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Secondary electron emission of graphene-coated copper

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ABSTRACT

The secondary electron emission of graphene-coated copper has very interesting properties. In this work, we prepared graphene-coated copper foil and measured both the secondary electron emission yield (SEY) and the secondary electron energy spectra. Compared with the copper base, there is a significantly reduction for the SEY. For the copper base without coating, the max value of SEY is beyond 2.1 for the primary electron energy of 300 eV. However, the corresponding value for the graphene-coated copper is about 1.5, reduced about 25%. For the secondary electron energy distribution, the elastically backscattered peak becomes higher and peak of the true secondary electrons is shifted from about 1.5 eV to 4 eV after coating the copper with graphene. The full width at half maximum of the true secondary electrons peak is also increased. Since the position of the peak is related to the surface potential barrier of the material, we believe that the graphene coating could increase the surface potential barrier of the material. This could also be the reason of SEY reduction because a higher potential barrier can reduce the electron emission from the material. A preliminary theoretical model of the surface potential distribution for copper surface with graphene coating was built and used to analyze the secondary electron emission of metal surface with graphene coating. The graphene coating is found to be an effective method to suppress the secondary electron emission.

1. Introduction

As a well-known effect of electron solid interactions, secondary electron (SE) emission plays an important role in an extremely vast field of research spanning from vacuum electronics, microscopic structure analysis, particle accelerators to space research [1–8]. Some devices, such as microchannel plate detector and scanning electron microscope make use of SEs. On the other hand, SE is known to be major cause of degradation of performance for some instruments as such the multipactor effect in high power microwave components, and electron cloud effect in accelerators [6,8]. When secondary electron emission is considered to be harmful, suppression of secondary electron emission is highly desired. Therefore, many investigations have been given into find effective technique of secondary electron emission suppression.

Secondary electron yield (SEY, often denoted as σ), which is defined as the ratio of the number of emitted secondary electrons to the number of incident primary electron, is frequently used to characterize the magnitude of secondary emission. Surface treatments are often introduced to reduce the SEY since secondary electron emission strongly depends on the surface condition. For example, carefully desired surface structures, such as micro-porous array structure, rectangle groove, were found to be effective for decreasing SEY of metal [9–14]. Another approach to secondary electron emission suppression is coating the surface by material with low SEY. The database summarized by Joy [15] can provide SEY data for many materials, which may be helpful for choice of coating material. Graphene was reported to be a material of ultralow secondary electron emission and carbon coating was found to be a way to reduce the SEY [16–18]. It was reported that electron bombardment could also decrease the SEY and the reason was considered to be the surface graphitization due to electron bombardment. It was believed that the sp3 type bond is the nature of SEY decreasing [19–21].

Besides the SEY, the secondary electron energy distribution is also an important knowledge and has been attracting many interests. Fine structures in energy spectra of secondary electrons and their dependence on primary electron energy have been carefully examined for graphene on nickel surface and been used for study the excited states of graphene interfaces [22–25]. Theoretical calculation using a plane-wave pseudo-potential method based on local density functional theory was also presented to study the graphene-substrate interaction [26]. Knowledge on energy distribution is helpful to understand the mechanism effect of graphene on secondary electron emission.

In this work, we studied the effect of graphene coating on the secondary electron emission of copper foil. Both the SEY and secondary electron energy spectra have been considered. Significant reduction for SEY was achieved by graphene coating. Investigation on the

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distribution of the secondary electron energy shows that the peak position of energy spectra shifts to higher energy and the full width at half maximum becomes wider. We also analyzed these effects by introducing the effective surface barrier related to the graphene coating. An example of suppression of multipactor in microwave devices is demonstrated as a possible application of graphene coating.

2. Experiment

2.1. Preparation of graphene coating on copper foil

Samples of copper foil both with and without graphene coating were prepared. The copper foil substrates with purity 99.8% and thickness 0.025 mm (Thermo Fisher Scientific #13,382) were used. The copper substrates were cleaned with isopropyl alcohol, acetone, ethanol and de-ionized water. Treatment using $FeCl_3$ solution with concentration of 0.01 mol/L was introduced for etching and oxidation of the substrate. About 0.1 mL of $FeCl_3$ solution was dropped onto each 1 cm^2 substrate and then dried out in the atmosphere. It was found that the graphene nucleation density can be reduced and the total graphene coverage increase-rate can be increased with the $FeCl_3$ solution treatment [27].

Graphene coating layer was grown using the chemical vapor deposition (CVD) method. The detailed information on growth behavior and characterization was reported in the previous publication [27]. Briefly, in a quartz tube furnace, the substrates were first heated up to 1000 °C and then annealed at this temperature for at least 20 min. In the CVD growth process, a two step introduction of CH_4 flows was optimized for high quality graphene growth: 1 sscm for 15 s and 0.1 sccm for 30 min, separately. Throughout the whole process, A 40 sccm H_2 flow was maintained. The CVD parameters are sketched in Fig. 1. The quality of samples were checked with scanning electron microscope (SEM) and Raman spectra as shown in Figs. 2 and 3, respectively. In the SEM image, it can be seen a uniform graphene lay was obtained. The Raman spectra indicate a single layer graphene on the substrate.

2.2. Measurement of secondary electron emission

The experiments of secondary electron emission measurement were performed in an ultra-high vacuum experimental system outlined in Fig. 4. First, the samples were shaped in a rectangle of about 1 × 1.2 cm^2 and loaded into the vacuum chamber with a condition of about 2×10^{-8} Pa. The SEYs of the prepared samples were measured at different primary electron energies with an incident direction perpendicular to the samples. The beam spot size of primary electrons was set to about 200 μm in diameter. Two sample currents I_p and I_m were measured at a high positive bias (500 V) and low negative bias (−20 V) of the sample, respectively. When the sample is high positive biased, almost all emitted secondary electrons were dragged back to the sample and thus I_p is equal to the primary electron current. The primary electron current was furthermore calibrated by using a Faraday cup. For the negative bias of the sample, on the other hand, all emitted secondary electron will be push out and we have $I_m = I_p - I_{se}$, where I_{se} is the secondary electron current. Therefore, the SEY can be determined as $\sigma = I_{se}/I_{pe} = 1 - I_m/I_p$. Here, three different points on a same sample were measured. The average value was taken as the SEY of the sample at certain condition and the deviations of the maximum SEY was less than 5%.

The secondary electron energy spectra was detected at a fixed primary electron energy of 300 eV by the spectrometer (DESA 150 analyzer) vertically above the sample. This spectrometer takes advantage of a cylindrical mirror electrostatic fields. It has a large acceptance solid angle of 6% of 2π, with an energy resolution of less than 0.1 eV. The secondary electron energy spectra collection was lasted for about 0.5 min. Here, a negative bias (−15 V), was applied to the sample to collect secondary electrons more effectively. To avoid the possible influence of primary electrons, the primary electron currents were controlled constantly as about 10 nA and 0.6 nA for measurements of SEY and energy spectra, respectively.

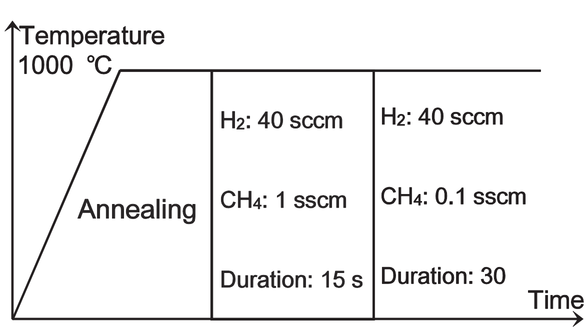

Fig. 1. Temperature and gas flow in CVD processing of graphene synthesis.

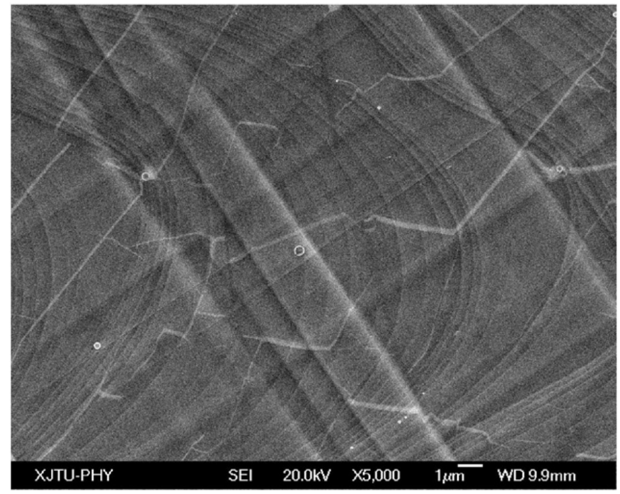

Fig. 2. SEM image of graphene on Cu substrate.

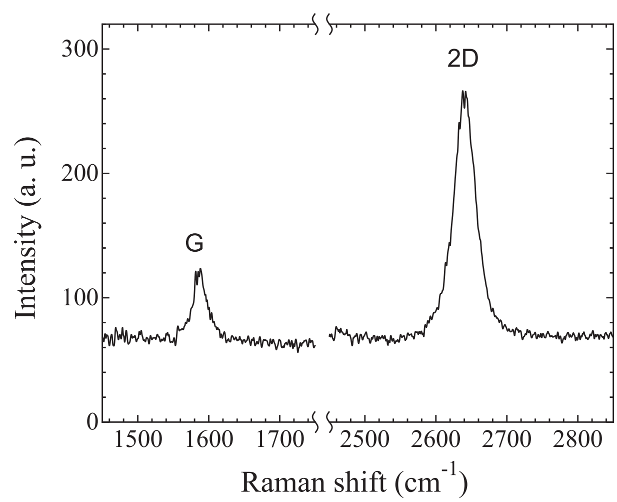

Fig. 3. Raman spectra of graphene on Cu substrate.

3. Results and discussion

3.1. SEY and energy distribution

Fig. 5 gives the measured SEY curves as a function of primary electron energy E_{pe} for copper samples both with and without graphene