1 (5)	1	1	1	1

Note: ¹ The total number of holes in design assuming 100% yield is also shown in parentheses.

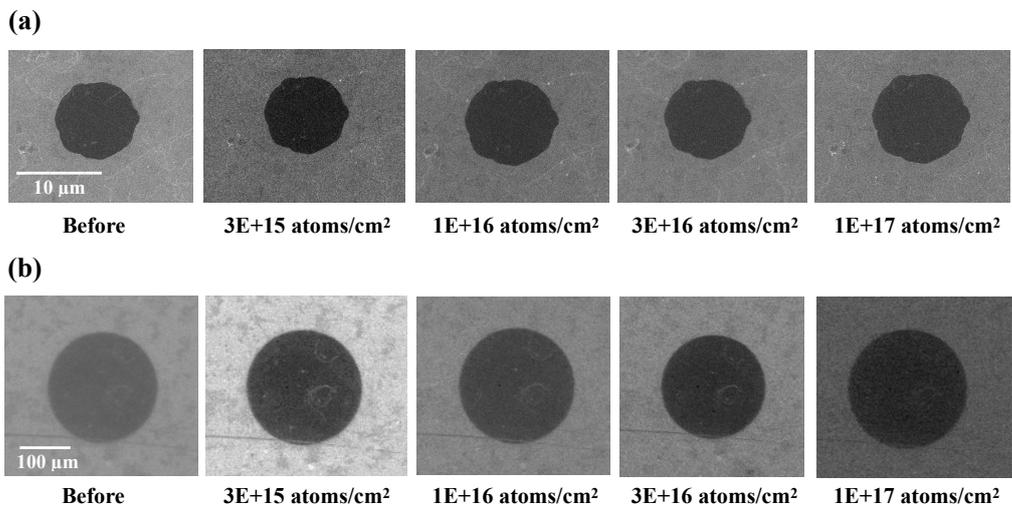


Figure 5. (a) Examples of SEM images of a φ10 μm free-standing structure in the single-layer graphene sample and (b) a φ200 μm free-standing structure in the bi-layer graphene sample before and after the high-speed AO irradiation tests.

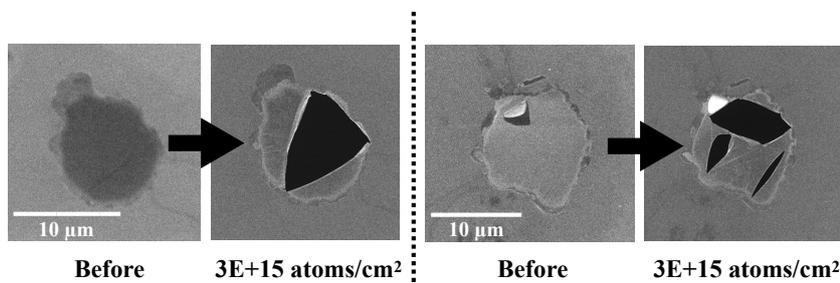


Figure 6. Examples of SEM images of φ10 μm free-standing structures in the single-layer graphene sample which show significant changes before and after the high-speed AO irradiation tests with a fluence of 3E+15 atoms/cm².

For five ruptured structures, four of them occur after the minimum fluence of $3E+15$ atoms/cm² and two had cracks initially before the irradiation tests and the free-standing structures were torn off along the cracks. Thus, there are two scenarios to explain our results. One is that only free-standing structures in the single-layer graphene sample with relatively small holes were broken, which suggests that the lifetime of the free-standing graphene structure can be longer by increasing the number of layers. Another is that any other causes such as accelerated metal outgassing contaminants remaining the vacuum chamber and detonation waves are not negligible for our results and almost no damages are seen through the high-speed AO irradiation up to the fluence value of 1×10^{17} atoms/cm².

4. FUTURE PROSPECTS

In the high-speed AO irradiation tests, we plan to conduct tests at a fluence of 1×10^{18} atoms/cm² or more and try to measure physical properties directly.

In addition, we have been working on establishing a unique transfer process aimed at realizing large-area free-standing graphene samples for ground- and space-based applications. In our current status, we have succeeded in forming free-standing graphene membranes with diameters of 300 and 900 μm using single- and bi-layer graphene sheets, respectively, as shown in Figure 7. As an example of a ground-based application using a large-area free-standing graphene membrane, we prepared *Transmission* Electron Microscope (TEM) grids with a large hole width of 100 μm covered with a bi-layer graphene membrane and nano-scale Pt particles were formed on the membrane by a sputtering method. A comparison of TEM images covered with different membranes with different thicknesses of 0.6 (bi-layer graphene), 15 (carbon), and 15-30 (collodion) nm is shown in Figure 8. The contrast becomes clearly with reducing the thickness.

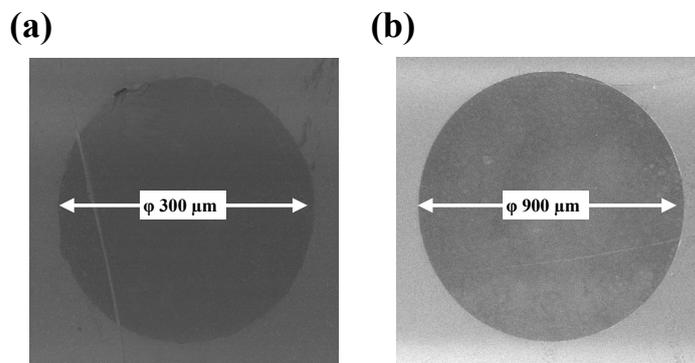


Figure 7. Free-standing graphene membranes with diameters of (a) 300 μm and (b) 900 μm using single- and bi-layer graphene sheets, respectively.

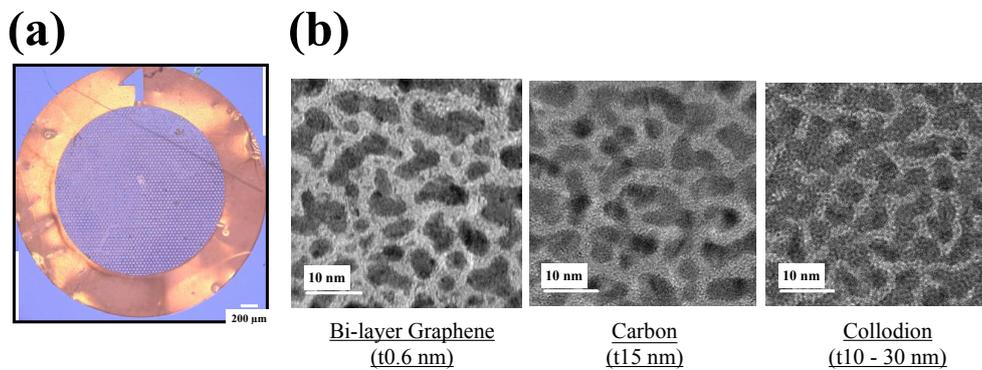


Figure 8. (a) TEM grids with a hole width of 100 μm covered with the bi-layer graphene. (b) TEM images of nano-scale Pt particles prepared by a sputtering method.

5. SUMMARY

Thin-film devices play an important role in X-ray astronomy and actually has been on board a variety of missions as passive temperature control systems and optical-blocking filters in mission payload systems. Polyimide and other polymer materials have been used, but there is still plenty of room for improvement in terms of transmittance in the soft X-ray energy region (especially ≤ 1 keV). Therefore, we proposed to utilize atomically thin graphene with very high mechanical strength instead of polymeric materials, to achieve ultimately high X-ray transmittance.

In this paper, high-speed AO irradiation tests were performed for the freestanding graphene structures to understand degradation in terms of mechanical intensity assuming the LEO case with fluence values of 3×10^{15} , 1×10^{16} , 3×10^{16} , and 1×10^{17} atoms/cm². We prepared two kinds of the samples using single- and bi-layer graphene sheets with diameters of $\phi 10$ μm and $\phi 10$ -200 μm , respectively. Consequently, the yield rate is found to be approximately 90% and 100% for the single- and bi-layer free-standing graphene samples, respectively. Almost all ruptured events occurred after the minimum fluence of 3×10^{15} atoms/cm². The results suggest that the lifetime of the free-standing graphene structure can be longer by increasing the number of layers or any other causes such as accelerated metal outgassing contaminants remaining the vacuum chamber and detonation waves are not negligible and almost no damages are seen through the high-speed AO irradiation up to the fluence value of 1×10^{17} atoms/cm².

Additionally, we have been working on establishing a unique transfer process aimed at realizing large-area free-standing graphene for ground- and space-based applications. We achieved free-standing graphene membranes with diameters of 300 and 900 μm using single- and bi-layer graphene sheets, respectively. Furthermore, we confirmed that the TEM images using the TEM grids covered with the bi-layer graphene membrane show the highest contrast for nano-scale Pt particles.

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