Minimizing sputter-induced damage during deposition of WS$_2$ onto graphene

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We demonstrate the sputter-deposition of WS$_2$ onto a single-layer graphene film leaving the latter disorder-free. The sputtering process normally causes defects to the graphene lattice and adversely affects its properties. Sputtering of WS$_2$ yields significant amounts of energetic particles, specifically negative S ions, and reflected neutral Ar, and it is therefore used as a model system in this work. The disorder-free sputtering is achieved by increasing the sputtering pressure of Ar thereby shifting the kinetic energy distribution towards lower energies for the impinging particle flux at the substrate. Monte Carlo simulations of the sputtering process show that W is completely thermalized already at relatively low sputtering pressure, whereas Ar and S need a comparably higher pressure to thermalize so as to keep the graphene film intact. Apart from becoming completely amorphous at 2.3 mTorr, the graphene film remains essentially disorder-free when the pressure is increased to 60 mTorr. The approach used here is generally applicable and readily extendable to sputter-deposition of other material combinations onto sensitive substrates. Moreover, it can be used without changing the geometry of an existing sputtering setup. Published by AIP Publishing.

Graphene, with its extraordinary electronic, optical, thermal, and mechanical properties,\textsuperscript{1} has attracted enormous interest within the scientific and engineering community both from fundamental and applied perspectives. In order to make functional devices, it is commonly required to deposit materials onto graphene without damaging it;\textsuperscript{2} damage can also be used as a means to tailor the chemical doping/functionalization.$^3$ This is not a trivial problem since the atomically thin layer of C, though one of the strongest materials known, is easily damaged by moderately energetic particles.$^4$

There are several kinds of defects that can be induced in graphene by energetic particles. As described in detail by Ahlberg \textit{et al.},\textsuperscript{4} there is no well-defined lower limit below which ions do not damage graphene. There is, however, a threshold energy at which graphene goes from barely unaffected to amorphous. This threshold is element specific, and it is experimentally determined to be 26 eV for Ar.$^5$ Moreover, the level of damage is dependent on the total number of energetic particles, i.e., the dose, before the deposit reaches a critical thickness beyond which the impinging atoms/ions do not interact with the underlying graphene film.

A scalable and commonly used industrial deposition technique is Physical Vapor Deposition (PVD) by DC magnetron sputtering. However, this process involves several types of energetic particles that may damage graphene sheets.$^4$ They consist of atoms sputtered of the target, Ar reflected from the target, and negative ions created at the target.

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onto a thermally oxidized Si wafer having a 300 nm thick SiO₂ layer.\textsuperscript{14} This approach is chosen because it is the viable manufacturing technique for industrial scale production of graphene.\textsuperscript{15}

All WS₂ coatings were sputter-deposited by magnetron sputtering in a high vacuum CS 600 von Ardenne system. The base pressure for all depositions was in the 10\textsuperscript{−7} mTorr range. A 100 mm WS₂ sputter target (K. Lesker Inc.) with a purity of 99.9\%, was used with a pulsed DC power at 200 W. Ar was used as the sputtering gas at a flow rate of 20 sccm. The processing pressure was varied from 2.3 mTorr to 60 mTorr with the deposition time adjusted so as to achieve a 5 nm thick WS₂ film on each sample. The deposition rate varied between 9 nm/min, at the lowest processing pressure, and 4 nm/min, at the highest pressure. The magnetron was located on the top lid of the deposition chamber with a 30° angle towards the substrate table at the center of the chamber bottom. The target to substrate distance was 16 cm. The graphene coated SiO₂/Si samples were located in front of the target at the conventional substrate position, i.e., on-axis in front of the target.

All WS₂ films were characterized by means of X-ray photoelectron spectroscopy (XPS) using a Physical Systems Quantum 2000 spectrometer with monochromatic AlK\textsubscript{α} radiation. XPS data indicate an under-stoichiometric WS₂,\textsubscript{2-x} at low processing pressure, whilst approaching stoichiometric WS₂ above 50 mTorr. Each sample was characterized before and after the WS₂ deposition using Raman spectroscopy (Renishaw "inVita" Raman spectrometer) with 532 nm laser excitation at 20× magnification.

In Figure 1(a), the Raman spectra for graphene at different processing pressures are exhibited; at the bottom of the graph, a spectrum of the as-grown graphene transferred onto an oxidized Si substrate is included as reference. For detailed interpretation of the Raman spectra and the labelling of the peaks, D, G, D’ and 2D, see Ferrari and Basko.\textsuperscript{16} The small peak at 2330 cm\textsuperscript{−1} comes from the N\textsubscript{2} gas present in the ambient air.\textsuperscript{17} The amount of induced damage in the graphene film is assessed by analyzing the Raman spectra in the following way: the ratio of the max intensity of the D peak to that of the G peak (D/G) is used as a measure of the amount of damage to graphene. This ratio is inversely correlated to the distance between two lattice defects, whereas the 2D to G ratio (2D/G) identifies the resemblance to monolayer graphene.\textsuperscript{4,13,16,18} At the lowest pressures, i.e., 2.3 and 10 mTorr, the spectra are significantly different from the reference spectrum, indicative of amorphization.\textsuperscript{4} At 20 mTorr, the spectrum shows clear D, D’ and 2D peaks, indicative of heavily damaged, but not amorphized, graphene. With increasing pressure, the D and D’ peaks become fainter while the G and 2D peaks keep their intensity and also become narrower, which is an indication of low-defect density graphene.\textsuperscript{4,16}

Sputtering at pressure above 60 mTorr resulted in spontaneous and randomly occurring discharges around the substrate table. Therefore, 60 mTorr is our highest processing pressure in this study. This upper limit of the pressure is dependent on the chamber geometry and process parameters used and can vary for other systems than the presently studied.

For the 2D/G and D/G ratios summarized in Figure 1(b), the maximum intensity of the peaks is used. Moreover, the peaks are fitted with Voigt profiles and a linear background using MATLAB using the built-in least-squares fit procedure. Each data point represents an average of up to 100 spectra collected on the sample. Analyzing a series of spectra this way, we also get an estimate of the variation of the sample as reflected in the error bars. Most of the error bars are within the size of the markers, indicating that the homogeneity of the samples is good throughout the sample series.

The horizontal line at the ratio 2.25 marked “Pre” in Figure 1(b) indicates the 2D/G ratio from the as-transferred graphene, the line at 0.1 indicates the corresponding D/G ratio. The D/G ratio marked “Post” represents the results after sputter-deposition. It varies with the processing pressure from a ratio of 2.5 at 20 mTorr to less than 0.5 above 50 mTorr. The 2D/G ratio marked “Post” varies between 2 and 2.25 in the 20–60 mTorr range. The graphene films receiving the WS₂ deposition at 2.3 and 10 mTorr were also analyzed, but as the films were completely destroyed, only the 10 mTorr data points are shown (as disconnected circles) in Figure 1(b). Above 50 mTorr, both the 2D/G and D/G ratios reach a regime where the graphene is only slightly damaged by the sputtering process.

The particle energy distribution was obtained by means of Monte-Carlo simulations, detailed elsewhere.\textsuperscript{11,12,19} In brief, (1) the initial energy and direction of the sputtered W atoms and the reflected Ar are calculated using SRIM.\textsuperscript{20} Negative ions, in this instance S, are given the target potential to define their initial energy with a direction along the target surface’s normal towards the substrate; (2) each atom then propogates a distance randomly generated using its mean free path; (3) if the vector between the old and new positions intersect a chamber wall (or substrate), the particle regarded adsorbed and the impact position is saved together with the energy; (4) if no wall/substrate adsorption occurs,

FIG. 1. (a) Representative Raman spectra at various pressures together with a reference spectrum of the pre-deposition material. (b) The 2D/G and D/G ratios for the sputter-deposited films, as well as for the as-transferred graphene prior to deposition. The circles indicate ratios for 10 mTorr disconnected from the other points in the series since the material is completely amorphous, with a 2D/G ratio of ~0.5 and a D/G ratio of ~1.3.
a hard-sphere collision occurs with a sputter gas atom (using theoretical atomic radii\textsuperscript{21}); and (5) the energy and direction of the atom is updated. Steps (2)–(5) are repeated for each atom until it is adsorbed. Results from such simulations are illustrated in Figure 2(a) where the kinetic energy distribution is shown for the different atoms/ions arriving at the substrate.

All simulations assume a simplified environment with a flat target and flat substrate. In real life, the target will not have a flat radial distribution, a race-track like groove is formed after some usage. This will affect the initial distribution of energy and direction of the atoms emanating from the surface. However, at higher pressures, this discrepancy will vanish due to large number of collisions. Furthermore, the mean free path of each atom/ion is calculated assuming a complete thermalization. This approach will somewhat underestimate the mean free path for high energy particles.\textsuperscript{11} The interaction between the particles is described with a hard sphere potential, which may also be considered a simplification compared to, e.g., the Lennard-Jones potential. But, at the kinetic energies considered here, this simplification does not affect the scattering properties in the collisions significantly. Despite approximations and idealizations outlined above, the same code has previously been used to successfully describe the compositional variations at different substrate positions and pressures in the case of WS\textsubscript{2}–x.\textsuperscript{12}

As shown in Figure 2(a), the S ions are accelerated with a target potential that varies from 390 V for lower pressures to 350 V at higher processing pressures. By increasing the processing pressure, the average energy of all particles decreases, i.e., the energy distribution shifts to lower energies. The energy distribution for S and Ar displays peaks above 100 eV whose intensity decreases with the increasing pressure. At a higher pressure, the peak between 0.01 and 0.1 eV predominates for all cases with W, S, and Ar. For the heavier element, this peak appears at a lower pressure since the collision cross-section is larger thereby giving rise to a comparatively larger number of collisions on the way to the substrate.

A high energy tail can be seen for both S and Ar, although much more pronounced for Ar. These particles are the ones with sufficient kinetic energy to damage the graphene film. To ascertain if S or Ar is the main culprit, one would need to determine the flux of the particles by multiplying the number of particles per unit time of each kind with their energy distribution. It is not straightforward to estimate an exact number of the different particles, but calculations using SRIM estimate that sputtered S and W atoms and reflected Ar are present at the target with an approximate proportion of 4/2/1. With the experimental conditions used, only a very small fraction of the sputtered S atoms are negatively ionized at the target surface. These ions, are (much) fewer compared to the number of reflected Ar atoms. This points toward the reflected Ar as the main cause of the damage to graphene for the considered system at higher pressure.

In Figure 2(b), the fraction of particles having a kinetic energy above the displacement energy (\(E_d\) in Equation (1)) or above 5 eV, that hit the substrate are plotted. The two thresholds are chosen to identify energetic atoms/ions that can create different types of defects. \(E_d\) is the minimum kinetic energy of a projectile required to remove a C atom from a free standing graphene sheet. To calculate \(E_d\) for a given atom, the expression for the maximum energy transferred in an elastic collision is used

\[
E_d = \frac{T_d(m_t + M)^2}{4m_t M}.
\]

Here, \(T_d\) is the lowest energy required to displace a C atom in graphene, and it is calculated to be 22.2 eV,\textsuperscript{22,23} \(m_t\) and \(M\) are the mass of a C atom and the incoming atom, respectively. \(E_d\) for Ar, W, and S are calculated to be 31.2, 96.4, and 28.0 eV, respectively. It has also been demonstrated that graphene may become damaged from particles having significantly lower energies than \(E_d\).\textsuperscript{4} Particles with a few eV of the kinetic energy may create the Stone-Wales type of defects that can deteriorate graphene at high doses. Therefore, we have chosen 5 eV as the lower energy threshold for this defect formation mechanism.

The complete thermalization of W is achieved at relatively low sputtering gas pressure, whereas the lighter atoms/ions stay energetic at a higher pressure. It can also be seen that the amount of Ar with energies above 5 eV has a lower decline rate than the amount of S with energies above 5 eV.

Comparing Figures 1(b) and 2(b), the same trend is observed for both the D/G ratio and the probability. When the probability of particles with an energy above \(E_d\) is high, the high D/G ratio indicates damaged graphene. When the sputtering pressure is increased and the probability of particles with energies above \(E_d\) decreases, the D/G ratio also decreases. At 50 mTorr, all W atoms are thermalized, and thus are not contributing to damaging the graphene. However, both S and Ar still have a significant fraction of their kinetic

![Figure 2](image-url)
energy distributions populated at energies that can damage the graphene film. At a higher pressure there will be some, although at a low probability, particles with an energy of several eV. This result also points toward the neutralized reflected Ar atoms as being the particles that are most likely to cause damage to graphene above 50 mTorr.

The deposited WS$_2$ films are of (nominal) equal thickness for all pressures, in order to attain doses of W and S unaffected by the processing pressure. The same should be true also for reflected Ar, since it has a mass and size similar to those of S. However, although the deposition time is more than doubled between the lowest and highest pressure points, the graphene film is not damaged for 60 mTorr – since the amount of high energy particles at the substrate is insignificant at the higher pressure.

The sputtering process may represent a rather difficult process to predict in great detail. As shown here, several kinds of particles can affect graphene during sputter-deposition. The energy distribution and amounts of the different species depend on the materials system. We choose to study the sputter-deposition of WS$_2$ because significant amounts of negative ions and reflected Ar are generated at rather high energies. Other materials can give dramatically different flux and energy distribution of energetic particles. In general, our simulations show that an increase in the sputtering gas is a key factor in keeping the sputter damage to a minimum.

In conclusion, we have shown that sputtering compound films onto graphene with controlled damage is possible by increasing the sputtering pressure and not requiring special substrate geometry or holders. Although WS$_2$ has been used in this work, the findings are applicable also to other transition metal dichalcogenides, e.g., MoS$_2$, MoSe$_2$, etc. Furthermore, we demonstrate that simulation can predict the suitable sputtering pressure regime, and that the sputtering gas is a key factor in keeping the sputter damage to a minimum.

The simulation results shown here are tailored for the sputtering and materials system used. This allows us to draw quantitative conclusions regarding the critical pressure at which S, W, or Ar can be thermalized. Since bombardment by energetic particles is material dependent, it is concluded that simulation is of importance in order to gain insight on what processing pressure is required for disorder-free sputtering onto graphene.

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