Since their discovery in 2004,1 n-layer graphenes have attracted intense interest due to their unique structure; interesting, novel properties;2,3 and significant dependence of properties on the layer number “n”.4,5 For example, in monolayer and bilayer graphene, the carriers correspond to massless and massive Dirac fermions and the quantum Hall effect occurs at different filling factors, respectively.6−9 In this work we report that gold deposited by thermal evaporation on graphenes interact differently with these substrates depending on the layer number of graphenes. This results in different morphologies of gold film on graphenes with different layer numbers. The differences observed with SEM (scanning electron microscopy) can be used to identify and distinguish graphenes especially if they are mixed with different layer numbers. Compared to the usual two methods reported previously, this technique with SEM is more convenient, has a higher throughput than that based on AFM (atomic force microscopy),10 and has a higher spatial resolution than that based on Raman spectroscopy.6−9

The n-layer graphenes investigated in this work were prepared with the micromechanical cleavage4 of natural graphite (Alfa Aesar) by using Scotch transparent tape 600 (3M).10 After repeated peeling, the graphenes were transferred to 300 nm SiO2/ Si substrates by adhering and taking off the tape. The n-layer graphenes left on the wafer were first selected based on their coordinates were found with regard to the marks in wafer. The Raman spectra of these n-layer graphenes were used to identify the layer number (Figure 1).6−9 The micro-Raman spectroscopy (Renishaw inVia Raman Spectroscope) experiments were performed under ambient conditions with 514.5 nm (2.41 eV) excitation from an argon ion laser. The laser power on the sample was ~1.0 mW to avoid laser induced heating. A 100× objective lens with a numerical aperture of 0.90 was used, which resulted in an ∼1 μm laser spot size.

To study the surface properties of n-layer graphenes,3,11 gold film was evaporated onto the wafer in a vacuum thermal evaporator at a deposition rate of 1.0 Å/s under a vacuum of ∼10−4 Pa. The morphologies of gold film as well as the size and density of nanoparticles on other metals is evaporated onto the wafer, and the morphologies on n-layer graphenes were studied by SEM (c) The wafer is treated at high temperature, and the size, density, etc. of nanoparticles on n-layer graphenes can be obtained.

Figure 1. (a) A typical photograph (in normal white light) of an n-layer graphenes. The layer number is estimated according to the color contrast. (b) Raman spectra of pristine n-layer graphenes, which can be used to confirm the layer number. The left and right peaks correspond to G and 2D bands, respectively.

Figure 2. Schematic diagram showing the technique to study the surface properties of n-layer graphenes using gold film or nanoparticles. (a) Graphenes with different layer numbers are found. (b) A thin film of gold or other metals is evaporated onto the wafer, and the morphologies on n-layer graphenes were studied by SEM (c) The wafer is treated at high temperature, and the size, density, etc. of nanoparticles on n-layer graphenes can be obtained.

As shown in Figure 3, the morphologies of gold film on n-layer graphenes are closely related to the layer number “n”. The grain size of gold and aperture among the grains are larger for the gold film on bilayer graphene compared to that on monolayer graphene (Figure 3a). Thus, a boundary can be found between the gold film on monolayer and bilayer graphene. The differences in morphologies, grain size, and apertures among grains can be more clearly seen from Figure 3b, where the left and right parts correspond to gold films on trilayer and monolayer graphene, respectively. Here the straight boundary is clearer. In Figure 3c, the morphologies of gold film are shown on the four layer graphene, substrate (SiO2), and bilayer graphene, respectively. In Figure 3d, a narrow ribbon of bilayer graphene in the left edge of monolayer graphene can be clearly seen and identified, which would be taken to be monolayer graphene by an optical microscope and Raman identification (see Supporting Information). The high spatial resolution of this technique can be further demonstrated by the circles in Figure 3, which are defects or contaminants on n-layer graphenes.

What is the mechanism of these thickness-dependent morphologies of gold on n-layer graphenes? Generally speaking, the final morphologies of gold are closely related to thermodynamic (e.g., energetics and stability) and kinetic (e.g., surface diffusion) factors.
Raman spectra, indicating the advantage of identifying the layer number of graphene from the monolayer graphene using an optical microscope or scanning electron microscope for bilayer, and monolayer graphene. It is difficult to distinguish the bilayer graphene (middle) and bilayer graphene (right). (d) Gold film on substrate, a narrow area of the SEM images of the morphologies of gold film on monolayer graphene (false-color). Differences in morphologies of gold film and clear graphenes. If the layer number is larger than 4, the difference is almost indistinguishable. Vacuum: 10⁻⁶ Pa. Deposition rate: 1.0 Å/s. Film thickness: 5.0 nm in (a, b, c) and 2.0 nm in (d). (a) Gold film on bilayer (left) and monolayer graphene (right). (b) Gold film on trilayer (left) and monolayer graphene (right). (c) Gold film on four layer graphene (left), substrate (SiO₂, 5.0 nm), and bilayer graphene (right). (d) Gold film on substrate, a narrow area of bilayer, and monolayer graphene. It is difficult to distinguish the bilayer graphene from the monolayer graphene using an optical microscope or Raman spectra, indicating the advantage of identifying the layer number with SEM.

One possible reason may be that the surface free energy of n-layer graphenes is dependent on the layer number. When the gold atoms are evaporated onto the surface of n-layer graphenes, they interact differently and result in different morphologies.

Another possible reason can be attributed to a kinetic factor: surface diffusion. When gold atoms are thermally deposited onto the silicon wafer, the arriving atoms can make random walks on the surface (SiO₂ or graphenes; see Supporting Information). An arriving atom may form a new island with other atoms (nucleation) or walk into an existing one (growth). The diffusion coefficient of the atoms determines how large an array of gold nanoparticles can be estimated by the density ratios. Therefore, the barrier difference between other layer numbers can be obtained after annealing at 1260 °C in vacuum for 30 s (false-color). Note that no gold nanoparticles are found in the substrate. (a) Gold nanoparticles on monolayer, bilayer, and trilayer graphene, respectively. (b) Statistics of the size and density of gold nanoparticles on n-layer graphenes.

The nanoparticle density of gold on n-layer graphene is closely related to the surface diffusion coefficient (D) according to classical mean-field nucleation theory. The scaling relationship between the nanoparticle density (N) and the surface diffusion coefficient (D) can be expressed as: N ~ (1/D)²/3 for isotropic surface diffusion. According to the Arrhenius equation of diffusion, the surface diffusion coefficient and the diffusion barriers (Eₓ) follow the scaling relation of D ~ exp(-Eₓ/kT), where K is the Boltzmann constant, T the temperature (see Supporting Information). Thus, combining these two equations, we can obtain: N ~ exp(Eₓ/kT). Therefore, the diffusion barrier Eₓ of gold is dependent on the layer number of the n-layer graphene. Although it is difficult to obtain the absolute value of barriers, the barrier difference between n-layer graphene can be estimated by the density ratios. Therefore, the barrier difference between monolayer and bilayer graphene can be calculated with ΔE = E₁ - E₂ = 3kT ln(N₁/N₂) = 504 ± 44 meV. The barrier difference between other layer numbers can be obtained.

Figure 3. SEM images of the morphologies of gold film on n-layer graphenes (false-color). Differences in morphologies of gold film and clear boundary can be found. The circles indicate defects or contaminants on graphenes. If the layer number is larger than 4, the difference is almost indistinguishable. Vacuum: 10⁻⁶ Pa. Deposition rate: 1.0 Å/s. Film thickness: 5.0 nm in (a, b, c) and 2.0 nm in (d). (a) Gold film on bilayer (left) and monolayer graphene (right). (b) Gold film on trilayer (left) and monolayer graphene (right). (c) Gold film on four layer graphene (left), substrate (SiO₂, middle), and bilayer graphene (right). (d) Gold film on substrate, a narrow area of bilayer, and monolayer graphene. It is difficult to distinguish the bilayer graphene from the monolayer graphene using an optical microscope or Raman spectra, indicating the advantage of identifying the layer number with SEM.

Figure 4. Morphologies, size, and density of gold nanoparticles on n-layer graphenes after annealing at 1260 °C in vacuum for 30 s (false-color). Note that no gold nanoparticles are found in the substrate. (a) Gold nanoparticles on monolayer, bilayer, and trilayer graphene, respectively. (b) Statistics of the size and density of gold nanoparticles on n-layer graphenes.
in a similar method, and they are $291 \pm 31$ meV ($E_2 - E_1$) and $242 \pm 22$ meV ($E_3 - E_2$), respectively.

What makes the surface diffusion coefficient and barrier of gold on n-layer graphene different? The quantum size effect (QSE)\textsuperscript{14,15} can modulate the band gap of semiconducting nanocrystals, and hence they exhibit size-dependent visible color.\textsuperscript{16} In ultrathin metal film, the electrons are confined in the vertical direction, and QSE is seen by the appearance of discrete energy levels of electrons.\textsuperscript{17,18} For monolayer graphenes, the pi-electrons are confined and reside above and below the graphene layer. The stacking of graphene layers does not increase the confinement of electrons. Recently it is discovered that the tunable band gap can be opened in bilayer graphenes.\textsuperscript{19–22} This suggests that the different surface diffusion coefficient and barrier of gold on n-layer graphenes may originate from QSE in a similar mechanism to that of semiconducting nanocrystals, which is closely related to van der Waals coupling between graphene layers.

We have tried to apply this methodology to graphenes obtained by reduction of graphene oxide.\textsuperscript{23–24} Although the morphologies of gold film on graphenes are different from that on SiO$_2$, the morphologies of gold are not uniform and show little dependence on the thickness of graphenes due to the higher density of defects or chemical contaminants (see Supporting Information).

It is worth noting that the gold film can be completely evaporated off the n-layer graphenes if annealing for several minutes at temperature above the melting point of gold (see Supporting Information). Micro-Raman spectra indicate that the nature of graphenes is not altered after the high temperature treatment (Figure 5). Meanwhile, similar results have been obtained if gold is replaced with other metals, indicating the universal phenomena reported here (see Supporting Information).

**Figure 5.** The micro-Raman spectra of the gold-covered and heat-treated n-layer graphenes. (a) Raman spectra of n-layer graphenes covered with gold film of 5.0 nm. (b) Raman spectra of n-layer graphenes after annealing.

In summary, gold thermally deposited onto n-layer graphenes interacts differently with these substrates depending on the layer number, indicating the different surface properties of graphenes. This results in thickness-dependent morphologies of gold on n-layer graphenes, which can be used to identify and distinguish graphenes with high throughput and spatial resolution. It plays an important role in checking if n-layer graphenes are mixed with different layer numbers of graphene with a smaller size, which cannot be found by Raman spectra and are deleterious to the electrical studies of n-layer graphenes.\textsuperscript{25–27}

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**Supporting Information Available:** The results of the corresponding optical images of Figure 3, a model of gold atom on graphenes, the calculation methods of the total volume of gold left on graphenes, a model to show the different diffusion barriers of gold on graphenes, gold film on graphenes obtained by reduction of graphene oxide, SEM and EDX showing that the gold film can be evaporated off graphenes, primary results with Cu, Ag nanoparticles on graphenes are given. This material is available free of charge via the Internet at http://pubs.acs.org.

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