Formation Mechanism of Secondary Electron Contrast of Graphene Layers on a Metal Substrate

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ABSTRACT: Scanning electron microscopy (SEM) is widely used to observe graphene on metal substrates. However, the origin of the SEM image contrast of graphene is not well understood. In this work, we performed in situ SEM imaging of layer-number-controlled graphene on a Ni substrate using a high-pass energy filter for secondary electrons. We found that the graphene layer contrast was maximized at 15−20 eV, corresponding to the π−π* interband transition in graphene. Our results indicate that the SEM image of graphene is produced by attenuation of the electrons emitted from the metal substrate by the monoatomic layers of graphene.

INTRODUCTION

Imaging is indispensable for the study of atomic-layered materials. Graphene research was accelerated by the fact that even monolayer graphene can be observed by an optical microscope when it lies on a 300 nm thick SiO₂ film and the thickness of graphene layers can be measured. Despite their atomic thickness, graphene and other atomic-layered materials can influence the optical index, reflectivity, or emissivity of the substrate material. Emissivity modification of a copper surface by graphene coverage is employed for in situ observation of chemical vapor deposition (CVD) processes of graphene on copper. Although optical imaging can be carried out using conventional microscopes, this approach severely restricts the combinations of atomic-layered material and substrate material and the spatial resolution is limited by the wavelength of light. By contrast, scanning electron microscopy (SEM) offers a versatility in terms of possible material combinations and a much higher spatial resolution. Graphene imaging by SEM has been widely used in many studies. SEM is also used for in situ imaging of graphene segregation or chemical vapor deposition (CVD) on metal surfaces. Although in situ imaging of graphene segregation can be nicely performed by low energy electron microscopy (LEEM), SEM is capable of in situ observation of graphene CVD with introduction of hydrocarbon or alcohol gases, which is unsuitable for LEEM because of a high voltage applied to the specimen. On the other hand, in contrast to LEEM for which the image formation mechanism is well understood, the formation mechanism of secondary electron (SE) images of atomic-layered material is complex and thus poorly understood. Considering the weak interaction between primary electrons and the atomic-layered material, the direct SE emission from graphene should be much smaller than that from the substrate. Nevertheless, monolayer graphene can be clearly imaged. There are many factors that can affect the SE emission from graphene-coated materials, such as work function, oxidation/nonoxidation, intercalation, charging, and attenuation of SEs. It is necessary to clarify the contrast formation mechanism and optimize the observation conditions.

In this study, we investigated the SE image contrast of graphene on metal surfaces using layer-number-controlled specimens prepared by segregation in the SEM chamber. We were able to optimize the contrast between graphene and the substrate by selecting the SE energy.

RESULTS AND DISCUSSION

SE Image Contrasts Depending on the Detector. The SEM instrument used (LEO 1530 VP, Carl Zeiss) has two types of SE detectors, in-column and out-lens detectors. SEM is also used for in situ imaging of graphene segregation or chemical vapor deposition (CVD) on metal surfaces. Although in situ imaging of graphene segregation can be nicely performed by low energy electron microscopy (LEEM), SEM is capable of in situ observation of graphene CVD with introduction of hydrocarbon or alcohol gases, which is unsuitable for LEEM because of a high voltage applied to the specimen. On the other hand, in contrast to LEEM for which the image formation mechanism is well understood, the formation mechanism of secondary electron (SE) images of atomic-layered material is complex and thus poorly understood. Considering the weak interaction between primary electrons and the atomic-layered material, the direct SE emission from graphene should be much smaller than that from the substrate. Nevertheless, monolayer graphene can be clearly imaged. There are many factors that can affect the SE emission from graphene-coated materials, such as work function, oxidation/nonoxidation, intercalation, charging, and attenuation of SEs. It is necessary to clarify the contrast formation mechanism and optimize the observation conditions.

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either bright (for the right edge in Figure 1) or dark (for the upper and left edges) depending on the inclination of the substrate surface or the nonuniformity of the detection efficiency. No such edge contrasts appear in the SE image acquired with the out-lens detector. Apart from the edge contrast, the brightness of the graphene-coated region is almost the same as that of the bare Ni surface. On the other hand, the graphene-coated regions appear more clearly, as a darker contrast. The even darker area seen in Figure 1d is the second layer of graphene segregated underneath the first layer. Although this second layer can also be recognized in the SE image acquired with the in-column detector, the contrast is less prominent and the edge contrast is absent. The differences in the SE images of graphene between the two types of detectors presumably stem from the difference in the energy ranges detected. Lower energy SEs are mainly collected by the in-column detector, whereas the remaining higher energy portion is collected by the out-lens detector.\[18\] To determine the effect
of SE energy on graphene contrast, we performed energy-filtered imaging by adding an energy filter into the specimen stage.

Energy-Filtered SE Images of Graphene. SEs were acquired with the in-column detector through an aperture 3 mm in diameter, set 4 mm above the specimen surface (see Figure S1). The filter can generate a retarding electric field between the specimen and detector, thus acting as a high-pass filter of the SE energy.

Figure 2 shows the retarding voltage dependence of SE images of graphene on the polycrystalline Ni surface observed at ≈800 °C. The contrast settings of the in-column detector were the same for all images. The brightness of each image in Figure 2 was adjusted so that the brightness of the Ni surface appeared the same for all of the retarding voltages. Figure 2a highlights monolayer, bilayer, trilayer (three layers), and tetralayer (four layers) graphene-coated regions with red, green, dark blue, and light blue shading, respectively. On a large crystal grain (center of the SEM images), there are monolayer, bilayer, trilayer, and tetralayer graphene regions on the surface at the initial stage. Because in situ imaging was performed at ≈800 °C, graphene segregation continued, causing a shape change while the retarding voltage was increased. At 0 V, similar to the SE images under ordinary conditions (Figure 1), monolayer graphene appears slightly darker than the bare Ni surface and the graphene-coated region becomes darker with increasing number of layers. At 5 V, where electrons with energies higher than 5 eV are going through the filter and being detected, monolayer graphene becomes slightly brighter than the bare Ni surface. The contrast between monolayer, bilayer, trilayer, and tetralayer graphene is very small. At 15 V, monolayer graphene becomes clearly darker than Ni and bilayer and thicker multilayer graphene films appear much darker than monolayer graphene, resulting in clear layer contrasts. At 25 V and higher, although the graphene-coated regions are darker than Ni, the contrast between layers is smaller than that at 15 V. The edge contrast of monolayer graphene is not so prominent even at 0 V and disappears at 10 V and higher voltages.

To quantify the contrast change, we digitized the brightness of graphene SE images and plotted the retarding voltage dependence of the SE image brightness for monolayer, bilayer, trilayer, and tetralayer graphene, as shown in Figure 3a. The image brightness shows a maximum around 3–10 V and rapidly decreases with increasing the retarding voltage, but detailed behaviors are different between the bare Ni surface and graphene-coated surfaces. The brightness increases at voltages lower than 3 V, which is unusual as energy distribution of SEs. This might be due to the fact that the acceptance angle of the in-column detector for emitted SEs changes with the SE energy. The collection efficiency of the in-column detector is especially high for the lower energy SEs. To compensate for the collection efficiency of the detector and to elucidate the difference in the graphene layer contrast, the data in Figure 3a are normalized relative to Ni and shown in Figure 3b. It can be seen that the brightness of monolayer graphene is maximized at 3 V and minimized at around 15 V. For thicker layers, although the maxima and minima shift to slightly higher voltages depending on the number of layers, their behavior is similar to that of monolayer graphene. More importantly, the difference in brightness between the mono-, bi-, and trilayers is maximized at around 15 V. The contrast between the bi-, tri-, and tetralayers is smaller for all voltages. Such voltage-dependent contrast changes cannot be explained simply by the work function difference between the films of varying layer numbers.

Origin of Graphene SE Image Contrasts. Given that most of the SEs are emitted from the Ni substrate, the fact that the graphene layer contrast is maximized at a retarding voltage of around 15 V means that the attenuation of SEs by graphene is maximized here. Furthermore, the smaller brightness difference for thicker layers indicates that SEs from the substrate are mostly suppressed by the graphene layers. Thus, the behavior shown in Figure 3b likely reflects the energy dependence of the inelastic mean free path (IMFP) of SEs.

To confirm this interpretation, we extracted the attenuation length from the data shown in Figure 3a. Because the data in Figure 3a represent the integrals of SE intensities over each retarding voltage, we calculated the SE intensity at a certain energy $I(E)$ as the numerical differentiation using the brightness of adjacent retarding voltages

$$I(E) \approx \frac{N(V) - N(V + \Delta V)}{\Delta V}$$

where $V$ is the retarding voltage at $E = eV$, $e$ is the elementary charge, $\Delta V$ is the retarding voltage increment ($=1$ V), and $N(V)$ is the brightness measured at retarding voltage $V$. Thus, we can obtain the attenuation length $\lambda(E)$ of an electron through graphene via
The energy loss peak at \( \approx 20 \text{ eV} \) is actually observed for suspended graphene is often referred to as \( \pi\sigma^+ \) plasmon;\(^{2,23}\) most SEs have a momentum nearly perpendicular to the graphene plane and excite the \( \pi\sigma^+ \) interband transition rather than inplane vibration of electrons in graphene.\(^{21}\)

The cause of the peculiar edge contrast of monolayer graphene on the Ni surface remains unclear. The present energy filtering results provide some clues. The edge contrast disappeared at higher retarding voltages (\( > 10 \text{ V} \)), suggesting that the edge contrast was created by lower energy SEs. For the in-column detector of the Gemini column, the accepting range of the takeoff angle of SEs depends on the SE energy.\(^{24}\) The detector accepts SEs emitted with a wide range of takeoff angles, including those emitted with small takeoff angles (i.e., nearly parallel to the specimen surface) in the case of lower energy SEs. With increasing energy, the lower limit of the detectable takeoff angle of SEs increases. Thus, if the edge contrast is generated by lower energy SEs emitted with small takeoff angles, it is reasonable for the edge contrast to disappear at higher retarding voltages. In addition, the energy filter can affect the selectivity for takeoff angle, resulting in a less clear edge contrast, as seen in Figure 2.

**Application to SE Imaging of Graphene on Cu.** The graphene contrast on a bare Cu surface is also maximized at a retarding voltage of \( \approx 20 \text{ eV} \). Figure 5 shows SE images of graphene islands nucleated on polycrystalline Cu observed at retarding voltages of 0 and 20 V. On a bare Cu surface, the graphene contrast is very faint in the absence of an applied retarding voltage.\(^{25}\) By contrast, under a retarding voltage, monolayer graphene islands appear much darker than the Cu surface, which makes graphene observation easier. Graphene on Cu also shows an energy loss peak at \( \approx 20 \text{ eV} \).\(^{26}\) This result confirms that the main origin of graphene SE contrast formation on metal surfaces is the graphene-induced attenuation of SEs generated in the metal substrate.

**CONCLUSIONS**

We performed energy-filtered SE imaging of graphene with controlled layer numbers utilizing in situ graphene segregation. We found that the SE contrast of graphene on Ni and Cu surfaces was maximized at retarding voltages of 15–20 V. In this voltage range, the layer contrast between monolayer and bilayers of graphene was also maximized. This was explained by the energy dependence of graphene-induced attenuation of SEs generated in the metal substrate. The maximum attenuation corresponds to the \( \pi\sigma^+ \) interband transition in the electronic states of graphene. This method is generally useful for observing atomically thin films on metal substrates.

![Image 1](https://example.com/image1.png)

**Figure 4.** Attenuation length of electrons derived from data in Figure 3a.

![Graph](https://example.com/graph.png)

**Figure 4.** Attenuation length of electrons derived from data in Figure 3a.

![Image 2](https://example.com/image2.png)

**Figure 5.** Energy-filtered SE images of graphene on polycrystalline Cu observed at \( \approx 800 \text{ °C} \) with retarding voltages of (a) 0 V and (b) 20 V.
EXPERIMENTAL SECTION

Graphene was synthesized by segregation on the Ni surface at elevated temperatures. We used an SEM instrument (LEO 1530 VP, Carl Zeiss) and modified the specimen stage to allow resistive heating by passing a direct current (dc) through the specimen. Thus, the SEM instrument could be used for in situ observation of graphene formation during segregation. The Ni specimen used was a 0.1 mm thick Ni (>99%) foil whose surface was mechanically polished. The foil was cut into a 0.3 × 20 mm² piece for heating to ≈1000 °C with a dc of ≈5 A in the SEM chamber. Before in situ SEM observation, the specimen was annealed at 950 °C in an Ar/H₂ (3% H₂ by volume) mixture gas in a quartz furnace to enlarge the Ni grains. Then, a carbon film (in the form of disordered graphite) was deposited by using ethanol vapor supplied by bubbling Ar/H₂ gas (total pressure of 800 Pa) through liquid ethanol at 900 °C for 20 min. During in situ observations, we estimated the specimen temperature on the basis of the behavior of graphene, which either dissolved (>900 °C) or underwent monolayer and multilayer segregation (≈790–900 °C), according to previous studies.²⁷,²⁸ The vacuum pressure of the specimen chamber was ≈7 × 10⁻³ Pa by pumping with a turbomolecular pump. Although this was not an ultrahigh vacuum, contamination of the specimen surface during observation was negligible at the elevated temperatures. To avoid the effect of contamination, all of the observations were done at the elevated temperatures.

The LEO 1530 VP has two types of SE detectors: (i) the so-called in-column detector set in the Gemini column,¹⁸ and (ii) a normal E–T detector (out-lens detector). The former collects lower energy SEs being intercepted by the weak electrical field of the objective lens, whereas the latter collects the remaining high energy SEs.¹⁸ In addition, we installed an energy filter on the specimen stage to measure the energy dependence of the SE contrast. As shown in Figure S1, SEs were acquired with the in-column detector through a 3 mm field of the objective lens, whereas the latter collects electron intensity stemming from individual graphene layers.¹⁸

Notes
The authors declare no competing financial interest.

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