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Reversible structure change in graphene/metal interface by intercalation and deintercalation

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Intercalation in two-dimensional materials is an important degree of freedom to modify the structural and electronic properties. In this paper, the atomic arrangements at the interface between single-layer graphene and Co(0001) with intercalated Ag and Au atoms were investigated using total-reflection high-energy positron diffraction. A structure analysis on the basis of dynamical diffraction theory demonstrates that by intercalation at annealing temperatures above 400 °C, the graphene height from the underlying atoms is shifted from 2.04 Å to 3.24 Å for Ag and 3.32 Å for Au. The Debye temperatures of graphene are changed from 430 K to 320 K for Ag and 368 K for Au by the intercalation. These changes indicate that intercalation results in the transformation to quasifreestanding graphene via a van der Waals interaction. For Ag, further annealing at 700 °C enables the graphene height and the Debye temperature to restore the pristine values by Ag deintercalation. However, for Au, the graphene height remains high up to 900 °C, which indicates the absence of deintercalation. The obtained results reveal a reversible structure change in the graphene/Co(0001) interface by Ag intercalation and deintercalation. The difference in the deintercalation between Ag and Au atoms can be explained by the activation energy of thermal desorption.

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I. INTRODUCTION

Graphene, an sp^2-hybridized two-dimensional honeycomb network of carbon, is one of the most extensively studied materials owing to the fascinating nature of Dirac fermions [1]. There are many useful features for possible technological applications; specifically, graphene is ultrathin, tough, and flexible, and in addition, it has an extremely high carrier mobility and large spin diffusion length. Thus, graphene-based technology is regarded as a good candidate for realizing future electronic and spintronic devices [2,3].

The characteristics of graphene can be changed by intercalation at the interface of graphene/substrate [4]. Angle-resolved photoemission spectroscopy studies have clearly demonstrated that intercalation allows to modify the electronic states of graphene. For single-layer graphene on the Ni(111) surface [5], the Dirac cone of linear energy dispersion for suspended graphene is considerably modified by the hybridization between p_z states of C atoms and d states of Ni atoms. The intercalation of noble metal atoms such as Ag and Au restores the Dirac cone by the decoupling between graphene and the intercalated layer [6,7]. In addition, Au intercalation leads to spin-split states derived from the Bychkov-Rashba effect [5] and the band-gap openings in the Dirac cone of graphene through the broken symmetry of two C sublattices [8]. Moreover, an intercalated Ag multilayer brings about the formation of quantum well states confined between graphene and a substrate [7]. An intercalated layer superimposed with graphene acts as a platform to synthesize versatile two-dimensional materials such as twisted plumbene, the lead counterpart of graphene [9]. Therefore, intercalation is an important route for modifying the structural and electronic properties of graphene-based materials and heterostructures towards novel functions.

The electronic states of intercalated graphene/metal substrate systems have been extensively investigated using photoemission spectroscopy. However, studies on the atomic structures of interfaces in intercalated systems are limited [10,11]. In particular, the height of graphene from the underlying atoms is an important structural parameter that is closely related to the appearance of a Dirac cone through the interaction between graphene and the substrate surface [12]. Therefore, the determination of the graphene height is of great importance in elucidating the origin of the electronic states of intercalated graphene/metal substrate systems. In this paper, we systematically investigated the structure changes in the graphene/transition metal interfaces associated with the intercalation and deintercalation of noble metal atoms Ag and Au using total-reflection high-energy positron diffraction (TRHEPD). Through the structure analysis using TRHEPD, we show the change in the graphene height and the Debye temperatures by Ag and Au intercalation and a reversible change by Ag deintercalation.

II. EXPERIMENT

Single-layer graphene on a Co(0001) surface was used as a sample [Fig. 1(a)]. A single-crystalline Co(0001) thin film with a thickness of 20 nm was grown on an α-Al_2O_3(0001)

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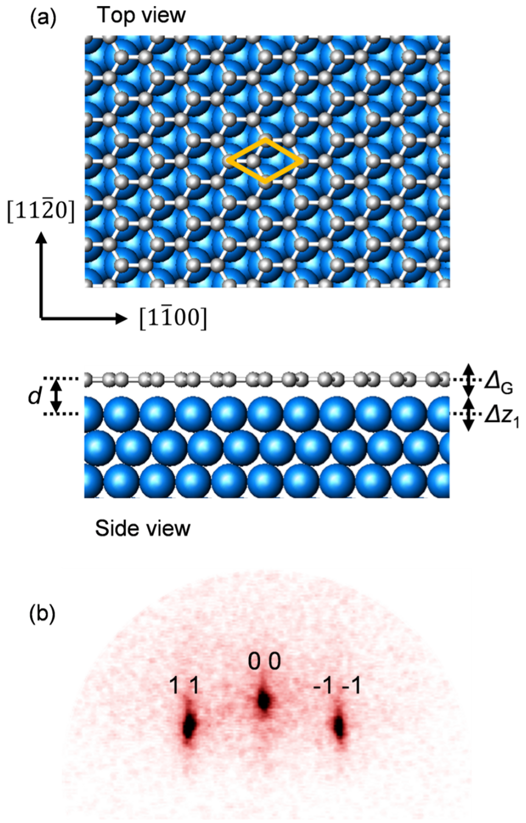

FIG. 1. (a) Structure model of single-layer graphene on a Co(0001) surface. Gray and blue circles represent C and Co atoms, respectively. The height of the graphene layer from the top Co layer is denoted as d. Δ_G and Δz_1 are the magnitude of buckling in the graphene layer and the shift of the top Co layer with respect to the ideal bulk position, respectively. The unit cell is shown by a yellow rhombus. (b) TRHEPD pattern observed for graphene/Co(0001). The incident azimuth and glancing angle are the $[11\bar{2}0]$ direction and 4.6°, respectively. The indices of diffraction spots, 0 0 (specular), 1 1, and −1 −1, are denoted.

substrate by the deposition of Co atoms at 350 °C. Subsequently, single-layer graphene was synthesized on the Co(0001) surface by exposing the surface to acetylene gas at 600 °C [13,14]. The formation of single-layer graphene was confirmed by x-ray photoelectron spectroscopy. A TRHEPD pattern is observed for pristine graphene/Co(0001), as shown in Fig. 1(b). Five monolayers (ML) of Ag or Au atoms were deposited on graphene/Co(0001) at room temperature, followed by annealing at each temperature (T_a) for 15 min.

TRHEPD experiments were carried out at the Slow Positron Facility of the Institute of Materials Structure Science, KEK. The details of the experimental setup were described elsewhere [15]. The positron beam energy was set at 10 keV. The rocking curves, i.e., diffraction spot intensity versus glancing angle (θ), were measured by rotating the sample up to 6° by 0.1° steps. The incident azimuth was chosen at 15° off from the $[1\bar{1}00]$ direction (the so-called one-beam condition [16]), where the intensity of the 0 0 (specular) spot depends on the surface-normal components of atomic positions and the number density of atoms in a layer. All measurements were performed at room temperature.

III. RESULTS AND DISCUSSION

Figure 2(a) shows a series of TRHEPD rocking curves for the 0 0 (specular) spot measured for Ag-adsorbed graphene/Co(0001) up to $T_a = 700\,^{\circ}\mathrm{C}$. Assuming a mean inner potential of 11.5 V for graphene [17], the critical angle (θ_c) of the total reflection can be estimated to be 1.94° using Snell's law. Thus, the intensity at $\theta < \theta_c$ carries information on the adsorbates on graphene.

The bottom of Fig. 2(a) shows the rocking curve for pristine graphene/Co(0001) before Ag adsorption. The peaks at $\theta = 2.8^{\circ}$, 4.3°, and 5.9° are clearly observable, whose profile coincides with a previous study [18]. After Ag deposition at room temperature (denoted as "as-depo"), the intensity considerably decreases throughout θ, and the profile becomes blurry. This result is obtained because the surface of graphene/Co(0001) is covered with Ag islands as identified from a new peak at approximately $\theta = 1.5^{\circ}$ (below θ_c) attributable to the transmission spot from Ag crystals. At $T_a = 300\,^{\circ}\mathrm{C}$, there is no dramatic change in the curve shape. However, after annealing at 400 °C, the peaks at $\theta = 4.3^{\circ}$ and 5.9° shift to 3.9° and 5.1°, respectively, although the intensity remains weak. The peak shift suggests the manifestation of intercalation. The onset temperature for Ag intercalation agrees with that in a previous report (300–500 °C) on Ag-intercalated graphene/Ni(111) [19]. According to the Bragg equation, the peak shift toward lower glancing angles is indicative of an increase in the graphene height. Above $T_a = 500\,^{\circ}\mathrm{C}$, the peak at approximately $\theta = 1.5^{\circ}$ disappears, and peak intensities gradually increase with an increase in annealing temperature. At $T_a = 600\,^{\circ}\mathrm{C}$, the peaks become sharp, and intensities below θ_c are nearly the same as those of pristine graphene/Co(0001). This result indicates that residual Ag atoms on the graphene surface disappear by annealing. Of note, the total number of intercalated Ag atoms is not necessarily equal to the one deposited (5 ML) because some Ag atoms on graphene are possibly desorbed without penetrating graphene, as has been indicated in a previous study [19].

The rocking curve profile changes with further annealing. The top curve in Fig. 2(a) shows that after annealing at 700 °C, the peak positions return to those of pristine graphene/Co(0001) before Ag deposition. This result indicates that the graphene height is shifted to that of pristine graphene/Co(0001) owing to the change in the interaction between graphene and the underlying layer. Therefore, Ag atoms are deintercalated at $T_a = 700\,^{\circ}\mathrm{C}$.

Such an intensity change is also observed for Au-adsorbed graphene/Co(0001). Figure 2(b) shows a series of rocking curves for Au-adsorbed graphene/Co(0001) up to $T_a = 900\,^{\circ}\mathrm{C}$. Similar to the Ag case, the new peak appears at approximately $\theta = 1.5^{\circ}$ when 5 ML of Au atoms are deposited at room temperature, which indicates the existence of Au islands on graphene. At $T_a = 400\,^{\circ}\mathrm{C}$, the peaks at $\theta = 4.3^{\circ}$ and 5.9° suddenly shift to $\theta = 3.9^{\circ}$ and 4.9°, respectively, and the peak at $\theta = 1.5^{\circ}$ disappears. The peak shift is ascribed to the upward displacement of the graphene height by Au intercalation. The intercalation temperature is also

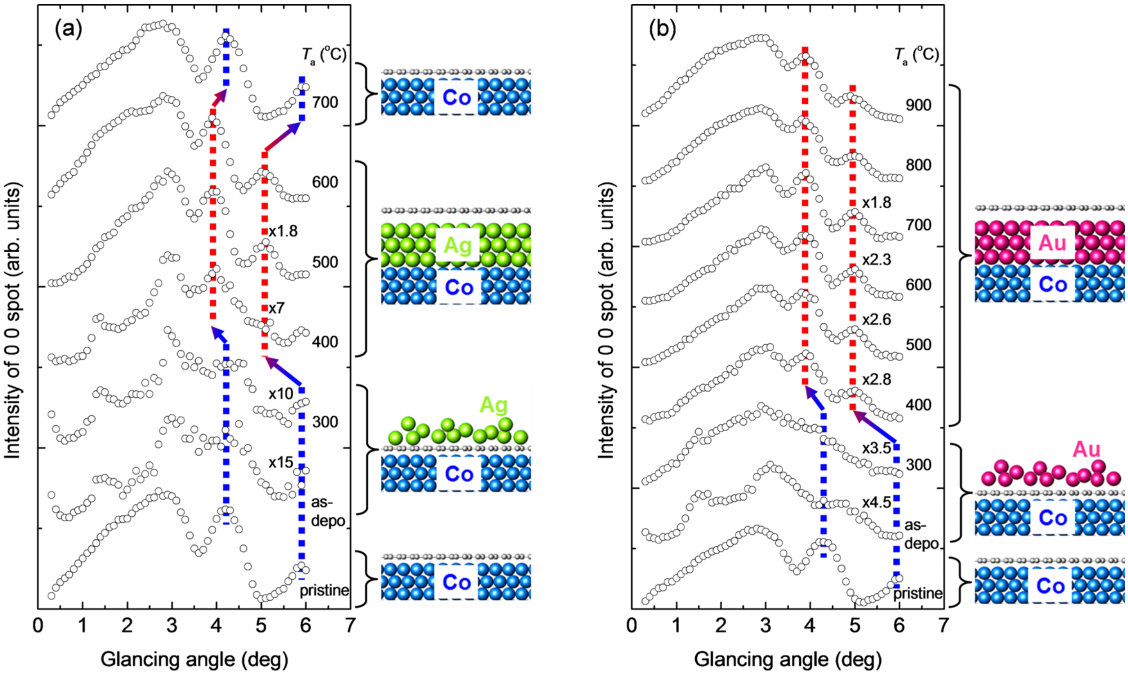

FIG. 2. TRHEPD rocking curves of 0 0 spots measured for (a) Ag-adsorbed and (b) Au-adsorbed graphene/Co(0001). The annealing temperature ($T_{\rm a}$) is labeled on the right-hand side of each curve. The bottom curve (denoted as "as-depo") is for pristine graphene/Co(0001) before deposition. The dotted lines are guides to the eye. Schematic drawing of the sample at each annealing stage is shown at the right-hand side of the figure.

consistent with that in a previous study on graphene/Ni(111) [5]. Up to $T_{\rm a} = 800\,^{\circ}\mathrm{C}$, the intensities gradually increase with an increase in annealing temperature, which indicates the disappearance of residual Au atoms on graphene. Compared to the Ag case, the peak positions remain unchanged up to $T_{\rm a} = 900\,^{\circ}\mathrm{C}$. Therefore, we conclude that Au atoms below graphene are not deintercalated in this temperature range.

To confirm the above-mentioned findings, we determined the atomic arrangements at the interface of graphene/substrate on the basis of dynamical diffraction theory [20]. We changed the graphene height (d) from the top Co (Ag and Au) layer, the deviation (Δz_1) of the top Co (Ag and Au) layer from the bulk position, and the magnitude of the buckling ($\Delta_{\rm G}$), which resulted in the height difference between the two sites of carbon atoms in the unit cell of graphene, to minimize the difference between measured and calculated curves [Fig. 1(a)]. In the calculations, we assumed that intercalated Ag and Au atoms form an fcc structure at the interface of graphene/Co(0001) [7]. Of note, owing to the limited penetration depth of the positron beam, the atomic layers below the second layer make a smaller contribution to the intensity. The graphene layer was taken to be commensurate and incommensurate with respect to the Co(0001) plane, and intercalated Ag(111) and Au(111) planes, respectively. The atomic positions below the second Co (Ag and Au) layer were fixed to be similar to those of ideal bulk layers. The Debye temperatures for graphene ($\Theta_{\rm DG}$) and the top Co (Ag and Au) layer ($\Theta_{\rm D1}$) were also treated as fitting parameters, while those below the second layer were fixed at the bulk values [21]. The absorption potentials originating from electronic excitations for C, Co, Ag, and Au layers were 0.88, 1.34, 1.11, and 1.39 V, respectively [22]. The goodness of fit was determined by the reliability factor (R) [23].

For pristine graphene/Co(0001), we have already obtained the optimum parameters in a previous study by analyzing the TRHEPD rocking curve [18]. The optimized parameters are listed in Table I. The rocking curve calculated using the optimum parameters is in good agreement with that measured for pristine graphene/Co(0001) ($R = 1.08\%$), as shown by the solid line in Fig. 3(a). The graphene height from the top Co layer is 2.06 ± 0.03 Å [18], which is much smaller than

TABLE I. Structural and nonstructural parameters for pristine, Ag-intercalated, Au-intercalated, and Ag-deintercalated graphene (Gr)/Co(0001).

	d (Å)	$\Delta_{\rm G}$ (Å)	Δz_1 (Å)	$\Theta_{\rm DG}$ (Å)	$\Theta_{\rm D1}$ (Å)
Gr/Co [18]	2.06 ± 0.04	0.01 ± 0.04	-0.15 ± 0.02	493	430
Gr/Ag/Co	3.24 ± 0.07	0.00 ± 0.07	-0.04 ± 0.03	320	161
Gr/Au/Co	3.32 ± 0.05	0.00 ± 0.05	-0.02 ± 0.03	368	103
Gr/Co (Ag deintercalated) [18]	2.06 ± 0.04	0.01 ± 0.04	-0.15 ± 0.02	493	430

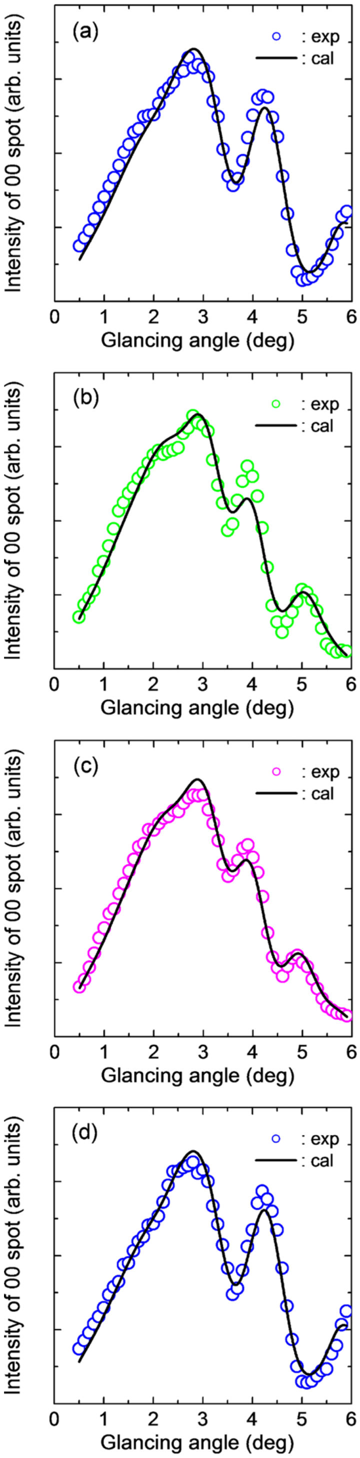

FIG. 3. TRHEPD rocking curves of 0 0 spots for (a) pristine, (b) Ag-intercalated, (c) Au-intercalated, and (d) Ag-deintercalated graphene/Co(0001). The open circles are the experimental data, and the solid lines are the curves calculated using the optimum parameters. The experimental data in (a)–(d) are the same as those in the bottom of Fig. 2(a), the data at $T_a = 600\,^\circ\mathrm{C}$ in Fig. 2(a), the data at $T_a = 900\,^\circ\mathrm{C}$ in Fig. 2(b), and the data at $T_a = 700\,^\circ\mathrm{C}$ in Fig. 2(a), respectively.

the interlayer distance in graphite (3.35 Å). The top Co layer is shifted downward ($\Delta z_1 = -0.15 \pm 0.02$ Å). There is no buckling in the graphene layer ($\Delta_G = 0.01 \pm 0.04$ Å). Thus, the graphene layer is strongly interacted with the Co(0001) surface owing to the hybridization between p_z states and d states [12].

Similar to pristine graphene/Co(0001), we also analyzed the rocking curves measured for Ag-intercalated graphene/Co(0001) at $T_a = 600\,^\circ\mathrm{C}$ [Fig. 3(b)] and for Au-intercalated graphene/Co(0001) at $T_a = 900\,^\circ\mathrm{C}$ [Fig. 3(c)]. The solid lines in Figs. 3(b) and 3(c) show the rocking curves calculated using the optimum parameters which explain well the measured curves ($R = 1.21\%$ for Ag intercalated, $R = 0.82\%$ for Au intercalated). We determined the graphene height from the top Ag- and Au-intercalated layer to be 3.24 ± 0.07 and 3.32 ± 0.05 Å, respectively (Table I). These values are more than 1 Å larger than that for pristine graphene/Co(0001) and are similar to the interlayer distance in graphite, which indicates the transformation to quasifreestanding graphene via a van der Waals interaction. The graphene height determined for Ag- and Au-intercalated graphene/Co(0001) is approximately the same as the values obtained by density functional theory (DFT) calculations for graphene/Ag(111) (3.33 [24], 3.26 [25], and 3.32 Å [26]) and graphene/Au(111) (3.31 [24], 3.27 [25], and 3.35 Å [26]) substrates. Therefore, Ag and Au intercalation leads to the decoupling of graphene with the Co(0001) surface.

The magnitude of buckling in the graphene layer was determined to be 0.00 Å for both Ag- and Au-intercalated cases. The result indicates that the graphene layer still remains flat (no buckling) after the intercalation. The shift of the intercalated top Ag and Au layer with respect to the ideal bulk position was determined to be -0.04 ± 0.03 and -0.02 ± 0.03 Å, respectively. The Debye temperatures (320 and 368 K) of graphene for Ag- and Au-intercalated graphene/Co(0001) are smaller than that for pristine graphene (430 K) and similar to the outermost layer of graphite (325 K for the surface-normal component [27]), which suggests the enhancement of thermal vibration of graphene owing to decoupling. The Debye temperatures of the top Ag and Au layers were determined to be 161 and 103 K, respectively, which are compatible with the surface Debye temperatures of Ag(111) (165 K [28]) and Au(111) (83 K [29]). The results strongly complement the intercalation of Ag and Au atoms and the formation of atomically thin Ag and Au layers with the (111) plane at the interface between graphene and Co(0001).

The profile of the rocking curve measured for Ag-deintercalated graphene/Co(0001) at $T_a = 700\,^\circ\mathrm{C}$ is almost the same as that for pristine graphene/Co(0001) and is reproduced well by considering the values (Table I) determined for pristine graphene/Co(0001) ($R = 0.96\%$), as shown by the solid line in Fig. 3(d). Thus, the Ag layers at the interface of graphene/Co(0001) are deintercalated at $T_a = 700\,^\circ\mathrm{C}$, and the graphene/Co(0001) interface recovers to its pristine structure, which shows a reversible structure change without degradation.

This difference in the deintercalation behavior between Ag- and Au-intercalated graphene/Co(0001) is closely related to the activation energy of thermal desorption. The thermal desorption of Ag and Au from the thin-film surfaces has been investigated using thermal desorption spectroscopy (TDS). At the interface of graphene/Co(0001), the intercalated layers have the fcc structure [7]. By considering the graphene heights and the Debye temperatures for Ag and Au intercalation, the discussion of the thermal desorption process on the thin-film surfaces can be straightforwardly applied to the intercalated layers in this study. The activation energies of thermal desorption for Ag and Au thin-film surfaces were determined to be 2.67 and 3.36 eV, respectively, in the process of thermal desorption from a thin film with a thickness of about 4 ML, which is considered to have little effect from the substrates [30]. The temperatures showing the maximum desorption rate were estimated as 707 and 947 °C for Ag and Au of ∼4 ML, respectively [30], which are almost independent of the substrate species [31]. The temperature difference in the thermal desorption between Ag and Au corresponds to 240 °C, giving rise to the difference in deintercalation. On the basis of the above TDS results, the Ag-intercalated layer undergoes thermal desorption (deintercalation) at around 707 °C, which is consistent with the observations in this study. On the other hand, since the thermal desorption temperature of Au is around 947 °C, the intercalated Au layer is hardly desorbed by the annealing at 900 °C (the maximum annealing temperature in this study), that is, the absence of Au deintercalation. The Au deintercalation probably occurs at an elevated annealing temperature of around 947 °C. In this temperature region, however, the initial stage of thermal desorption for Co will progress [32], accompanied by the thermal desorption for Au. In actuality, the Au deintercalation could not be observed in this study because the dewetting of the Co(0001) thin film on the $Al_2O_3(0001)$ substrate was caused by the annealing above 900 °C.

IV. SUMMARY

In summary, we investigated the structure change in graphene/Co(0001) by Ag and Au intercalation using the TRHEPD technique. The Ag and Au atoms are intercalated at the interface of graphene/Co(0001) at $T_a = 400\,^\circ\mathrm{C}$. Upon Ag and Au intercalation, the graphene heights from the underlying atoms are lifted from 2.04 Å to 3.24 and 3.32 Å, respectively. The Debye temperatures of graphene accordingly decrease from 430 to 320 K for Ag and 368 K for Au. The intercalated Ag atoms are removed at $T_a = 700\,^\circ\mathrm{C}$, and the graphene height and the Debye temperature are restored to 2.04 Å and 430 K, respectively, i.e., the pristine graphene/Co(0001) interface structure before intercalation. However, Au atoms still exist at the interface up to $T_a = 900\,^\circ\mathrm{C}$. Therefore, the Ag deintercalation exhibits a reversible structure change in the graphene/Co(0001) interface. Because of the difference in the activation energy of thermal desorption, Au deintercalation cannot be observed in the temperature range up to 900 °C.

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