Secondary electron emission characteristics of graphene films with copper substrate*

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Abstract: For modern and future circular accelerators, especially high-intensity proton synchrotrons or colliders, the electron cloud effect is a key issue. So, in order to reduce the electron cloud effect, exploring very low secondary electron yield (SEY) material or coating used in vacuum tubes becomes necessary. In this article, we studied the SEY characteristics of graphene films with different thicknesses which were deposited on copper substrates using chemical vapor deposition. The SEY tests were done at temperatures of 25 ℃ and vacuum pressure of $(2-6)\times10^{-9}$ torr. The properties of the deposited graphene films were investigated by X-ray photoelectron spectroscopy (XPS) and Raman spectroscopy. The SEY curves show that the number of graphene layers has a great effect on the SEY of graphene films. The maximum SEY of graphene films decreases with the increase of the number of layers. The maximum SEY of 6–8 layers of graphene film is 1.25. These results have a great significance for next-generation particle accelerators.

Keywords: secondary electron yield, graphene films, low SEY film

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1 Introduction

The build-up of electron cloud generated by residual gas ionization, synchrotron radiation, etc., in the beam pipes considerably affects the stability of particle beams in a particle accelerator. For example, the suppression of secondary electron emission is important for the Super Proton Synchrotron (SPS) accelerator and the future super proton-proton collider (SPPC) [1–4]. Therefore, it is critical to look for stable and very low SEY material for future high intensity accelerators.

Graphene has been the subject of extensive research, due to its high carrier mobility, good optical transmittance, and excellent thermal conductivity [5]. It has huge prospects in many areas, such as optoelectronic devices, energy storage, waste water treatment etc. [6–9]. On the other hand, the characteristics of vacuum chamber materials for modern and future particle accelerators are: high electrical conductivity, low impedance, low outgassing rate, good thermal conductivity, especially low secondary electron emission and so on [10–12].Most of the features of graphene fit the characteristics of vacuum chamber materials for modern and future particle accelerators. Hence, graphene films are considered to treat the surface of vacuum tubes for future particle accelerators. However, the SEY properties of graphene films with copper substrates has not been fully investigated.

In this article, the optical properties and SEY of different thickness graphene films with copper substrates are characterized and investigated.

2 Experiment

A Kimball Physics EGL-2022 electron gun was installed and directed towards the sample at a 90° angle. The electron gun scans over an energy spectrum of 50 eV to 5000 eV on the samples at Emission Current Control (ECC) mode. The background pressure in the test chamber was $(6-8)\times10^{-10}$ Torr and it was $(2-6)\times10^{-9}$ Torr during the SEY test, when the test temperature was about 300 K. A schematic diagram of the secondary electron yield test device is shown in Fig. 1.

The Faraday cup was biased to +50 V, and the sample was biased to −40 V. The size of the samples was 10 mm ×10 mm × 0.5 mm. The electron dose per unit surface during the measurement was 1×10^{-7} C/mm^2. The precision of the SEY values is about 2.6%.

The copper sample was ultrasonically cleaned in ace-

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tone and ethyl alcohol. Then it was dipped into the prepared HF solution, washed by deionized water and dried in nitrogen gas.

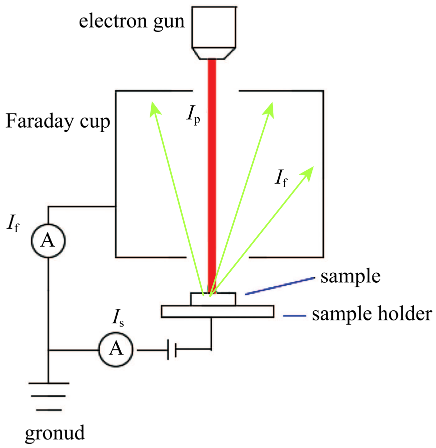

Fig. 1. (color online) Schematic diagram of secondary electron yield test device.

The SEY is the ratio of the current of secondary electrons, I_{SEY}, to the current of incident electrons, I_p. Sample-to-ground current I_s measured at the sample and Faraday cup-to-ground current I_f were measured by two Keithley 2400 Source Meters and the SEY, δ, is obtained as equation (1):

$$\delta_{SEY}=\frac{I_f}{I_p}=\frac{I_f}{(I_f+I_s)}. \quad (1)$$

Graphene films were obtained from Nanjing XF-NANO Materials Tech Co. Ltd. (China), with 25μm copper substrate [13]. These films were prepared by the chemical vapor deposition (CVD) method. The Raman spectra of graphene films in this article were characterized by LABRAM-HR with two lasers. One was an Ar laser (514.5 nm) and the other was a semiconductor laser (785 nm). In this article, the Ar laser (514.5 nm) was used.

3 Results

3.1 Characterization of graphene films

As shown in Fig. 2, the Raman spectra of all the graphene films samples show similar characteristics for the position of the D, G and 2D peaks. Graphene films with 1, 2, 3−5 and 6−8 layers all have strong 2D and G peaks, and weak D peaks. Table 1 shows the specific values of Raman parameters of four different graphene films with 1, 2, 3−5, and 6−8 layers, respectively. The ratio of I(2D)/I(G) decreases with the increase of graphene film thickness.

Table 1. Raman parameters of graphene samples with 1, 2, 3−5, 6−8 layers, respectively.

sample	D		G		2D		I(2D)/ I (G)
	Raman shift/cm^{-1}	intensity(au)	Raman shift/cm^{-1}	intensity(au)	Raman shift/cm^{-1}	intensity(au)	
1 layer	1354.74	763	1589.57	913	2687.55	1162	1.27
2 layers	1376.98	966	1599.56	1217	2709.48	1477	1.21
3−5 layers	1390.63	461	1582.9	1217	2710.94	1072	0.88
6−8 layers	1414.48	940	1582.9	3887	2705.1	1872	0.48

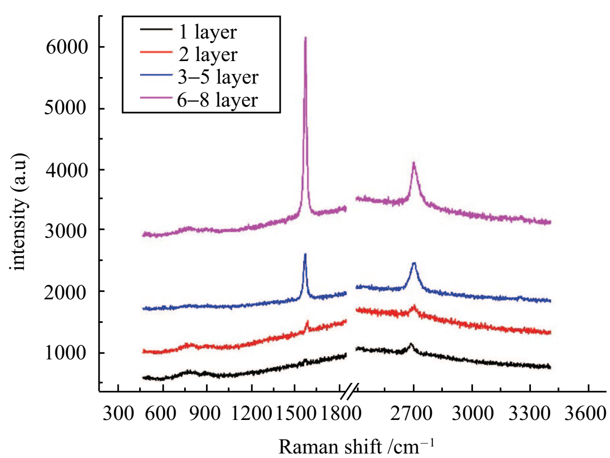

Fig. 2. (color online) Raman spectra of graphene films with 1, 2, 3−5, 6−8 layers, respectively.

A Thermo-VG Scientific ESCALAB 250 XPS was used to test the composition of these samples. Usually the detection depth of XPS for metal is about 4 nm. The surface composition of 6−8 layer graphene film was tested. Table 2 shows that the carbon content is about 84.69%. In addition, there is a small amount of oxide on the film surface. Due to the substrate of the graphene films being copper, the XPS test results show traces of Cu, about 2.69%. Figure 3 shows that the binding energy of C1s is 285 eV, and it is 532.5 eV for O1s.

Table 2. Surface composition of 6−8 layer graphene film.

element	At. %
C1s	84.69
Cu2p	2.69
O1s	12.62

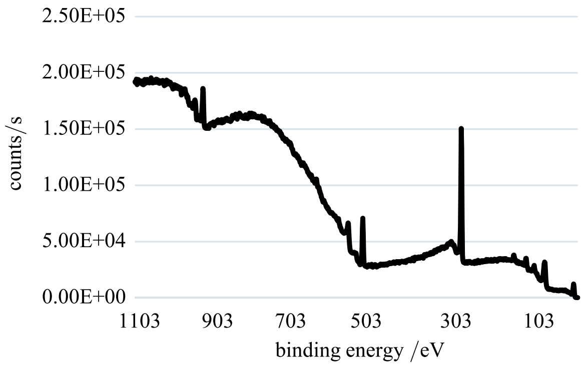

Fig. 3. The XPS spectrum of 6−8 layer graphene film.

3.2 SEY test

Figure 4 shows that the $\delta_{\rm max}$ of graphene films with different layers are 1.51, 1.43 1.41 and 1.25, respectively, when the incident charge per unit surface (Q) is 1×10^{-7} C·mm^{-2}. The primary electron energy $E_{\rm max}$ at which the maximum yield is obtained is $E_{\rm max}$ = 500, 470, 450 and 500 eV, respectively. Moreover, the $\delta_{\rm max}$ of the Cu substrate is 1.57. Under the same test parameters, the SEY of materials is mainly influenced by the material properties of the sample surface within ∼10 nm. The thickness of 1 layer graphene is too small and the SEY of 1 layer graphene with Cu substrate is mainly determined by the properties of Cu. So, the SEY of 1 layer graphene film is the nearest value to the SEY of Cu. With the increase in the number of graphene film layers, the SEY of graphene film will decrease, as shown in Fig. 4.

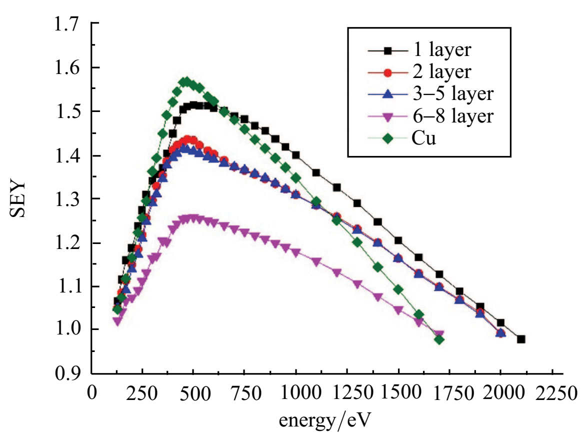

Fig. 4. (color online) SEY of graphene films with different layers, and that of the copper substrate.

4 Discussion

4.1 SEY of the graphene films

According to Ref. [14], the SEYs of metals increase under air exposure. Air exposure is generally unavoidable. Therefore, the SEY of pure graphene films may be lower than the results shown in Fig.4.

In Ref. [15], it shows that the elemental surface composition changes in the dose range of 10^{-6}–10^{-1}C·mm^{-2}. Moreover, Ref. [16], shows that the electron bombardment will induce increased graphitization, resulting in the decrease of SEY. Therefore, the dose we chose is 1×10^{-7} C·mm^{-2}.

The SEY of copper reported varied between 1.85–1.4 [17, 18]. In our experiment, the SEY of copper which was polished is 1.57. The difference may induced by different test devices, different test conditions etc. In Fig.4, the trend of the slopes is different from the trend in Ref. [19] at high energy. This difference may be caused by different time intervals of data acquisition and energy range. If the maximum energy is 3000 eV, the slopes of the SEY curve will be more and more negative.

For the SPS, the threshold value of the build-up of electron cloud is 1.3, while for the SPPC, it should below 1.4 or even 1.2 [20]. Is graphene film applicable to the SPPC? The answer is determined by the threshold value of electron cloud build-up, film lifetime, SEY properties of graphene thin films and other factors. For graphene samples with copper substrate prepared by the CVD method, the SEY of 6–8 layers graphene films is about 1.25.

Reference [21] shows that the SEY of 1 −2 and 6 −7 layers of graphene fakes were all below 1, 0.8 and 0.5, respectively. These results are different from our experimental results. The difference may be caused by different test parameters, characteristics of the substrates and physical properties of graphene, etc. To be specific, the difference is mainly focused on the following aspects. 1) Different calculation methods. The formula of SEY used in Ref. [21] is as follows:

$$\delta_{\rm SEY} = 1 - I_{\rm m}/I_{\rm p}, \tag{2}$$

where $I_{\rm m}$ is the sample current to ground. Since the signals which were collected are different in these two formulas, this will induce SEY difference to some extent. 2) They used a pulsed-beam mode, while we use emission current control mode. Pulsed-beam mode can minimize surface charging effects. Sample charging will affect signal collection. In other words, different beam modes mean different beam conditions. Hence, the SEY for the same sample will be different under different beam conditions. Using emission current control mode may cause surface charge accumulation, then $I_{\rm f}$ will increase. Therefore, according to equation (1), the $\delta_{\rm SEY}$under emission current control mode will be higher than in pulsed-beam mode. 3) Different substrates. The substrates of the graphene films in Ref. [21] are Al foils, while it is copper in our experiment.

Ref. [22] shows that the intrinsic SEYs of monolayer graphene with silicon dioxide substrates are around 0.10

at 1000 eV primary electron, while our results for the SEY of 1 layer graphene film with copper substrate is about 1.40 at 1000 eV primary electron. This difference is mainly caused by the following reasons. 1) Different substrates. 2) Different testing mechanism. The SEY in their article is the intrinsic secondary electrons, while in our experiment it includes the intrinsic secondary electrons, escaped secondary electrons and scattered electrons. So, this is the mainly reason that our test results are higher than theirs.

All in all, there is currently no standard test device for SEY testing. The SEY test devices in different laboratories are diverse. On the other hand, for the same kind of material samples, it is difficult to guarantee that the test parameters and their surface states, such as surface cleanliness etc., are the same in different SEY test devices. So, for the same kind of material samples, test results will be different to some extent.

4.2 Application of the graphene films

The preparation of graphene films by the CVD method needs a high temperature, so the deposition of graphene films directly on the inner surface of copper pipes is difficult to implement. High temperatures will cause copper pipes to be mechanically unstable – for example, they might partly deform. Keeping the temperature of the long copper pipes at around 1000℃ is also a difficult problem. Therefore, we propose a solution, lining the graphene films with copper substrates in the inner surface of the pipes. In this way, 6 −8 layer graphene films meet the threshold limit of the SPS.

As a very promising material, graphene film has stable physical properties and low secondary electron yield. Also, with the development of graphene preparation processes and technologies, graphene film with several layers may be implemented in accelerator vacuum chambers to solve the problems related to electron cloud effect for future accelerators.

5 Conclusion

In this study, the SEY of graphene film samples, with 1 layer, 2 layers, 3−5 layers and 6−8 layers of graphene respectively, with copper substrates, were tested. Experimental results suggest that the number of layers significantly influence the SEY of the graphene films. The $\delta_{\max}$ of 6−8 layer graphene film is 1.25. In order to obtain low SEY, it is important to choose the 6−8 layer graphene film for electron cloud mitigation. Moreover, taking into account the stability of the graphene films, it will be of great value for beam screen construction of next generation accelerators such as the SPPC.

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