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Probing the uniformity of silver-doped epitaxial graphene by micro-Raman mapping

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Abstract

We present a Raman spectroscopy study on epitaxial graphene decorated with thin Ag films (2-15 nm), which are deposited using magnetron sputtering. We find that the presence of Ag on the graphene surface induces doping, the uniformity and efficiency of which is determined by Ag nominal thickness. Deposition of Ag films with thicknesses up to 5 nm favors the effective electron transfer from Ag to epitaxial graphene. A significant redshift and broadening of the 2D peak are observed with increasing the Ag-layer thickness above 5 nm, which is indicative of large strain and doping fluctuations. We also observe a non-trivial linear growth of 2D/G peak intensity ratio with increasing D/G ratio for all Ag-decorated samples, which is explained by increase of peak amplitude due to surface enhanced Raman scattering and charged impurity-induced screening caused by the presence of Ag on the graphene surface.

Keywords: epitaxial graphene, silver, Raman mapping, doping, strain

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Introduction

As a unique member of the graphene family, epitaxial graphene grown on different polytypes of SiC (EG/SiC) possesses a wide range of intriguing properties, including large area, high quality, low defectiveness, chemical and thermal stability, and transfer-free growth [1-5], thereby triggering an enormous interest within scientific community during last 15 years and provoking researches that yielded a more subtle understanding how to exploit this material in real applications, especially in electronics [6, 7], optics [8] and sensorics [9-12]. It is obvious that the development of next-generation devices based on EG/SiC requires its incorporation/integration into/with classical semiconductor technologies (p - n junctions, transistors, Schottky contacts etc.) and achieving uniform doping over prescribed nano-scale

regions. These interrelated tasks are still very challenging due to poor reproducibility of the doping methods (substitutional doping or electron charge transfer) that usually cause the significant reduction of the electrical performance of epitaxial graphene and its structural and morphological damage. Eventually, the trade-off in the framework of triad “doping efficiency – EG conductivity – structural homogeneity” must be reached to push graphene closer to high performance devices. In this regard, any attempts to bring new insights into doping mechanisms of graphene toward reliable manipulation of its electronic properties on centimeter-scale are of high scientific and technological relevance. In this study, we are focusing on investigating the doping phenomena induced by deposition of thin silver (Ag) films on large-area epitaxial monolayer graphene.

The choice of Ag as a model metal to dope graphene is justified by its unique properties with respect to graphene [13]. It is known that the deposition of Ag nanoparticles on graphene may produce *n*-type doping driven by the work function difference between the two materials [14]. This is because the Fermi level alignment makes it easier for charge carriers to move from the Ag to graphene, thereby lifting Fermi level of graphene above the Dirac point. Furthermore, according to earlier density functional theory (DFT) calculations, Ag interacts with graphene mainly through van der Waals forces enabling formation of ultra-thin Ag films weakly bonded to substrate [15]. Such features combined together provide excellent prerequisites for fabrication of damage-free large-area uniformly *n*-type doped epitaxial graphene, since low defect density and pronounced electron charge transfer at the interface are expected as a result of interaction between defect-free graphene structure and Ag.

Despite the large technological potential of Ag/EG/SiC nanoarchitectures, only few reports in the literature have studied the effect of Ag directly interfacing with epitaxial graphene [16-22]. Earlier studies on the formation of Ag films on EG/SiC employed high-vacuum thermal evaporation [20] and Ag deposition from chemical solution [17]. Sekine *et al.* [20] reported a synthesis of highly crystalline Ag nanosized islands with a face-centered cubic structure and a distance to epitaxial graphene of ~ 3.14 Å, pointing out the physisorbed state without formation of chemical bonding. It was also found that the decoration of epitaxial graphene with Ag causes increase of the graphene electron density from $1 \times 10^{12} \text{ cm}^{-2}$ (pristine graphene) to $1.9 \times 10^{13} \text{ cm}^{-2}$. Chadhari *et al.* [17] reported the formation of pyramidal-shaped silver islands with average diameter of 18 nm. There have been also several attempts to grow ultra-thin films by evaporation from a water-cooled Knudsen cell onto EG/SiC samples with different thicknesses at a substrate temperature of 77 K [19, 21]. Adjusting the thermal decomposition temperature of 6H-SiC Liu *et al.* [19] controlled the thickness of graphene prior

to Ag deposition, thereby providing different templates (from “pure” buffer layer to few-layer graphene) for synthesis of the metal nanoparticles. It was claimed that Ag-island size during the initial film growth stages is virtually insensitive to the thickness of epitaxial graphene, while increase of the graphene layer thickness causes reduction of n -type doping due to the weakened interaction between Ag islands and thicker EG layers. In their more recent work [21], the same group showed substantial evidence of substitutional doping of EG with Ag, and Ag intercalation via penetration through edge and defect sites in the topmost graphene layers. In this case, Ag atoms preferentially form covalent bonds with carbon atoms. Similar chemical interaction phenomena occurring at the interface between liquid silver and graphene-coated SiC substrate were independently examined by Homa *et al.* [18] by using sessile drop method. Moreover, an enhanced Ag island nucleation density was reported when depositing on the buffer layer (carbon rich surface reconstruction of the 4H-SiC) [21].

The findings highlighted in the previous paragraph suggest that the quality of graphene plays an important role for the Ag-layer nucleation and growth. A high number of intrinsic defects and edge states in graphene may significantly enhance the adsorption ability of Ag on graphene and hence yield a more irregular Ag/graphene interface and/or Ag-C intermixing. Thus, only high-quality defect-free graphene could ideally satisfy the requirements of effective n -type doping during deposition of Ag films. In the light of that, epitaxial monolayer graphene with high thickness uniformity is regarded as promising template for deposition of electron-donating Ag-layers. In this context, achieving control over both the graphene uniformity after Ag deposition and Ag-induced doping efficiency is an important precondition for further progress in conceptualization of the EG-based devices.

Micro-Raman mapping analysis is an excellent approach to elucidate the nature of structural changes in epitaxial graphene upon Ag deposition and to draw conclusions with respect to doping uniformity and mechanisms. This is because the intrinsic Raman modes (namely G and $2D$) of epitaxial graphene are strain- and doping-dependent [23, 24], then any variations in the position and intensity of these peaks enable to gauge strain/doping changes due to Ag presence on the substrate surface. Furthermore, statistical analysis of Raman data [25-28] can be used to estimate the degree of spatial fluctuations of the carrier concentration in the Ag-coated EG/SiC. This route has not been explored in the literature so far.

In the present paper, we investigate the formation of thin Ag films deposited on epitaxial graphene/SiC by magnetron sputtering and study their effect on the vibrational properties of epitaxial graphene. A deep understanding of carrier density modulation induced by Ag

deposition is of special interest because it provides critical knowledge toward optimization of the graphene doping conditions.

Experimental procedures

Thin Ag films were deposited by direct current (dc) magnetron sputtering in an ultra-high vacuum chamber (base pressure $\sim 10^{-8}$ Pa) at room temperature. Ar gas (purity 99.999%) at a pressure of 1.7 Pa was used to generate plasma and sputter a magnetron source which was equipped with an Ag target (diameter 76.2 mm; thickness 6 mm; purity 99.99%). The nominal thickness of the Ag films was varied between 2-15 nm by changing the deposition time. As substrates for growth, we used 7 mm $\times$ 7 mm on-axis 4H-SiC (0001) wafers covered by monolayer graphene. Prior to deposition, the substrates were cleaned with ethanol followed by N₂ drying.

Epitaxial graphene was synthesized by high-temperature thermal decomposition of the Si-face SiC in argon atmosphere. Additional technical details on this sublimation technique can be found elsewhere [29]. The formation of monolayer graphene was confirmed by optical reflectance mapping (not shown here) [30] and subsequent Raman scattering studies.

The Ag-layer surface morphology was investigated using plan-view scanning electron microscopy (SEM) in a Leo 1550 Gemini SEM instrument at an operating voltage ranging from 10 kV to 20 kV and a standard aperture value of 30 μ m. The film crystal structure was studied by X-ray diffractometry (XRD) Bragg-Brentano geometry, using a Panalytical X'pert Pro instrument with Cu K α radiation ($\lambda=0.1542$ nm). XRD patterns (not shown here) show that Ag films have a fcc crystal structure, they are polycrystalline, and grown preferably along the [111] crystallographic direction. Raman mapping analysis was performed by using a micro-Raman setup based on a monochromator (Jobin-Yvon, model HR460) equipped with a CCD (couple-charged device) camera. The objective lens has a magnification of 100 $\times$ and numerical aperture NA = 0.95 resulting in a ~ 0.85 μ m diameter of the laser spot focused on the sample surface. A 532 nm diode-pumped solid-state laser with 1 mW power was used as an excitation source. The spectral resolution of the system is ~ 5.5 cm⁻¹. 121 Raman spectra on a square map (3 μ m $\times$ 3 μ m, 0.3 μ m pitch) were collected to construct two-dimensional micro-Raman maps.

Results and discussion

Figure 1 displays the plan-view SEM images of Ag films deposited on EG/SiC substrates for nominal thicknesses ranging from 2 to 15 nm. The surface of the 2 nm film (Fig. 1(a)) consists of isolated circular islands. Analysis of multiple images corresponding to the same nominal thickness showed that the mean island size is 17.6 nm with standard deviation of 5.3. Increase of the nominal film thickness to 5 nm (Fig. 1(b)) yields elongated islands with mean

size of 42.3 nm with standard deviation of 15.9. Further deposition of Ag results in increase of island size which form an interconnected island network (10 nm in Figs 1(c)) which eventually leads to the formation a nearly continuous layer (15 nm; Fig. 1(d)). The morphological evolution observed in Fig. 1 is consistent with results for noble metal film growth on a variety of weakly-interacting substrates, including SiO₂ and graphite [31, 32], and it is the result of the dynamic competition between island nucleation, growth, and coalescence [33].

Figure 1. Plan-view SEM images of Ag films grown by magnetron sputtering on EG/SiC substrates at various nominal thicknesses: (a) 2 nm; (b) 5 nm; (c) 10 nm; and (d) 15 nm.

In order to establish the effect of Ag-layer morphology on the vibrational and structural properties of graphene we performed Raman spectroscopy measurements. Figure 2 shows the representative Raman spectra of the pristine and Ag-decorated (nominal thickness 2 to 15 nm) epitaxial graphene. The spectrum of the pristine epitaxial graphene sample is dominated by two strong peaks at 1611 cm⁻¹ and 2733 cm⁻¹, which are attributed to characteristic *G* and 2*D* Raman in-plane vibrational modes, corresponding to atomic displacements of *sp*²-bonded carbon species in graphene lattice [34]. We also notice the presence of the low-frequency scattering from the left side of *G* peak (1200 cm⁻¹-1600 cm⁻¹ spectral region), which is related to the buffer layer (interfacial C-rich layer between graphene and 4H-SiC, in which 30 % C atoms are covalently bonded to Si atoms) [35]. Defect-related vibrational modes are absent or very weak

compared to the two main epitaxial graphene Raman peaks, suggesting the high-quality (close to defect-free) of the monolayer graphene before Ag deposition.

The decoration of the epitaxial graphene with Ag leads to the following changes in the recorded Raman spectra: (i) activation of intervalley scattering from K to K' (D peak), intravalley scattering from K to K (D' peak) and combination scattering ($D+G$ peak) [36, 37] (see Figure 2 and inset of Fig. 2), which is indicative of generation of in-plane and out-of-plane defects; (ii) red shift and broadening of G and $2D$ modes, which may originate from synergetic influence of both strain and doping [38]; and (iii) enhancement of Raman signal, which can be ascribed to a combination of surface-enhanced Raman scattering (SERS) phenomena induced by both pronounced charge transfer at the interface Ag/graphene interface and plasmonically-active Ag nanoparticles [39, 40]. Moreover, Fig. 2 shows a continuous shift from 1611 cm^{-1} to 1590 cm^{-1} and split of the G peak with increasing Ag-layer thickness. The frequency shift is more pronounced for $2D$ mode, for which the peak shifts from 2705 cm^{-1} (for epitaxial graphene decorated with 2nm Ag film) to 2689 cm^{-1} (for epitaxial graphene decorated with 15 nm Ag film).

Figure 2. Representative Raman spectra of epitaxial graphene before and after deposition of Ag films with different thicknesses. Inset demonstrates the deconvoluted spectral region in the proximity of the G peak, suggesting the G peak splitting as a result of Ag decoration (nominal thickness 2 nm).

Figure 3 presents a plot of the $2D$ vs. G peak position for all recorded spectra, for pristine graphene and Ag-decorated EG/SiC substrates at various nominal thicknesses, with the aim to

decouple the effects of strain and doping on characteristic Raman scattering modes [41, 42]. The data points for pristine graphene sample before Ag deposition scatter mostly along a line with a slope of about 2.3 (blue circles in Fig. 3). This group of points is parallel to so-called strain line that agrees well with the literature data for purely stressed graphene subjected to biaxial compressive strain (due to the substrate effect) with negligible doping effect [43].

Compared to pristine graphene, there is no linear dependency seen for substrates interfacing with ultra-thin Ag deposits (2 nm and 5 nm; purple diamonds and green squares respectively) and the spread of the data points takes place in very narrow region. This behavior implies uniform doping over the scanned area of the Ag-decorated epitaxial graphene and is consistent with electron doping regime, for which the slope of $2D/G$ line is negative (~ -0.1) [44].

The data points for epitaxial graphene decorated with 10 nm thick Ag film (red asterisks in Fig. 3) are neatly arranged along a strain line (from the left side), suggesting screening effect [45]. From this analysis it appears that 10 nm Ag film is not suitable for uniform doping, since large non-uniform compressive strain occurs possibly due to coalescing process. During this process, the interconnections between initially separated Ag nano-islands start to appear, thereby favoring local strains and screening effects. On the other hand, 15 nm thick Ag film is more continuous in nature and, according to Figure 3 (violet triangles), is partly relaxed (since the corresponding data points scatter primarily along a line with the small negative slope), indicating nearly the same strain degree, but large carrier density fluctuations. It is most likely that compressive strain on graphene induced by the substrate effect from one side and Ag deposition at the early stages from another side can be released by structural transformation from the nano-island film to continuous silver layer.

Figure 3. Mutual dependence of $2D$ peak frequency and G peak frequency for pristine and Ag-decorated epitaxial graphene obtained from two-dimensional Raman mapping. The light red point ($G=1582\text{ cm}^{-1}$ and $2D=2670\text{ cm}^{-1}$) denotes the strain- and doping-free graphene. Theoretical dependences of the $2D$ peak position on G peak position for graphene subjected only to strain or hole doping are also plotted for reference (blue and red lines, respectively).

To further support the conclusions from the results presented in Fig. 3, we then consider the evolution of FWHM of $2D$ peak with Ag-layer thickness (Figure 4). Since this parameter is very sensitive to doping and structural quality of the graphene [41, 45], it can be also used to probe the uniformity of electronic properties of Ag-decorated epitaxial graphene. We observed dramatic changes of the width of the $2D$ peak with Ag nano-film thickness increasing (see $2D$ frequency versus G frequency dependences color coded by Γ_{2D} , which are shown in Figure 4). To be more exact, the extracted values of FWHM of $2D$ peak are 33.3, 49.3, 44.54, 77.8 and 64.1 cm^{-1} (the corresponding histograms of Γ_{2D} distribution are shown in Fig. 4f). Such band broadening can be explained by large strain fluctuations [45] and doping-induced phenomena [41], also indicating that only extremely thin silver films (2 and 5 nm, respectively) may produce, to some extent, uniform n -doping.

Figure 4. (a-e) Dependency of the $2D$ peak position on the G peak position for pristine and Ag-decorated epitaxial graphene color-coded by FWHM (full width at half maximum, Γ_{2D}) of $2D$ peak. (f) Histograms of Γ_{2D} values for pristine and Ag-decorated epitaxial graphene.

The variation in the $2D/G$ amplitude ratio versus G peak position shows also striking contrasts between the electronic properties of the epitaxial graphene before and after silver decoration (Figure 5a). Particularly, we revealed a weak dependence of the $2D/G$ ratio on G mode frequency and overall decrease in amplitude from 0.75 (for pristine graphene) to 0.1 and 0.06 for graphene affected by 2 nm and 5 nm Ag layers, respectively. This finding provides additional evidence to support the claim on n -type doping of graphene [24] that is in good agreement with previously reported data on Ag-induced n -doping in exfoliated graphene [46-48]. Unlike to effect of the ultra-thin Ag films on properties of epitaxial graphene, deposition of thicker films (10 and 15 nm) leads to stronger dependence of the $2D/G$ ratio on G peak position and more random spread of data points, suggesting the large strain and doping fluctuations.

To gain more insights into the nature of Ag effect on epitaxial graphene, we also plotted the dependence of the $2D/G$ amplitude ratio on D/G amplitude ratio (Figure 5b). The linear behavior of such dependences is supposed to be related to the influence of Ag-induced defects. Nevertheless, these results contradict literature data, according to which the intensity of the $2D$ line monotonously decreases with increasing the defect concentration [49]. We suggest that the observed linear dependences can be explained by: (i) different degrees of the enhancement (due to SERS effect) of D and $2D$ peak amplitudes, depending on the resonance frequency or energetics of the charge transfer channel; and/or (ii) local charged impurity-induced screening of the graphene π electrons, followed by reduction of electron density and subsequent increase in $2D/G$ ratio [24].

Figure 5. (a) $2D/G$ amplitude ratio plotted as a function of the Raman shift of the G mode pristine and Ag-decorated epitaxial graphene samples. (b) Correlation between $2D/G$ amplitude ratio and D/G amplitude ratio for Ag-decorated epitaxial graphene on 4H-SiC

By ascribing the carrier concentration and compressive strain values to each of the data points shown in Figure 3 for pristine epitaxial graphene and samples affected by the deposition of thin Ag silver films with thickness 2 and 5 nm (this approach is well documented in literature and successfully approbation for doped graphene under biaxial strain [24, 42, 44, 50, 51]), we constructed the carrier (electron) concentration maps (Figure 6) and strain distribution maps (Figure 7) with corresponding histograms,

The results in Figure 6 reveal that large area and quite uniform n -type doping is achieved as a result of Ag deposition. An increase in film thickness and area of coverage results in increase in doping level and an increase in spatial fluctuations of carrier concentration.

Figure 7 shows an overall decrease in compressive strain. Furthermore, local strain variations correlated with electron density distribution over the map regions of enhanced carrier density correspond to regions of reduced compressive strain. Such a correlation can be interpreted in terms of fundamental relationship between carrier concentration and strain proposed by Schmidt *et al.* [52]: an increase in the compressive strain gives rise to the decrease of in-plane length of C-C sp^2 -bond and, consequently, the increase in Fermi velocity. Due to this reason, the electrons density becomes smaller. Therefore, biaxial compressive strain in epitaxial graphene after Ag deposition can be partly released by enhancement of the local electron concentration due to produced n -doping.

Figure 6. Electron density maps for pristine (a) and Ag-decorated epitaxial graphene (b, c), showing the effect of extremely thin silver film (2 nm and 5 nm) on electronic properties of

graphene. The bottom panel represents the corresponding histograms fitted with a Gaussian function, mean values of the carrier density and standard deviations.

Figure 7. Compressive strain maps for pristine (a) and Ag-decorated epitaxial graphene (b, c), showing the effect of thin Ag film (2 nm and 5 nm) on electronic properties of graphene. The bottom panel represents the corresponding histograms fitted with a Gaussian function, mean values of the compressive strain and standard deviations.

Conclusions

Large-area uniform electron doping of epitaxial graphene ($0.95\text{--}1.36 \times 10^{13} \text{ cm}^{-2}$) is achieved by room temperature deposition of extremely thin Ag nano-island films as dopant source. In-depth Raman mapping analysis followed by statistical analysis has been performed to extract the critical information on Ag-induced doping of epitaxial graphene depending on thickness of Ag nano-film. Epitaxial graphene after decoration with very thin Ag films of $<5 \text{ nm}$ exhibits comparatively narrow red-shifted $2D$ peak with quite small $2D/G$ amplitude ratio, suggesting that the successful n -doping occurs due to electron transfer from Ag to epitaxial graphene. Thicker Ag films (10 and 15 nm) are found to be inappropriate doping sources due to the presence of large strain and doping fluctuations as well as generation of structural in-plane and out-of-plane defects. Interestingly, increase in defect density in all Ag-decorated epitaxial graphene samples causes the unexpected increase the $2D/G$ amplitude, which can be explained by both inequivalent increase of peak amplitude due to SERS effect and screening effect originating from accommodation of charged impurities at the graphene surface. By constructing the compressive strain and electron doping maps, we revealed the simultaneous reduction of

the compressive strain and increase in carried density. This observation can be attributed to the partial strain relaxation through a local enhancement of the carrier density. Our results gain deep insights into the Ag effect onto electronic and vibrational properties of epitaxial graphene, and, therefore, can be further utilized to reach better control on doping efficiency.

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