Exploring the Interface Landscape of Noble Metals on Epitaxial Graphene

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1. Introduction

Self-assembly of noble metals (NMs) on weakly interacting 2D materials, including graphene, is a promising strategy for the synthesis of novel hybrid materials with nonconventional functionalities for electronics,[1–3] sensors,[4–6] and catalytic applications.[7–10] The resulting synergy between graphene, which possesses extraordinary physical properties,[11–14] and plasmonically/catalytically active NMs[15–17] enables achieving enhanced output performance and stability in broadband and ultrafast photodetectors,[18] dye-sensitized solar cells,[19] large area surface-enhanced Raman scattering (SERS) substrates,[20] and effective electrocatalysts for the hydrogen evolution reaction in water splitting.[21]

Further progress in the study of fundamental properties of NMs-graphene systems and their implementation into next-generation realistic devices necessitates significant modification of the NMs components of the hybrid system up to discovery of true 2D metals—one-atom-thick NM layers. In this regard, great efforts are, nowadays, directed toward synthesis of 2D metals on graphene.[22–26] Although the attempts to accommodate 2D metals on the hexagonal lattice of sp2-bonded carbon atoms were initially inspired by the first experimental observation of confined growth of 2D Fe inside nanopores of graphene, a common approach today is the use of graphene–SiC interface as a platform for stabilization of 2D metal layers through metal intercalation processes.[27–30] Some intriguing results on the formation and the properties of 2D Au and Ag layers have been recently reported by Forti et al.[28] and Briggs et al.[29] For instance, it was demonstrated that the 2D-Au monolayer is a semiconducting material with the valence band maximum 50 meV below the Fermi level,[28] whereas the intercalated Ag layers retain their metallic and plasmonic nature.[29] It is believed that due to a very weak interaction between the newly formed quasi-free-standing monolayer epitaxial graphene (MLG) and NMs layers, the corresponding hybrid systems might be referred to as a class of van der Waals heterostructures with potential applications in nonlinear optics and spintronics.

It is worth noting that the morphology and, thereby, the quality of vapor-deposited thin NMs layers on graphenized surfaces

Understanding the interaction between noble metals (NMs) and epitaxial graphene is essential for the design and fabrication of novel devices. Within this framework, a combined experimental and theoretical investigation of the effect of vapor-deposited NM (silver [Ag] and gold [Au]) nanostructures on the vibrational and electronic properties of monolayer epitaxial graphene (MLG) on 4H-SiC is presented. Large sets of Raman scattering data are analyzed using supervised classification and statistical methods. This analysis enables identification of the specific Raman fingerprints of Au- and Ag-decorated MLG originating from different dispersion interactions and charge transfer at the metal nanostructure/MLG interface. It is found that Raman scattering spectra of Au-decorated MLG feature a set of allowed phonon modes similar to those in pristine MLG, whereas the stronger Ag physisorption triggers an activation of defect-related phonon modes and electron doping of MLG. A principal component analysis (PCA) and linear discriminant analysis (LDA) are leveraged to highlight the features in phonon dispersion of MLG that emanate from the NM deposition process and to robustly classify large-scale Raman spectra of metal-decorated graphene. The present results can be advantageous for designing highly selective sensor arrays on MLG patches decorated with different metals.
of SiC are strongly dependent on the growth regime governed by: 1) the metal deposition conditions; 2) the overall NMs–substrate interaction strength; and 3) the intercalation temperature. Hence, a holistic understanding of the growth-related phenomena on graphenized surfaces of SiC and their interrelationships acquires great fundamental and practical significance. Knowledge on NMs-epitaxial graphene interaction during the early film-formation stages (adsorption and nucleation) could facilitate the optimization of growth conditions, thereby promoting smarter growth kinetics control and formation of NMs layers with desired performance. In this context, Raman spectroscopy followed by a comprehensive multivariate data analysis can not only be helpful to probe the quality of graphene, but can also be adapted for probing the aforementioned interaction and providing insights into the phonon dispersion of the NMs-decorated graphene.

Our focus is on the interaction among NMs and epitaxial graphene on 4H-SiC, which is a specific type of graphene family materials. As epitaxial graphene has unique surface energetics, distinct from that of, e.g., free-standing graphene, one can anticipate that the growth of NMs on it will occur in a unique manner that cannot be understood in light of well-established knowledge pertaining to the effect of NMs on single-layer free-standing (exfoliated) graphene. To our understanding, Raman activity of metal-decorated epitaxial graphene must be the subject of a separate study.

Because there are many metal growth methods (thermal evaporation, electrodeposition, magnetron sputtering, chemical vapor deposition, electrophoretic deposition, etc.) and each of them has some specific features, the selected metal growth method requires specific attention. To the best of our knowledge, the direct current magnetron sputtering of metals on epitaxial graphene/4H-SiC is poorly investigated while it may be the technic of choice due to the observed robustness of epitaxial graphene. Hence, in the present study, we explore the interaction of magnetron-sputtered Au and Ag with epitaxial graphene on 4H-SiC using Raman mapping in conjunction with the principal component analysis (PCA), linear discriminant analysis (LDA), and correlation analysis. The same amount of material (equivalent to a nominal thickness of 2 nm) was deposited onto the MLG surface, enabling a direct comparison of the Au/MLG/SiC and Ag/MLG/SiC interaction strengths. It is worth noting that, here, we are investigating the two systems independently from each other. More specifically, we choose explicitly different conditions to study two scenarios: one with close to thermalized flux and the other with hyperthermal flux (Au and Ag, respectively). Independently of the growth conditions, we believe that both Ag-epitaxial graphene/SiC and Au-epitaxial graphene/SiC systems are interesting by their own strength. The considered NMs are expected to have different catalytic and sensing performance, and thus, there are no restrictions to apply different synthesis conditions to form Ag and Au nanoflakes with desired morphologies on the same substrate. This brings us to the concept of the sensor array, as an example. Indeed, different metals will uniquely interact with analyte molecules, therefore providing conditions for highly selective detection. Furthermore, as the material properties that are particularly essential for the applications are extremely sensitive to the metal particle size/shape, the growth under specified technological conditions is justified in terms of structure–property relationship. Considering that, we stress the importance of in-depth investigation of Ag-epitaxial graphene/SiC and Au-epitaxial graphene/SiC systems by making use of complex statistical methods. In fact, the statistical analysis of Raman data may be helpful not only for rational design of metal–graphene-based sensor arrays, but also for building appropriate pattern recognition algorithm to process the response signals from the individual sensing elements within a sensor array. Furthermore, by choosing two different metals, we demonstrate the usefulness and versatility of the proposed approach as a tool for analyzing Raman spectra of graphene decorated with arbitrary NMs. Finally, by performing density functional theory (DFT) calculations, it can be shown that the current results may be helpful for the development of arrayed optical sensor platform for selective detection of different species. Carbon monoxide (CO) will be tested to demonstrate a different interaction strength with Ag- and Au-decorated epitaxial graphene.

2. Results and Discussion

By comparing the morphologies of as-deposited 2 nm-Au and 2 nm-Ag (deposition rates of 0.1 and 1 Å s⁻¹, respectively; see Section 4 for experimental details) films on epitaxial graphene substrates (Figure S1, Supporting Information), we notice the formation of discontinuous Ag film comprising of small, isolated nanoscale islands (with a mean particle diameter of ~15 nm, see Figure S2, Supporting Information) and the appearance of an overall interconnected network structure of large, ramified Au islands. In a recent work, we deposited gold layers on epitaxial graphene by thermal evaporation at a deposition rate of 1 Å s⁻¹ and observed morphologies similar to those obtained for the sputtered layer in the present work. This implies that the deposition rate change from 0.1 to 1 Å s⁻¹ when thermalized fluxes are used does not affect the morphology substantially. Furthermore, the observed difference in growth morphologies of Ag and Au can be explained by the difference in metal–substrate interaction. A nominal thickness of 2 nm is small enough to prevent the formation of entirely continuous films, thereby enabling investigation of the early stages of metal nucleation, which are mainly governed by the metal–substrate interaction. This means that, depending on its binding affinity, the epitaxial graphene substrate determines, in different ways, the surface kinetics of the same amount of deposited gold and silver species. That is an important reason for the observation of unique structural evolution of gold and silver on epitaxial graphene.

More insights into how the as-deposited metal layers interface to epitaxial graphene are extracted from the analysis of the Raman spectra of epitaxial graphene before and after decoration with the NMs. Ag deposition gives rise to pronounced changes in the Raman spectrum of the bare epitaxial graphene (Figure 1), which manifest themselves as: 1) an appearance of defect-related Raman peaks of graphene, namely, D, D', D + D', G, and D** modes; 2) a significant red shift of the 2D peak; and 3) a pronounced decrease in the 2D/G amplitude ratio. The latter can be ascribed to the effect of surface plasmon resonance. More specifically, due to better matching between Ag plasma
According to our analysis, the peak position correlates very well with the threshold energy for carbon vacancy formation in graphene. More specifically, the kinetic energies of sputtered target atoms (Ag and Au) are on the order of few eV, which is lower than the kinetic energy of sputtered species on the phonon dispersion of bare MLG, suggesting that the gold exposure has minimal impact on structural, vibrational, and electronic properties of MLG. Similar to bare epitaxial graphene, Au/MLG Raman fingerprint is found to consist of only three dominating vibrational modes (G, 2D, and 2D') and weak spectral features related to the vibrational density of states of buffer layer. No defect-related phonon modes were observed, indicating negligibly small effect of both Ar plasma and sputtered Au species on the phonon dispersion of graphene. Our overall conclusion is that the observed defect-related Raman peaks in Ag-decorated epitaxial graphene can be related to stronger interaction between silver and topmost graphene layer than between gold and graphene.

Raman analysis also revealed that the spectral features related to the buffer layer are still resolved after metal deposition, suggesting that no intercalation of metals beneath the buffer layer under the considered growth conditions occurs. In our process, dc magnetron sputtering, the sputtered species are primarily neutrals (degree of ionization for dc magnetron sputtering discharges for sputtered metal is on the order of a few percent) with energies determined by the Thompson distribution. More specifically, the kinetic energies of sputtered target atoms (Ag and Au) are on the order of few eV, which is lower than the threshold energy for carbon vacancy formation in graphene. Therefore, we expect that the just-arriving metal species will preferentially occupy in-plane nucleation sites on the top of graphene layer rather than to migrate beneath buffer layer. Furthermore, the observation of symmetric line shape of 2D peak (Figure S3, Supporting Information) for metal-decorated graphene excludes a partial formation of quasi-free-standing bilayer graphene. Also, it was earlier shown that full-width at half-maximum (FWHM) (2D) for epitaxial graphene is larger than that for exfoliated graphene (≈46 cm⁻¹ vs >30 cm⁻¹) and becomes significantly broader (64 and 74 cm⁻¹) for the bilayer and trilayer epitaxial graphene on SiC. According to our analysis, the 2D peak for all three samples can be well fitted by a single narrow Lorentzian peak with an FWHM of 32, 47, and 49 cm⁻¹ for bare, Au-decorated, and Ag-decorated graphene, respectively (Figure S3, Supporting Information). These values are below the limit of 64 cm⁻¹ for bilayer graphene. Therefore, we are confident that the metal deposition mainly occurs on monolayer graphene regions. The observed 2D peak broadening after metal deposition can be interpreted as related to the metal-induced strain and doping fluctuations.

To shed additional light on the nature of NMs effect on the properties of MLG, we analyze the squared Pearson correlation coefficients, $R^2$, of the interrelationships between all pairs of parameters of main characteristic peaks of bare and metal-decorated MLG (Figure 2). The more positive the $R^2$ value, the more pronounced the linear correlation between the corresponding parameters. A careful inspection of the correlation matrices for bare and Au-decorated MLG samples indicates that the 2D peak position correlates very well with G peak position (Figure 2a,b), which can be explained by the presence of a constant doping level and varying strain values in the considered samples. Indeed, the data points for bare and Au-decorated MLG samples (filled green and filled blue circles, respectively) are partly overlapping and located in the so-called forbidden area of 2D–G space on the left-hand side of the strain line (Figure 3a, see also Figure 3b,c). This suggests a small decrease in the electron doping and an appearance of large nonuniform compressive strain. Concomitantly, the 2D peak positions of the Ag/MLG sample do not present linear relationship with respect to G peak positions (Figure 2c). Considering 2D–G space, we notice a very narrow spread of the experimental data points of Ag/MLG (marked by filled red circles) between strain and doping lines. This implies large-area uniform n-type doping of MLG (with a mean carrier density of $9.5 \times 10^{12}$ cm⁻² determined by a graphical method proposed by Lee et al. due to the charge transfer from Ag to MLG. To ascertain the charge transfer direction, DFT-based calculations of charge density difference (CDD) for
both Au/MLG and Ag/MLG interfaces were performed (Figure 4a–c). As shown in Figure 4b,c, both Au and Ag adatoms are surrounded by cyan regions, indicating a pronounced charge depletion because of the donation of electrons. Thus, the charge transfer at the interface occurs from metal adatoms to MLG, which is in good agreement with the experimental results. In this regard, it is important to note the emergence of more extended yellow region (charge accumulation) in the case of Ag adsorption (Figure 4b), which can be explained by a larger charge transfer between Ag and MLG than between Au and MLG. Figure 4a demonstrates the xy-plane averaged charge redistribution as a function of distance along the z-direction. The CDD curve in the middle of the Au/MLG structure (between Au and MLG layer) contains deep minimum related to a charge depletion region around graphene and a weak local maximum around zero. However, the analysis of CDD curve for Ag/MLG indicates much larger charge redistribution at the interface, which is confirmed by an appearance of a stronger CDD peak in the middle of the structure. A distinct difference between both structures is also revealed by performing a charge population analysis using Voronoi and Hirshfeld schemes. It is calculated that Hirshfeld (Voronoi) charge on Au is about 0.249 e\(^-\) (0.271 e\(^-\)), which is smaller than the charge on Ag of 0.299 e\(^-\) (0.321 e\(^-\)).
As in the description of the Raman spectra in Figure 1, the unique growth conditions of Ag island-like film also cause the appearance of the nominally forbidden defect-related phonon modes. Interestingly, as can be seen from the corresponding correlation matrix (Figure 2c), there is a strong mutual correlation between $2D/G$ and $D/G$ amplitude and area ratios. More specifically, the gradual increase in the $D/G$ ratio is accompanied by an increase in the $2D/G$ ratio (Figure 5). Such a dependence can be explained by several factors. First, because of the statistical distribution of Ag island areas (Figure S2, Supporting Information), the MLG regions are subjected to different Ag exposures, which causes both defect density and electron concentration fluctuations. Apparently, larger Ag islands (from 20 up to 50 nm) can donate more electrons to MLG and induce more defects. $D/G$ ratio may depend not only on the defect density, but also on the electron density. Up to a specific critical value of carrier concentration, an increase in the carrier concentration leads to increase in the $D/G$ ratio. However, under high-doping level, Pauli’s exclusion principle restricts the double resonance process related to Raman $D$-band. As the corresponding quantum pathways are partially blocked by doping the epitaxial graphene, Raman intensity of $D$-band decreases. While $2D/G$ ratio is determined by electron–phonon scattering rate ($\gamma_{ep}$) and electron–electron scattering rate ($\gamma_{ee}$), the latter is

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**Figure 4.** a) Laterally (xy-plane) integrated CDD curves of epitaxial graphene interacting with Au and Ag, respectively. Vertical dotted lines denote z coordinates (spatial positions) of topmost graphene layer (green) and adsorbed metal species (Ag position is represented by violet line, whereas orange corresponds to Au position). The 3D CDD plots with an iso-surface value of $0.001 \text{ e Å}^{-3}$ for b) Au and c) Ag adsorbed on epitaxial graphene surface. Yellow and cyan regions demonstrate charge accumulation (positive) and depletion (negative) regions, respectively.
affected by doping level ($\varphi_{ee} \approx 0.06|E_{0}|$). Therefore, we assume that the co-existence of the graphene regions with low $D/G$ and $2D/G$ ratios as well as with high $D/G$ and $2D/G$ ratios may be related to the different doping levels in these regions. This phenomenon may occur due to the nonuniform Ag island size distribution, because variations in size/shape of the Ag islands can induce local variations in the charge transfer between silver and epitaxial graphene. Indeed, according to the DFT calculations (Figure S4, Supporting Information), $Ag_{8}$ planar cluster adsorbed on MLG donates more electrons (0.616 $e^{-}$) to the epitaxial graphene than the smaller $Ag_{2}$ and $Ag_{4}$ clusters (0.232 $e^{-}$ and 0.552 $e^{-}$, respectively), which additionally corroborates our assumption that the island area may affect the total interfacial charge transfer. Thus, local charge transfer fluctuations cannot be ruled out as a possible reason for doping inhomogeneity and the revealed correlation between $2D/G$ and $D/G$ ratios.

Another reason for the mentioned correlation is that the size and shape of certain Ag nanoscale islands could provide much better way to satisfy the plasmon resonance excitation conditions for $D$ peak amplitude enhancement rather than for $G$ peak amplitude enhancement. In other words, under such conditions, $G$ peak would experience smaller changes in amplitude and area, thereby causing synchronous changes of $D/G$ and $2D/G$ ratios. Indeed, the size and the shape of silver nanoparticles are known to strongly influence their SERS activity. Earlier, it was shown that the maximal enhancement of $G$ and $2D$ peak intensity in graphene can be obtained for Ag ellipsoids with a major axis length of $\approx 175$ nm, which is extremely far from the mean particle size in our samples. Nevertheless, even in the case of the weak SERS activity of Ag nanoparticles, we cannot neglect its possible relationships with the intensities of the characteristic Raman peaks. Careful analysis of the scanning electron microscopy (SEM) image of Ag-decorated MLG indicates that the Ag island shapes cannot be approximated by an exact ellipsoid or sphere. In our case, the formation of irregularly shaped Ag nanoislands occurs, and the observed changes in the Raman signal of graphene are originating from the combined contributions from all irregularly shaped Ag nanoislands. Interestingly, the island with sharp edges or even facets may exhibit increased electric field, providing better conditions for local SERS enhancement. Therefore, the observed spot-to-spot variation in Raman intensity of $D$- or $G$-band may indicate the existence of hotspots with different electric field magnitudes. It is reasonable to assume that the size of selected Ag nanoislands is more appropriate compared with others to provide better matching between Raman $D$-band energy and plasmon resonance energy than between Raman $G$-band energy and plasmon resonance energy.

Through performing PCA and LDA, it was revealed that Ag-covered MLG regions can be easily discerned from uncovered and Au-covered MLG regions. Based on the preprocessed Raman spectra, we initially show that the scores plot of the first four principal components (PCs) for the Au/MLG sample (Figure 6a) resembles, to some extent, the same plot for bare MLG sample (Figure S5, Supporting Information), thereby indicating that PCs represent only the characteristic phonon modes of graphene. Contrary, Ag deposition was found to have a stronger effect on the phonon dispersion of MLG, as shown in the rich structure of PC2 loading plot that is related to defect-mediated activation of initially forbidden Raman modes (Figure 6b). Despite this method enabling to understand quantitatively the whole internal difference between the samples, PCs values partly overlap (not shown here), thereby complicating their discrimination. To overcome this drawback, we constructed a new training data set based only on the parameters (position, width, amplitude, and area) of the observed Raman peaks (from 121 to 1681 observations and eight variables) and applied the PCA-LDA approach to classify experimental data points. It is worth noting that the first three PCs interpret more than 97% variances. Figure 7a demonstrates score cluster plot of the three considered samples. A clear separation of the data points belonging to the Ag/MLG sample from those of the remaining two was observed, whereas PCs of Au/MLG could not be clearly distinguished. Indeed, as shown in the confusion matrix (Figure 7b), the PCA-LDA model misclassifies small fraction of experimental Raman data of Au/MLG as those of bare MLG in the test set, whereas it successfully classifies 100% of the Ag/MLG data. Spectral discrimination of Raman signal from Ag-covered MLG and Au-covered MLG using supervised classification methods is critically important for design of novel bimetallic sensor arrays. As was demonstrated by Li et al., such a bimetallic sensor array comprising five gold nanoparticles and two silver nanoparticles with different sizes as sensing elements can be utilized for simultaneous detection of proteins and bacteria. Furthermore, considering the advantage of epitaxial graphene as an electrical transducer for sensing of toxic heavy metals and carcinogenic volatile organic compounds, we believe that the integration of epitaxial graphene with NMs may boost the development of versatile discriminative detection platform for fast recognition of chemical substances with potential health hazards. In this regard, Raman spectroscopy combined with the PCA-LDA method can provide more reliable detection and quantitation of hazardous substances. In line with this, the current research shows the applicability and advantages of such a combined approach to quantify the differences and separation between the Au-covered and Ag-covered graphene monolayer regions.

To examine the feasibility of the idea of bimetallic sensor arrays, we performed additional DFT calculations. Large $8 \times 8$
epitaxial graphene slab with two Si–C bilayers was used as a substrate model. Then, two clusters—\(\text{Au}_5\) and \(\text{Ag}_5\)—were placed onto the surface of epitaxial graphene simultaneously so that to avoid any interaction between them. Such an approach enables to mimic a sensor array consisting of three regions, which are available for different kinds of interactions (physisorption or chemisorption) with external molecules in the proximity of the epitaxial graphene surface: uncovered MLG, Ag-covered MLG, and Au-covered MLG, respectively. Figure 8 demonstrates the optimized structure of the \(\text{Ag}_5\text{Au}_5\)-MLG/SiC system.

It is important to note that \(\text{Ag}_5\) and \(\text{Au}_5\) clusters interact with MLG/SiC in different ways. As separated metal clusters are presumed to be noninteracting, it is possible to calculate local interaction energies for two pairs (\(\text{Ag}_5\)-MLG and \(\text{Au}_5\)-MLG, respectively) using the following equations

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\begin{align*}
E_{\text{int}}^{\text{Ag}_5\text{Au}_5-\text{MLG}} &= E_{\text{tot}}^{\text{Ag}_5\text{Au}_5-\text{MLG}} - E_{\text{tot}}^{\text{Ag}_5-\text{MLG}} - E_{\text{tot}}^{\text{Au}_5-\text{MLG}} \\
E_{\text{int}}^{\text{Ag}_5\text{Au}_5-\text{MLG}} &= E_{\text{tot}}^{\text{Ag}_5\text{Au}_5-\text{MLG}} - E_{\text{tot}}^{\text{Ag}_5-\text{MLG}} - E_{\text{tot}}^{\text{Au}_5-\text{MLG}}
\end{align*}
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where \(E_{\text{tot}}^{\text{Ag}_5\text{Au}_5-\text{MLG}}\) is a total energy of the whole interacting system, \(E_{\text{tot}}^{\text{Ag}_5-\text{MLG}}\) and \(E_{\text{tot}}^{\text{Au}_5-\text{MLG}}\) are the total energies of the system without \(\text{Ag}_5\) and \(\text{Au}_5\) clusters, respectively, and \(E_{\text{tot}}^{\text{Ag}_5\text{Au}_5}\) and \(E_{\text{tot}}^{\text{Au}_5\text{Ag}_5}\) are the total energies of isolated metal clusters. Except \(E_{\text{tot}}^{\text{Ag}_5\text{Au}_5}\), all remaining energy terms were obtained by single-point calculations using Cartesian coordinates for relaxed geometrical configuration of the \(\text{Ag}_5\text{Au}_5\)-MLG/SiC structure. The interaction energy between \(\text{Ag}_5\) and epitaxial graphene (\(-3.7109\text{ eV}\)) is greater than that obtained for the \(\text{Au}_5\)-MLG system (\(-2.9149\text{ eV}\)). The average cluster-substrate distance in the case of \(\text{Ag}_5\)-MLG is found to be smaller than that in \(\text{Au}_5\)-MLG.
(2.4184 vs 2.6019 Å) that explains the larger total charge transferred from Ag₅ to MLG (0.522 e⁻, according to Voronoi population analysis) in comparison with that from Au₅ to MLG (0.468 e⁻). The results of CDD analysis also show that a charge depletion exists near the metal clusters (Figure 8b), confirming that both clusters donate electrons to epitaxial graphene. Figure 9 demonstrates the map of Voronoi partial atomic charges on carbon atoms belonging to the topmost graphene layer, according to which more negatively charged regions on the graphene surface are being formed in the proximity of the metal–graphene contact area. As the Raman spectrum of epitaxial graphene is sensitive to the doping level, it is reasonable to assume that on a large scale, each of the regions will generate intrinsic Raman spectrum, and thus, the Raman mapping analysis followed by K-means clustering analysis (KMCA) or PCA-LDA will enable classification into three groups (uncovered MLG, Ag-covered MLG, and Au-covered MLG, see also Figure 10a). This is an important step in designing a sensor array, because a set of clearly identifiable reference Raman signals can be further utilized to monitor the presence of external gas molecules or biomolecules. In this context, we investigated the adsorption of three CO molecules onto the Ag₅Au₅-MLG surface (Figure 10b). When each of the selected regions is exposed to CO, a charge redistribution at the interface is initiated, and the corresponding graphene regions experience peculiar changes (different doping degrees). This enables CO adsorption to be manifested in Raman spectra. Because silver and gold are plasmonically active metals, Raman signal in the selected regions can be enhanced due to the SERS phenomena, which can also be beneficial to CO detection in living cells.

We noticed that the CO molecule is physically adsorbed on the uncovered graphene region, whereas a formation of strong metal–CO bonding occurs during CO adsorption above Ag₅ and Au₅ clusters. It is worth noting that the CO prefers to sit above the top site of the Ag₅ cluster, whereas the bridge site is the most favorable for CO adsorption on the Au₅ cluster. Ag–CO bond length (≈2.1 Å) is found to be shorter than Au–CO bond length (≈2.3 Å). From a practical point of view, the revealed difference in adsorption behavior and related interfacial charge redistribution in the selected regions suggest that combined statistical and classification analysis of experimental multidimensional spectral data sets for Ag₅Au₅-MLG sensor array before and after interaction with CO molecules can provide high-accuracy identification of CO even at extremely small concentrations. The importance of this finding lies in the possibility of precise recognition of different analyte molecules based on different interaction strengths with Ag/MLG and Au/MLG sensors.
Ag and Au layers were deposited onto epitaxial monolayer graphene on 4H-SiC substrates by means of a direct current magnetron sputtering technique. Au on graphene/4H-SiC self-assembles into interconnecting ramified islands, whereas Ag forms a network of largely separated nanoscale islands. Different morphologies are the first experimental evidence of different interaction strengths between the metals and graphene substrate. Raman spectroscopy in conjunction with PCA, LDA, and correlation analysis enabled gaining deep insights into the effect of the NMs on the phonon dispersion of epitaxial monolayer graphene. Minimal impact of Au on the vibrational properties of graphene was revealed, which is contrasting with the effect of Ag. Raman spectra of epitaxial graphene undergo substantial changes upon Ag deposition expressed by the increasing role of the defect-related scattering processes. As was predicted by CDD calculations, deposited Ag induces more pronounced charge transfer to the graphene than Au, causing large-area n-type doping. The developed classification model allowed high accuracy discrimination between three considered cases (bare MLG, Au/MLG, and Ag/MLG) and can be advantageous for development of sensor array technologies including multiple NMs simultaneously present onto monolithic MLG platform for selective detection of gases and biomolecules. As an example, we have modeled MLG-based sensing platform comprising spatially separated Ag5 and Au5 nanoclusters and discussed its capacity for detection of CO. Being deposited onto MLG surface, gold and silver nanoclusters affect Raman signatures of underlying MLG areas in different ways due to diverse metal–template binding distances and demonstrate different binding affinities to CO, which highlights the possibility of selectively detecting analyte molecules using appropriately designed sensor arrays.

3. Conclusion

Ag and Au layers were deposited onto epitaxial monolayer graphene on 4H-SiC substrates by means of a direct current magnetron sputtering technique. Au on graphene/4H-SiC self-assembles into interconnecting ramified islands, whereas Ag forms a network of largely separated nanoscale islands. Different morphologies are the first experimental evidence of different interaction strengths between the metals and graphene substrate. Raman spectroscopy in conjunction with PCA, LDA, and correlation analysis enabled gaining deep insights into the effect of the NMs on the phonon dispersion of epitaxial monolayer graphene. Minimal impact of Au on the vibrational properties of graphene was revealed, which is contrasting with the effect of Ag. Raman spectra of epitaxial graphene undergo substantial changes upon Ag deposition expressed by the increasing role of the defect-related scattering processes. As was predicted by CDD calculations, deposited Ag induces more pronounced charge transfer to the graphene than Au, causing large-area n-type doping. The developed classification model allowed high accuracy discrimination between three considered cases (bare MLG, Au/MLG, and Ag/MLG) and can be advantageous for development of sensor array technologies including multiple NMs simultaneously present onto monolithic MLG platform for selective detection of gases and biomolecules. As an example, we have modeled MLG-based sensing platform comprising spatially separated Ag5 and Au5 nanoclusters and discussed its capacity for detection of CO. Being deposited onto MLG surface, gold and silver nanoclusters affect Raman signatures of underlying MLG areas in different ways due to diverse metal–template binding distances and demonstrate different binding affinities to CO, which highlights the possibility of selectively detecting analyte molecules using appropriately designed sensor arrays.

4. Experimental Section

Material Synthesis: MLG substrates with high thickness uniformity (more than 85% monolayer graphene, as confirmed by optical reflectance mapping[56], see Figure S6, Supporting Information) studied here were synthesized by a patent-protected sublimation method.[57] It covers high-temperature (≥1900 °C) thermal decomposition of the Si-face of nominally on-axis 4H-SiC (0001) substrates in 1 atm Ar gas ambience. Heating means is by radio frequency (RF) coil fed from RF generator. Silver and gold films with an average thickness of 2 nm were prepared by direct current (dc) magnetron sputtering on epitaxial graphene on 4H-SiC at room temperature under ultrahigh vacuum conditions (base pressure <10–8 Pa). Growth rates were 0.1 and 1 Å s–1 for gold and silver, respectively. The total pressure of plasma-forming gas (argon with purity of 99.999%) was kept at 50 mTorr during gold deposition and at 6.5 mTorr during silver deposition, respectively. As compared with recently reported plasma etching conditions to produce defects in epitaxial graphene on SiC,[25] the total pressure of the plasma-forming argon gas (≈6.3–50 mTorr) we used can be referred to the case of mild plasma treatment, which does not cause graphene damage. Therefore, plasma-forming gas treatment during magnetron sputtering can be excluded as a main factor inducing defect-related Raman peaks. In this regard, we note that the difference in total pressures can be considered as an additional minor factor determining the difference in morphologies of the resulting metal layers. We realize that, ideally, it would be preferable to study the effect of identical nanoislands of silver and gold on the Raman spectra of the epitaxial graphene. However, as the sputtering yields for the two target metals are different,[58] it is obvious that the growth of metals on epitaxial graphene at the same conditions (cathode power, argon pressure, and deposition time) would not lead to the formation of identical gold and silver nanostructures. In fact, we experimentally confirmed that applying the silver growth conditions to the gold deposition on epitaxial graphene led to the formation of Au layer of a different thickness. To avoid comparing Raman properties of graphene affected by different amounts of gold and silver, we optimized the growth conditions to provide the same quantum yield of deposited metals, setting the nominal thickness of the gold and silver films to 2 nm. By choosing the film thickness as a fixed parameter, here, we are mainly attempting to understand the nature of the Raman
response of the epitaxial graphene with the self-assembly of the deposited gold and silver on its surface.

Characterization: To probe the interaction between MLG and NMs, we used a micro-Raman setup based on a monochromator (Jobin-Yvon, model HR460) equipped with a coupled-charged device (CCD) camera using 100× objective lens having the numerical aperture of 0.95. The Raman spectra were obtained with a diode-pumped solid-state laser emitting 1 mW at 532 nm. The diameter of the laser spot focused on the sample surface was ≈0.85 μm. The spectral resolution was ≈5.5 cm \(^{-1}\). Removing the substrate signal was performed through subtraction of Raman spectrum of bare 4H-SiC substrate (Figure S7a, Supporting Information) from the observed raw Raman spectra of the graphenized 4H-SiC (typical raw spectrum of pristine epitaxial graphene is demonstrated in Figure S7b, Supporting Information). The subtraction algorithm also uses automatically determined factor to multiply the substrate spectrum prior to subtraction. Such subtraction algorithm provides well-distant Raman spectra of the epitaxial graphene with no background signal from the substrate. The characteristic Raman bands of epitaxial graphene before and after metal decoration were fitted by single Lorentzian functions. The morphology of as-deposited NMs layers was investigated using SEM (Leo 1550 Gemini SEM instrument) at an operating voltage ranging from 10 to 20 kV and a standard aperture value of 30°.

Multivariate Data Analysis: As large data sets of Raman spectra are generated, the combined statistical and correlation analysis is mandatory not only to get a full picture of Raman activity in the selected regions, but also to uncover partly hidden interrelationships between different variables. In this regard, raw Raman spectra of bare and NMs-decorated MLG samples were first normalized and then smoothed using the Savitzky–Golay algorithm with a polynomial order of 3 and a window length of 11 points. Thereafter, the PCA[1] was applied to reduce the dimensionality of initial dataset (number of Raman spectra) and to identify the dissimilarities between the samples. The most important parameters derived from the analysis of the Raman spectra (position and widths of characteristic peaks, peak amplitude, and area ratios) are finally utilized to calculate Pearson correlation coefficient matrices, enabling identifying the linear interrelationships between any two parameters as well as to construct a PCA-LDA model to classify the Raman data. Being a supervised classification method, LDA, in our case, enables to assign unlabeled Raman signal to a specific already known class (bare MLG, Ag-MLG, or Au-MLG) based on the spectral features of this unlabeled Raman signal and on a trained model. In this regard, the PCA-LDA model, all Raman data were randomly divided into a training set (90% of data) and a test set (10% of data). The calculation of the pairwise Pearson correlation matrices for the parameters of the characteristic peaks makes it possible to highlight initially hidden relationships between parameters, which are then subjected to a suitable interpretation using the existing theory. Such an approach creates a broad picture of Raman activity of epitaxial graphene and elucidates the nature of the metal decoration effect on the phonon dispersion of the epitaxial graphene. In addition, one can possibly exclude the relationships with small or even negative linear regression coefficients, which usually have no physical meaning. By selecting the feature pairs having the most positive correlation coefficients, we also propose an explanation for the revealed trends.

Density Functional Theory: To better understand the NMs–MLG interaction, we performed DFT calculations using SIESTA code[2] within the van der Waals Density Functional (vdW-DF) functional.[3] To simulate the NMs adsorption process and the charge transfer at the interface, 4 × 4 MLG/BuL/4H-SiC slab was exploited as MLG/BuL/4H-SiC substrate with a 6\(\times\)3 × 6\(\times\)3 R30° surface reconstruction (Figure S8, Supporting Information). The 8 × 8 MLG/BuL/4H-SiC slab with two Si-C bilayers was utilized to model bimetallic sensor array for detection of CO. The pseudopotentials for H, Si, C, O, Ag, and Au were generated using the Troullier–Martins scheme using the ATOM code.[4] A vacuum layer of 20 Å was added above the MLG/BuL/4H-SiC slab along the normal direction to prevent unwanted interaction with neighboring unit cells. Double-\(\zeta\)-polarized (DZP) basis set with an energy shift of 200 meV was chosen. The Cartesian coordinates of the Au/MLG/BuL/4H-SiC and Ag/MLG/BuL/4H-SiC structures were relaxed until the force on each atom reached less than 0.02 eV Å\(^{-1}\). A Monkhorst–Pack k-point 3 × 3 × 1 mesh was used to sample Brillouin zone during the optimization process. The mesh cutoff was set at 400 Ry.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

density functional theory, epitaxial graphene, gold, Raman spectra, silver

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