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GAS PERMEABILITY MEASUREMENT OF GRAPHENE FILMS*

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Abstract

Graphene has extremely high strength and thermal conductivity, which can possibly be used for high-power beam window in accelerator. In this paper, gas permeabilities of different graphene films have been measured by the permeation measurement facility. According to the results, the possibility of the graphene-made beam windows will be discussed.

INTRODUCTION

In large particle accelerators, beam windows are usually used to isolate the high-vacuum environment and other atmospheric environments. Its design requirements mainly contain heat dissipation, mechanical strength, irradiation lifetime, etc.[1]. The commonly used window materials are Beryllium (such as the interface between the beam line and the accumulating ring in BEPC II), Nickel alloys, Aluminum alloys (such as the proton beam window and neutron beam window in CSNS[2,3]), etc.

With the development of high-intensity and high-power accelerators, existing beam windows will not meet requirements in terms of thermal conductivity, light transmission performance, etc. Graphene is currently the thinnest and hardest nano material with the best electrical and thermal conductivity properties. Meanwhile, large-scale graphene production technology is becoming more and more mature[4]. The application of graphene to the high-power beam window will solve the problems of heat dissipation and strength, etc, and will bring new technological breakthroughs to the development of the beam window.

The heat dissipation, vacuum performance and pressure resistance of the graphene window need to be verified experimentally to provide data support for the pre-study, selection and design of the beam window. Therefore, this article has done the following work. The permeability of the films including the substrate material PET with a thickness of 180 μm, the 180 μm PET substrate with a few layers CVD graphene attached, 180 μm PET substrate with 2 μm graphene film attached and 100 μm graphene film were measured by a differential pressure method, meanwhile, the diffusion coefficient, solubility and permeability of different films were obtained by Fourier series method. Based on these results, the vacuum performance parameters of several films are analyzed and compared.

GAS PERMEABILITY

A monolayer graphene membrane is impermeable to standard gases including helium[5]. The gas permeability of the large-scale graphene film, especially the commercially available graphene product on the market requires a thorough study. Parameters that characterize the vacuum properties of the film material include helium leakage rate of the film material, diffusion coefficient, solubility and permeability and so on. The leakage rate of film can be measured with a helium mass spectrometer leak detector under normal conditions. However,the thin film is a flexible material, it is greatly influenced by the time of pumping during the measurement process, and the leakage rate of the film will change at different time. So only when the value of the diffusion coefficient, solubility, and permeability of the film reach an equilibrium state,the measured gas permeability of the film under a certain atmosphere is veritable.

Principle of Gas Permeability Measurement and Data Processing

In the vacuum field, $\boldsymbol{Q}$ is the leak rate, which represents the amount of gas entering the vacuum system per unit of time. Ignoring the case of system outgassing, we can see that

$$Q = \frac{dp}{dt} V \ . \tag{1}$$

V is the volume of the measured chamber.

$$\frac{dp}{dt} = K \frac{A}{V} \frac{P_0}{h} \ . \tag{2}$$

Where $\boldsymbol{K}$ is the permeant rate, which characterizes the gas permeant velocity of the specimen in equilibrium, h is the thickness of the specimen, $\boldsymbol{A}$ is the effective area of the specimen with gas permeation, and $\boldsymbol{P_0}$ is the pressure in the high pressure chamber.

After leaking for a long time, the dissolution and the diffusion is in an equilibrium state, the relationship between the gas pressure and the measured time is regarded as approximately linear [6,7], the gas pressure in the measured chamber at any time is

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$$p = P_0 \frac{ADS}{Vh}\left(t - \frac{h^2}{6D}\right). \quad (3)$$

D is the diffusion coefficient of the specimen. ***S*** is the solubility coefficient.

If this beeline is extended, the intercept at the time and the pressure axes is t_c and p_c, respectively. Thus the diffusion coefficient ***D*** and the solubility ***S*** are:

$$D = \frac{h^2}{6t_c} \qquad S = -\frac{6V}{Ah}\frac{p_c}{P_0} \quad (4)$$

Finally the permeant rate ***K*** is

$$K = DS = -\frac{Vh}{AP_0}\frac{p_c}{t_c}. \quad (5)$$

The data processing is as follows:Use Labview for data acquisition, draw the curve of the *p-t*. Then select the data of equilibrium state and perform linear fitting to obtain a straight line:

$$p' = kt + b. \quad (6)$$

Put *t=0* and *p'*=0 into the relation (6), get

$$p_c = b; t_c = -b/k. \quad (7)$$

Bring the results into Eq.(1), Eq. (4) and Eq.(5) to get the values of ***Q, D, S,*** and ***K***.

To obtain the stable value, *dp/dt*, in the equilibrium state, an attenuation exponent function is used to fit the curve *dp/dt-t*

$$y = A_1 \exp\left(-\frac{x}{t_1}\right) + y_0. \quad (5)$$

As a result of similar fitting, the slope of the straight line, *k,* is close to y_0, which indicates that the fitting result is effective.

Measuring Facility and Measurement Procedure

Using the differential pressure method, the measuring facility was built as shown in Fig.1, V1 is a high pressure chamber, V2 and V3 are measurement chambers whose volume are much larger than V1; P1 and P2 are vacuum gauges to detect the pressure of measured chamber and high pressure chamber; RGA is residual gas analyzer ; F is film to be tested, sealed by fluorine rubber seal;GV1,GV2 and GV3 are all metal angle valves to control the direction of gas flow; Meanwhile, GV4 is a safety valve and work pressure is 0.11 MPa, when the pressure is large than 0.11 MPa, it will be opened to protect the film.

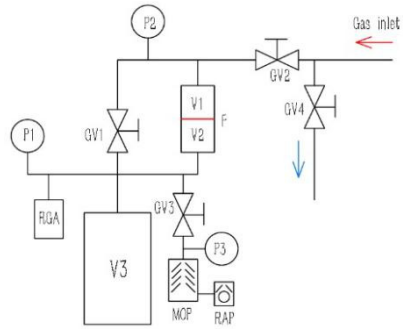

Figure 1: Schematic diagram of the permeation measurement facility.

The Measurement Procedure is as follows:

Step 1: After installation and leak detection, measure the leakage rate at the clamping point of the film flange and front of the film;

Step 2: Open GV1, GV3 valve, close the GV2 valve, start the dry pump, start the molecular pump when the vacuum degree is less than 100 Pa. And then after 3 hours of normal operating of the molecular pump, bake the entire vacuum chamber and its connecting pipelines to 300°C with the heating rate of 0.5 °C/min. Cool down the facility to room temperature after 24 hours of baking;

Step 3: Measure the *p-t* curve (background), and use RGA to perform gas analysis in the vacuum chamber to ensure that the vacuum chamber is free from contamination;

Step 4: Close GV1, open GV2, inflate 1 atm of helium, close GV2, record *p-t* curve;

Step 5: With the method of Fourier series in the Reference [6] to process the data, obtain the permeation rate, the solubility, the diffusion coefficient of different thin films to helium gas;

Step 6: Using the Eq.(1), calculate Q_1 caused by the vacuum chamber background, and Q_2 caused by the film ventilation (including the vacuum chamber background) .Then the film's leak rate can be obtained, $Q=Q_2-Q_1$.And then compare the value Q by helium mass spectrometer leak detector;

Step 7: Change the different films and repeat 1-6 steps, we can get the vacuum performance parameters of different films; By inflating different test gases, we can get vacuum performance parameters of different films for different gas;

Step 8: Compare the above data and get valid conclusions.

Measurement Results and Analysis

The pressure and time curves of the different films were measured using the facility and measurement method described above, including: **a)** The 100 μm graphene film, **b)** The 2 μm graphene film on 180 μm PET substrate, **c)** The 180 μm PET film, **d)** The few layer CVD

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graphene on 180 μm PET substrate. Figure 2 shows the pressure increase of measurement chambers. Figure 3 is the pressure increase rate of different films for helium.It indicates that the *dp/dt* rate of the measured chamber background is much smaller than the *dp/dt* rate of different films, and the relationship is *dp/dt*(c)> *dp/dt*(b)> *dp/dt*(d)> *dp/dt*(a) > *dp/dt*(background).

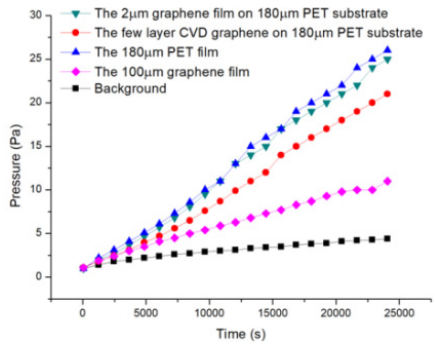

Figure 2: The pressure increase of measurement chamber.

Gas permeation characteristics of four different materials are shown in Table 1.Where the V is the volume of the measurement chamber (2.493×10^{-3} m^3), R is the gas constant (8.315 J/(K·mol)) and T is temperature (293 ± 1 K).

Table 1 shows that when the measured chamber background is sufficiently small, the following are the numerical value relation of ***Q***, ***K***, ***S***, and ***D***. In the presence or absence of background, the size relationship is the same. ***Qa<Qd<Qb<Qc***; ***Ka<Kd<Kb<Kc***; ***Sc<Sb<Sd***; ***Dd<Db<Dc***.

Graphene film and graphene attached to the PET film can prevent the passage of gas, the film leakage rate ***Qa<Qd<Qb<Qc***, but the overall difference is not very large, one order of magnitude smaller than the leak detector test results. This is owing to that the membrane goes further with the pump down time, its penetration reaches a balance, so the calculated ***Q*** result is credible.

Permeability is another important parameter to represent the gas flux of the membrane. The permeability is ***Ka<Kd<Kb<Kc***, which indicates that the adhesion of other substances on the membrane can prevent its permeability from increasing. We can see that fewer helium molecules reach the contact surfaces between PET and graphene or graphene film because graphene and graphene film with certain resistance. According to the parameters ***S*** and ***D***, PET has the largest the diffusion coefficient but the smallest solubility, which shows that the saturation time is short, and the analysis is due to its smaller thickness.

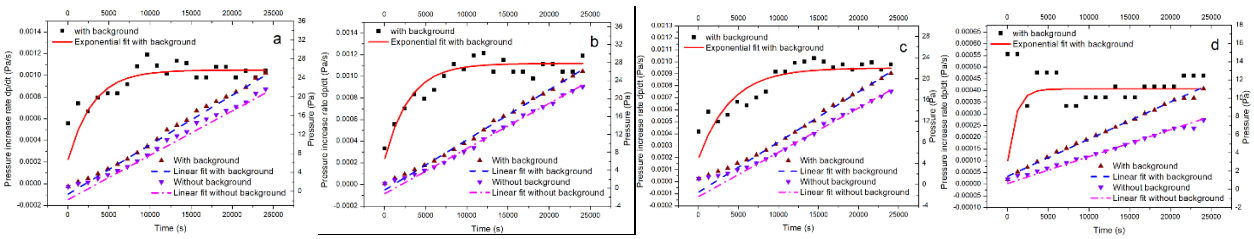

Figure 3: Pressure increase rate of different films for helium.

Table 1: Gas Permeation Characteristics of Four Different Materials

	(a)	(b)	(c)	(d)	(a)	(b)	(c)	(d)
		With background				Without background		
Q_1($\times10^{-7}$Pa.m^3/s)	0.084	1.8	4.9	4.2	0.084	1.8	4.9	4.2
Thickness($\times10^{-4}$m)	1	1.82	1.8	1.8	1	1.82	1.8	1.8
dp/dt($\times10^{-4}$Pa/s)	4.07	10.5	11.2	9.49	2.95	9.4	1.01	8.4
P_c(Pa)		-0.654	-0.449	-1.48		-1.78	-1.28	-2.31
tc(s)		623	401	1560		1900	1270	2750
D($\times10^{-12}$Pa.m^3/s)		8.86	13.5	3.46		2.91	4.27	1.96
S($\times10^{-4}$mol/Pa/m^3)		1.92	1.33	4.39		5.23	3.79	6.86
K($\times10^{-16}$mol/Pa/m/s)	3.62	17	17.9	15.2	2.63	15.2	16.2	13.5
Q_2($\times10^{-6}$Pa.m^3/s)	1	2.62	2.79	2.37	0.735	2.34	2.52	2.09

Q_1 is Helium leak rate measured by the helium leak detector and Q_2 is calculated by Eq.1

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CONCLUSIONS

Through the experiments, it is verified that the graphene film has good gas barrier capability and can be used independently. But it is necessary to select a suitable thickness of graphene film, and a large number of engineering experiments and simulation analysis are required to ensure its reliability. It is expected that a graphene beam window will be used with the improvement of graphene's preparation process.

REFERENCES

[1] H. Wang *et al*., "Design of High-power graphene beam window", In *Proc. 5th Int. Particle Accelerator Conf. (IPAC'14)*, Dresden, Germany, June 2014, paper MOOCA03.

[2] H. Wang *et al*., "Material Test of Proton Beam Window for CSNS", In *Proc. 6th Int. Particle Accelerator Conf. (IPAC'15)*, Richmond, USA, May. 2015, paper WEPMN008.

[3] L. Y. Zhang *et al*., "Design of back-streaming white neutron beam line at CSNS", *Applied Radiation and Isotopes*, 2017.

[4] D. Li and R.B. Kaner, "Graphene-Based Materials", *Science*, 2008, vol. 320, no. 5880, pp. 1170-1171.

[5] J. S. Bunch *et al*., "Impermeable atomic membranes from graphene sheets", *Nano Lett*, 2008, vol.8, no. 8, pp. 2458-62.

[6] X. F. Yao *et al*., "Experimental study of helium leakage parameters in flexible composite", *Journal of Applied Polymer Science*, 2010, vol. 116, no. 6, pp. 3562-3568.

[7] D. Dong *et al*., "Helium gas permeability measurements of polymeric membranes using the difference method", *Vacuum*, 2015, vol. 121, Supplement C, pp. 173-176.