Full Length Article

Energetic bombardment and defect generation during magnetron-sputter-deposition of metal layers on graphene

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A B S T R A C T
In the present work, we elucidate the interplay among energetic bombardment effects in magnetron sputtering and defect generation in two-dimensional (2D) materials. Using deposition of gold (Au) layers on single-layer graphene (SLG) as a model system, we study the effect of pressure-distance (pd) product during magnetron sputtering on the pristine SLG properties. Raman spectroscopy, complemented by X-ray photoelectron spectroscopy, shows that for pd = 8.2 Pa⋅cm, Au layer deposition causes defects in the SLG layer, which gradually diminish and eventually disappear with increasing pd to 82.5 Pa⋅cm. Stochastic and deterministic simulations of the sputtering process, the gas-phase transport, and the interaction of sputtered and plasma species with the substrate surface suggest that defects in SLG primarily emanate from ballistic damage caused by backscattered Ar atoms with energies above 100 eV. With increasing pd, and thereby gas-phase scattering, such high energy Ar species become thermalized and hence incapable of causing atomic displacements in the SLG layer. The overall results of our study suggest that control of backscattered Ar energy is a potential path toward enabling magnetron sputtering for fabrication of multifunctional metal contacts in devices founded upon 2D materials.

1. Introduction
Deposition of multifunctional metal contacts on two-dimensional (2D) materials is a key step in the fabrication of a wide array of optoelectronic, catalytic, and sensing devices [1–6]. For the performance of such devices to be optimized, metal layers (i.e., contacts) should exhibit a well-defined morphology. Moreover, control of the structure and chemistry of the metal/2D-crystal interface is also required, without substantially modifying the pristine properties of the 2D material [7–14]. Nowadays, metal layers (i.e., thin films) are routinely synthesized on 2D materials via vapor condensation using thermal or electron beam evaporation [1,15–17]. Besides vapor-based methods, wet-chemistry approaches and electroless deposition have been employed for decorating graphene-based surfaces with metal nanoparticles [18–22]. All the above-mentioned deposition strategies suffer from lack of lateral film thickness and property uniformity, while they do not provide the ability to control atomic assembly kinetics during growth; a prerequisite for tuning metal-layer morphologies and film/substrate interface properties.

Magnetron sputtering is a vapor-based deposition technique that meets the requirements of large-scale film thickness and properties uniformity, while it offers access to a wide range of process parameters for tuning growth kinetics [23]. However, it has been, up to now, deemed incompatible with metal-layer deposition on 2D materials, as it generates ample amounts of energetic neutral and ionized species, which create defects that compromise the pristine electronic and transport properties of the 2D crystals [24–31]. Hence, a fundamental understanding of the interplay among energetic bombardment effects during magnetron-sputter deposition and defect generation in 2D crystals is required for enabling magnetron sputtering in 2D-material technologies and applications.

In the present work, we contribute to the afore-mentioned understanding by studying magnetron-sputter-deposition of gold (Au) layers on single-layer-graphene (SLG). The choice of the Au/SLG model system is motivated by the fact Au is a highly inert material, suitable for contacts [3,32], while SLG offers a sensitive platform for identifying defect...
formation by spectroscopic techniques, including Raman spectroscopy [33–35]. To tune the energy of species arriving at the SLG substrate, we vary the working pressure-distance (pd) product during sputtering from 8.2 to 82.5 Pa-cm, and we deposit films with a nominal thickness of 2 nm. Morphological analysis of the film surface shows that Au grows in a pronounced three-dimensional (3D) fashion on SLG, such that only ~50% of the SLG surface is covered by the deposit at all synthesis conditions. Moreover, the increase of the pd product causes a transition from a surface that hosts partially elongated islands to a dendritic island morphology. This type of 3D morphology allows for post-deposition studies of the vibrational properties of SLG by Raman spectroscopy. Our Raman data show that deposition at pd = 8.2 Pa-cm results in considerable damage of the pristine SLG structure, which is diminished as pd increases, and effectively disorder-free growth conditions are established for pd = 82.5 Pa-cm. The Raman analysis is supported by X-ray Photoelectron Spectroscopy (XPS) measurements, which show that the fraction of sp² bonded carbon atoms in the substrate decreases with decreasing the pd value, i.e., smaller pd products favor the formation of defect-related structures.

Seeking to establish an atomistic understanding of the phenomenological correlations between deposition parameters and SLG properties observed in our experiments, we employ Monte Carlo (MC) simulations for estimating the energies of plasma species (sputtered Au and back-sputtered Ar) arriving at the SLG surface. We find that at pd = 8.2 Pa-cm, Au and Ar species exhibit broad energy distributions extending up to ~100 and ~200 eV, respectively, which become thermalized for pd = 82.5 Pa-cm. Gas-phase transport MC simulations are coupled with Classical Molecular Dynamics (CMD) to model the interactions of energetic species with SLG. CMD data show that point defects in the SLG network are primarily caused by backsputtered Ar with energies above 100 eV, which is consistent with the gradual disappearance of defect-related modes in the Raman spectra of Au/SLG heterostructures as pd values are increased. The overall results of this study provide knowledge for optimizing energetic input to the substrate during magnetron sputtering, such that strategies for the non-invasive growth of metal layers on 2D materials can be developed.

2. Research methodology

2.1. Film synthesis and characterization

Gold (Au) layers (i.e., thin films), with a nominal thickness of 2 nm, are grown by direct current magnetron sputtering (dcMS) on single-layer-graphene (SLG) synthesized by chemical vapor deposition on copper (Cu) substrates. It should be noted that films are deposited directly on SLG/Cu, i.e., graphene is not transferred, to avoid defect formation and explicitly study the effect of the sputtering process on the pristine graphene structure. Deposits are carried out in an ultra-high vacuum chamber (based pressure ~ 10⁻⁸ Pa) using argon (Ar) as a sputtering gas (gas purity 99.999%). The magnetron source, equipped with an Au target (diameter 7.62 cm, purity 99.99%), is placed at a distance d = 12.5 cm from the substrate, and at an angle of 45° with respect to the substrate surface normal. To tune the energy of the species arriving at the substrate, the working pressure p is varied in the range 0.6 to 6.7 Pa yielding pressure-distance (pd) products between 8.2 and 82.5 Pa-cm. In the remainder of the article, we present and discuss results with reference to pd (instead of p), since pd is a universal and deposition-geometry-independent parameter describing gas-phase scattering, and its effect on particle transport [36] and energy of species arriving at the substrate [37]. Ar discharges are operated at a constant current mode, and the deposition rate is held at ~0.1 Ås⁻¹ by increasing the target current density from 0.13 to 0.8 mA cm⁻² (corresponding to target current 6 to 37 mA) as pd is increased from 8.2 to 82.5 Pa-cm. The deposition rate at the various conditions is determined from in situ spectroscopic ellipsometry [38] by measuring the thickness of continuous films grown on silicon (100) substrates covered with a 530 nm thick, thermally grown, silicon dioxide overlayer [39].

The effect of sputtering conditions on the film morphology is investigated by scanning electron microscopy (SEM). Top-view images are collected using a LEO-Zeiss (1550 Gemini) Field Emission Gun SEM at an operating voltage of 4 kV. At the nominal thickness of 2 nm, the film is expected to feature isolated islands and/or clusters [40–44]. Hence, SEM data are analyzed using the ImageJ freeware [45] to determine the fraction q of the SLG surface covered by islands, as well as to define the island number densities, from which we extract the mean island projected size (MS). We also quantify the island shape by approximating the islands with ellipsoids and computing the in-plane aspect ratio (AR), i.e., the ratio of the major to the minor ellipse axis on the substrate plane.

Raman spectroscopy is employed to identify disorder in the sp² network of graphene at the various deposition conditions by recording changes in the characteristic D, G, and 2D Raman bands [46–51]. Raman spectra, averaged from areas 10 × 10 μm², are recorded using a LabRam HR micro-spectrometer (HORIBA) equipped with a Peltier-cooled charge coupled device detector. We use the 514 nm line of a diode-pumped solid-state laser, the 633 nm line of a He-Ne laser, and the 785 nm line of a diode laser as excitation wavelengths, which are focused on the sample by means of a standard 100× objective lens. The laser power applied on the sample is kept at 0.1 (514 nm laser), 0.4 (633 nm laser), and 3.5 mW (785 nm laser) to avoid laser-heating-induced changes of the SLG properties and the Au morphology. The spectrometer is calibrated using a Si wafer and/or a Ne lamp.

Raman analysis is complemented by X-ray Photoelectron Spectroscopy (XPS). Photoelectron spectra are recorded in a Kratos AXIS Ultra DLD UHV system (base pressure ~ 10⁻¹⁰ Pa), equipped with a monochromated aluminum Kα X-ray beam (hv = 1486.6 eV), a hemispherical sector analyzer, and a multichannel detector. A 20 eV pass energy, resulting in a full width at half maximum (FWHM) for the Ag-3d₅/₂ peak of less than 500 meV with a step size of 0.1 eV, is used in order to obtain information from the core-level spectra. XPS data are analyzed using the Kratos Vision software and the build-in relative sensitivity factors.

2.2. Simulations

To estimate the energy of species arriving at the substrate, we use Monte-Carlo simulations for modeling the sputtering process and the interaction of species generated at the target with Ar gas en route to the substrate. The sputtering of a 4 mm thick Au target by 400 eV Ar⁺ ions (the Ar⁺ ion energy corresponds to the typical target voltage of 400 V in our experiments) is modeled using the SRIM (Surface and Range of Ions in Matter) software package [52,53]. Besides the energy distribution of sputtered Au atoms, we also use SRIM to extract the distribution of backscattered Ar particles. Such backscattered particles may constitute a considerable fraction of the total energetic flux to the substrate, most notably in the case of large ion-target mass mismatch [54,55]. The data obtained from SRIM simulations, along with the deposition chamber geometry, are used as input for modeling the transport of species through the gas phase via the SIMTRA software package [56]. Simulations are performed for pd products consistent with experiments (see Section 2.1), while the interaction of target-eminating particles (i.e., sputtered Au and backscattered Ar) with Ar gas is described using a screened Coulomb potential with Molière screening function [56,57]. The SIMTRA simulations yield energy distributions of sputtered Au and backscattered Ar species impinging on the substrate. These simulations guide classical molecular dynamics (CMD) simulations of the interactions of the energetic species with the SLG/Cu substrate. The above-described simulation strategy is schematically illustrated in Fig. 1. The CMD simulations are carried out in the framework of the LAMMPS [58] freeware. The C-C interaction in the SLG layer is modeled using the adaptive intermolecular reactive bond order (AIREBO) potential by Stuart et al. [59], which has been successfully used in the
packages) are used for modeling sputtering of Au target by Ar\cite{60,61}. Au-C, Ar-C, and Ar-Ar interactions are described by the Ziegler–Biersack–Littnark (ZBL) potential\cite{52}, which is a universal repulsive formalism widely used for modeling the collisions between energetic species and carbon-based materials\cite{60,62,63}. The C-Cu interaction at the SLG/Cu interface is described using the Lennard–Jones (LJ) potential with its parameters taken from Refs.\cite{64,65}, while Cu-Cu, Au-Au, and Au-Cu interactions are modeled using the Finnis-Sinclair interatomic potential developed by Ackland et al.\cite{66}.

Simulations are performed using a Cu fcc substrate consisting of 24,192 atoms in an $8 \times 8 \times 4.5$ nm$^3$ box with the z-axis oriented along that (1 1 1) direction. In this configuration, the substrate consists of 21 atomic layers, which suffice for avoiding forward sputtering during impingement of energetic Au and Ar species. The bottommost four layers of the Cu slab are frozen to describe the bulk of the substrate. The next 12 layers are kept at a constant temperature of 300 K using a Langevin thermostat, while the topmost five layers along with SLG (consisting of 2508 C atoms) and impinging Au and Ar atoms constitute the reaction zone. Periodic boundary conditions are applied in the x and y directions, while the SLG/Cu(1 1 1) system is relaxed at the temperature of 300 K prior to impingement of Au and Ar atoms.

Arrival and impingement of energetic species at and on the SLG/Cu substrate are simulated by releasing pulses of 10 Ar or Au atoms (the time between each pulse is 50 ps) at distances between 20 and 40 Å above the substrate surface. The species are given initial velocities toward the substrate surface corresponding to energies up to 175 eV, consistent with the energies predicted by the SRIM/SIMTRA simulations (see Section 3 for more information). We use an adaptive time step of up to 0.25 fs. After arrival of the last particle pulse, the simulated systems are left to relax, and runs are completed when the temperature reaches 300 K and no considerable changes in the SLG/Cu structure are observed. The simulation output is visualized using Visual Molecular Dynamics software\cite{67}. A schematic representation of the simulation system and representative snapshots before and after particle impingement as shown in Fig. S1 in the Supporting Information. The effect of energetic species on SLG/Cu substrate is quantified by calculating the broken and newly-created bonds in the SLG layer after particle impingement, as explained in Section S.1 and Fig. S2 in the Supporting Information.

3. Results and discussion

Fig. 2(a–d) display top-view SEM images of 2 nm Au films deposited on SLG/Cu substrates at various pd values. For pd = 8.2 Pa-cm (Fig. 2(a)), the film surface features isolated and partially elongated islands with areal coverage $q$ of ~51%. Increase of pd to 16.5 Pa-cm (Fig. 2(b)) yields islands that have more elongated shapes and a slight decrease of the $q$ value to ~49.5%. By further increasing pd to 41.2 Pa-cm (Fig. 2(c)), the islands become larger, obtain dendritic shapes, and the substrate areal coverage becomes $q$ = 49%. At the maximum pd value of 82.5 Pa-cm, (Fig. 2(d)), the island shapes remain dendritic and $q$ decreases further to ~46%. The evolutions of the island projected size, MS and their in-plane aspect ratio, AR vs. pd are also plotted in Fig. 2(e and f), respectively, to better demonstrate that the islands become larger and their shape more elongated by increasing the sputtering pressure.

The data presented in Fig. 2 show that Au grows in a 3D fashion on SLG under all process conditions, since a significant fraction of the substrate surface remains exposed after depositing 2 nm (corresponding to ~ 10 monolayers) of material. This growth behavior is typical for weakly-interacting film/substrate systems\cite{40,41,68–73}, and it is consistent with the significantly smaller free surface energy of SLG (0.046 mJ/m$^2$)\cite{74,75} relative to Au (1.5 J/m$^2$)\cite{76}. Moreover, the tendency of Au islands to exhibit dendritic shapes at relatively large pd values is an indication that the increase of the gas-phase scattering frequency (caused by the increase of pd) results in a smaller amount of energy transferred from the plasma particles to the film-forming species, such that their effective diffusion length is reduced. A more detailed discussion on the correlation between pd and the energy of species arriving at the substrate is provided later in the present section.

The effect of film growth conditions on the vibrational properties of the underlying SLG substrate is demonstrated in Fig. 3, which plots Raman spectra from pristine SLG/Cu and from 2 nm thick Au/SLG/Cu samples, whereby Au layers are grown at various pd values. Spectra measured with the excitation laser wavelength of 514 nm are presented,
Fig. 2. Top-view SEM images of sputter-deposited 2 nm thick Au layers on SLG/Cu for pd product values of (a) 8.2 Pa cm, (b) 16.5 Pa cm, (c) 41.2 Pa cm, and (d) 82.5 Pa cm. Panels (e) and (f) plot the evolution of the island size MS and the in-plane aspect ratio AR vs. pd, whereby the standard error of both quantities is represented by error bars.

since this is the most widely used wavelength in the literature. The pristine SLG/Cu spectrum (Fig. 3(a)) exhibits peaks at ~1585 cm\(^{-1}\) since this is the most widely used wavelength in the literature. The and (d) 82.5 Pa cm. Panels (e) and (f) plot the evolution of the island size MS and the in-plane aspect ratio AR vs. pd, whereby the standard error of both quantities is represented by error bars.

attributed to the transformation from a defective to a highly-disordered carbon (graphite and graphene) structure upon increasing defect density [51,80]. Qualitatively consistent trends with regards to the integrated intensity ratios of the Raman peaks are also observed in spectra recorded with excitation wavelengths at 633 and 785 nm, see Fig. S3 (Section S.2) in the Supporting Information.

Further insights into the effect of Au deposition on the SLG/Cu properties are obtained by XPS measurements. Fig. 4(a) shows the high-resolution C-1 s core level spectrum of an Au/SLG/Cu sample, whereby the Au layer is deposited at pd = 41.2 Pa cm. The spectrum reveals the existence of two main peaks, centered at binding energies ~289 and ~285 eV. Detailed analysis, using a Shirley background, shows that the two-peak structure can be deconvoluted into four components attributed to the sp\(^2\) carbon bonds of graphene (binding energy 284.6 eV [81,82]), C=O and C=O bonds from surface contamination (binding energy 286.5 eV and 288.5 eV [83], respectively), defect-related sp\(^3\) bonds (binding energy 285.2 eV [84–90]). Qualitatively similar features in the C-1s core level spectra are observed for samples grown at all deposition conditions, as well as in spectra recorded from pristine SLG/Cu substrates, as shown in Fig. S4 in the Supporting Information (Section S.3). Based on the data presented in Fig. 4(a) and S4, we plot in Fig. 4(b) the integrated intensity ratio of the sp\(^3\)-to-sp\(^2\) related components, as a function of pd. The plot shows that the ratio decreases with increasing pd and asymptotically approaches that of pristine SLG/Cu, which is consistent with the Raman data in Figs. 3 and S3.

The experimental data presented in Figs. 3 and 4 show that the pd parameter has a pronounced effect on the structural quality of graphene, whereby decrease of pd yields a larger density of defects. It is also known that the pd product determines the frequency of collisions in the gas phase and, thereby, the energy of species arriving at the substrate during film growth. We quantify this effect by combining SRIM and SIMTRA simulations to determine the energy distributions of Au and Ar at the
substrate position for the various deposition conditions (see Section 2.2 for details), which are plotted in Fig. 5. For $p_d = 8.2$ Pa cm, both Au and Ar species exhibit broad energy distributions (Fig. 5(a) and (e), respectively) with tails extending up to ~200 eV. However, the distribution of Ar is more uniform resulting in a mean energy $E_{\text{mean}}$ of 23.4 eV, as opposed to the distribution of Au which decays strongly as function of energy, yielding $E_{\text{mean}} = 4$ eV. With increasing $p_d$, the energy distributions of both species become narrower and $E_{\text{mean}}$ decreases until monoenergetic thermalized fluxes with $E_{\text{mean}} = 0.04$ eV are obtained for $p_d = 82.5$ Pa cm (Fig. 5(d) and (h)).

The data presented in Fig. 5 indicate that for $p_d$ values 8.2 and 16.5 Pa cm the substrate is subjected to bombardment by species having a wide range of energies, such that defect formation in SLG may be the result of all energetic contributions. Designing CMD simulations to account for and model the simultaneous arrival of all species (Au and Ar) on SLG/Cu, with energies and relative fluxes consistent with the distributions in Fig. 5, is a non-trivial task. Instead, we chose here to study the effect of each species and energy represented in the data in Fig. 5 separately and assess their propensity to cause defects in SLG. To this purpose, we simulate by CMD the impingement of Au and Ar atoms with energies exhibiting relative statistical frequencies down to $10^{-3}$ in their respective distributions, i.e., up to 90 eV for Au and 175 eV for Ar. The results show that Au atoms with energies up to 50 eV cause no defect formation in the SLG layer. Increase of the Au projectile energy to 90 eV leads to the appearance of Stone-Wales defects [91], i.e., C atoms are rearranged in a way that four neighboring hexagonal rings are transformed into two pentagons and two heptagons (see Fig. 6(a)). With regards to backscattered Ar species, the simulation data show that the Ar species with energies below 100 eV have no effect on the SLG structure, while their effect becomes more pronounced at energies 110 eV and above. For impinging energies in the range 110–130 eV, Ar atoms cause transformation of the hexagons into pentagons, heptagons and nonagons (see Fig. 6(b)). Increasing the Ar atoms energy above 130 eV yields sputter-removal of carbon atoms from the SLG and the formation of vacancies (Fig. 6(c)). All type of bombardment-induced defects evidenced in the CMD simulations are consistent with the appearance of clear D and D’ peaks in the Raman spectra (Figs. 3 and S3) and $sp^3$ components in the XPS spectra (Figs. 4 and S4) for samples grown at $p_d < 82.5$ Pa cm [34,92–94].

To further assess the extent of the damage caused by Ar atoms (irrespective of the type of defect), we use the CMD data to compute and present in Fig. 7 the ratio $\frac{\sum N_b}{\sum N_C}$ of the total number of broken C-C bonds.

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**Fig. 4.** (a) XPS C-1 s spectra of 2 nm Au deposited on SLG/Cu at $p_d = 41.2$ Pa-cm. Open circles represent the experimental spectrum, black, blue, green, and magenta lines represent the individual fitting components, while their sum is represented by the red line. (b) The $sp^3/sp^2$ ratio, calculated from the blue and black components, respectively, as a function of $p_d$.

**Fig. 5.** Energy distributions of (a) – (d) sputtered Au and (e) – (h) backscattered Ar species impinging on the substrate, as determined by SRIM and SIMTRA simulations. Simulations are performed for $p_d$ products from 8.2 to 82.5 Pa-cm to be consistent with the experiments.
values are computed. The data show that for energies below 110 eV no defects are formed and hence no values are computed. The data show that \( \sum \frac{N_a}{N_c} \) increases monotonically with Ar atom energy, which can be interpreted as an increase in the defect density. The overall results of the CMD simulations suggest that the majority of defects in SLG in our deposition process primarily emanate from ballistic damage caused by Ar atoms with energies above 100 eV. Moreover, the sputtering and gas-phase transport simulations (SRIM and SIMTRA, respectively) show that the flux of defect-causing Ar atoms gradually diminishes and eventually disappears with increasing sputtering pressure. This can explain the nearly defect-free SLG structure observed in the Raman and XPS data for films grown at pd = 82.5 Pa·cm. We also note that Ar gas heating and rarefaction \[95,96\] —caused from collisions between sputtered Au and gas Ar atoms—is unlikely to have a pronounced effect on the transport and mean energy of species arriving at the substrate, due to the relatively small discharge currents (6–37 mA, see Section 2.2 for details) used in our experiments.

### 4. Summary and outlook

We present a systematic study on the effect of magnetron-sputter-deposited gold (Au) layers (i.e., thin films) on the structural integrity of single-layer graphene (SLG). Films with a nominal thickness of 2 nm are deposited for pressure-distance (pd) products in the range 8.2 to 82.5 Pa·cm. Analysis of the SLG vibrational modes (probed by means of Raman spectroscopy), complemented by X-ray photoelectron spectroscopy measurements, show that film deposition at pd = 8.2 Pa·cm results in formation of defects in the graphene substrate. This deleterious effect is diminished with increasing pd values, and a nearly defect-free SLG structure is achieved when depositing at pd = 82.5 Pa·cm. Seeking understand the atomistic origin of this behavior, we employ Monte-Carlo and classical molecular dynamics simulations to model the processes of sputtering, gas-phase transport, and impingement of sputtering-related species on the substrate. The simulation data show that defects in SLG primarily originate from ballistic damage caused by energetic Ar species that are backscattered at the target surface and arrive at the substrate with energies above 100 eV. With increasing pd, gas-phase scattering causes the gradual thermalization of high-energy species, such that no atomic rearrangement and defect generation occurs at pd = 82.5 Pa·cm. Our overall results highlight a potential path, e.g., by using complex pd patterns, for enabling sputtering in the synthesis of metal contacts on graphene and other 2D materials, which is a key step toward industrial-scale fabrication of key enabling devices.

### CRediT authorship contribution statement

N. Pliatsikas: Conceptualization, Methodology, Formal analysis, Investigation, Writing – original draft. O. Karabinaki: Formal analysis, Investigation, Writing - review & editing. M. Zarshenas: Methodology, Formal analysis, Investigation, Writing - review & editing. G.A. Almyras: Methodology, Writing - review & editing. I. Shtepliuk: Conceptualization, Writing - review & editing. R. Yakimova: Conceptualization, Writing - review & editing. J. Arvanitidis: Conceptualization, Methodology, Formal analysis, Investigation, Writing - review & editing, Supervision. D. Christofilos: Conceptualization, Methodology, Formal analysis, Investigation, Writing - review & editing, Supervision, Funding acquisition. K. Sarakinos: Conceptualization, Methodology, Writing - review & editing, Supervision, Funding acquisition.

### Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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