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Direct Epitaxial CVD Synthesis of Tungsten Disulfide on Epitaxial and CVD Graphene

G. V. Bianco,1† M. Losurdo,1 M. M. Giangregorio,2 A. Sacchetti,1
P. Prete,3 N. Lovergine,1 P. Capezzuto,3 and G. Bruno3

The direct chemical vapor deposition of WS2 by W(CO)6 and elemental sulfur as precursors onto epitaxial-graphene on SiC and CVD-graphene transferred on SiO2/Si substrate is presented. This methodology allows the epitaxial growth of continuous WS2 film with homogeneous and narrow photoluminescence peak without inducing stress or structural defects in the graphene substrates. The control of the WS2 growth dynamics for providing the localized sulfide deposition by tuning the surface energy of the graphene substrates is also demonstrated. This growth methodology opens the way towards the direct bottom up fabrication of devices based on TMDCs/graphene van der Waals heterostructures.

Introduction

Whereas the “hype” on graphene seems to be weakening, a renewed interest in families of different layered materials such as dichalcogenides (e.g., MoS2 and WS2), nitrides (e.g., h-BN), and even oxides (e.g., TiO2) is emerging.1-4 Indeed, the quality of graphene continues to improve and its integration into heterostructures with other 2D materials represents an attractive technological perspective.3 In particular, monolayers of transition metal dichalcogenides (TMDCs) such as MoS2 and WS2 have recently caught great interest as materials with properties complementary to those of graphene. In contrast to graphene, whose zero energy gap represents a limit for applications in logic electronics and field-effect transistors, monolayers of MoS2 and WS2 are semiconductors with a direct gap in the visible and, consequently, with a strong photoluminescence.5-10 Therefore, their combination into heterostructures held together by van der Waals interactions (often referred as “van der Waals heterostructures”) provides a great potential for the development of 2D electronic and optoelectronic devices.1, 11-14

Currently, many physical and chemical methodologies15-28 are employed to prepare TMDCs and, among these, the direct growth of TMDC on other bidimensional materials represents a promising approach for the fabrication of van der Waals heterostructures.27-31 This approach can provide cleaner and more defined interfaces if compared to the staking of 2D materials by transfer methods which often result in impurities trapped at the heterojunction interface.20, 32 In fact, the interface quality has a fundamental role in defining the properties of TMDCs as well as of atomic-layered materials in general since substrate roughness and charged impurities can act as scattering centers strongly affecting their transport and optical properties. The important role of the interface quality on the properties of a TMDC has been highlighted by Okada et al. for the deposition of WS2 on hexagonal boron nitride (h-BN).27 They demonstrated an intense and narrow (fwhm of 26 meV) photoluminescence (PL) emission peak for WS2 when deposited on an hexagonal and atomically flat surface. Similar results have been reported by Kobayashi et al. for the growth of WS2 on graphite where micrometer WS2 2D crystals presented a narrower PL peak rather than that shown by WS2 grown on Al2O3 or SiO2/Si.33 Such PL responses are indicative of an improved structural quality that derives from the absence of dangling bonds on h-BN or graphite surfaces as well as on the face of a TMDCs layer which allows the WS2 growth by Van der Waals epitaxy: the two van der Waals surfaces facing each other result in a heterostructure with an atomic order thickness and a very abrupt interface by drastically relaxing the lattice matching condition between the two materials.34 Nevertheless, although van der Waals epitaxy has been demonstrated effective for providing micrometer-sized WS2 crystals with high structural quality, TMDCs applications into van der Waals heterostructures need the controlled growth of layered materials as continuous film with homogeneous optical properties.
In this contribution, we report on the direct growth of WS\(_2\) onto both epitaxial graphene (epi-G) and CVD graphene (CVD-G). To the best of our knowledge, this is the first study that shows how to deposit atomic layers of WS\(_2\) by using elemental sulfur (S) and tungsten hexacarbonyl (W(CO)\(_6\)) as precursors. If compared with the commonly used WO\(_3\) powder,\(^{21,33}\) such metal organic W precursor can provide a more precise control over the gas-phase chemistry for deposition on large area (as previously demonstrated for the WSe\(_2\) growth).\(^{29,35}\) Moreover, the WS\(_2\) deposition by direct reaction of gaseous precursors on the substrate surface, rather than by substrate metalization and subsequent sulfidization,\(^{10,17}\) offers important advantages in terms of process scalability. We also demonstrate the flexibility of this new chemistry for providing the controlled WS\(_2\) growth from isolated triangular crystals, to continuous few layer films, up to quasi-unidimensional nanostructures.

The photoluminescence responses of deposited WS\(_2\) films as a function of their morphologies are investigated. Moreover, SEM analysis is performed for defining the WS\(_2\) growth dynamic in order to achieve the controlled, also localized, WS\(_2\) growth with homogenous thickness, and hence, optical properties.

**Results and discussion**

The WS\(_2\) film growth is carried out by the thermal decomposition of W(CO)\(_6\) in presence of sulfur vapor according to the following reaction:

\[
\text{W(CO)}_6 + \text{S}_2 \rightarrow \text{WS}_2 + 6\text{CO}
\]  

The scheme of the CVD system used for the growth of WS\(_2\) is reported in fig. 1a. The quartz reaction tube for thermal CVD has two heated zones for the sulfur-powder boat and for the growth susceptor where the graphene substrate is loaded. After evaporation of the solid tungsten precursor (W(CO)\(_6\)) at 50°C (T\(_1\)), the last is mixed with helium carrier gas and passes through the quartz tube system where the small capsule with elemental sulfur is heated at 170°C (T\(_2\)). Then, the S\(_2\) vapor is also mixed to the gas flow that reaches the graphene substrate heated at 600°C (T\(_3\)). When epi-G/SiC is used as substrate, the WS\(_2\) growth is evidenced by the colour changes of the transparent sample.
which becomes grey/blue in colour (insets of fig. 1 b), and it is confirmed by the elemental composition obtained from the EDS-SEM microanalysis (fig. 1b).

Fig. 2 reports the real ($\varepsilon_1$) and imaginary ($\varepsilon_2$) parts of the pseudodielectric function ($\varepsilon = \varepsilon_1 + i\varepsilon_2$) of WS$_2$ grown on epi-G/SiC (deposition time of 10 min).

show a consistent blue shift with decreasing layer numbers. In particular, a C transition located above 2.75 eV has been typically correlated to WS$_2$ monolayer.$^{9,37}$ The achieved WS$_2$ growth can be also attested by the comparison between Raman spectra of epitaxial graphene on SiC before and after the deposition process (fig. 3). In the range 1200–2000 cm$^{-1}$, the spectra present the Raman peaks of the SiC substrate overlapping the characteristic D and G peaks of graphene (approximately at 1350 and 1590 cm$^{-1}$, respectively). Conversely, the graphene 2D is clearly visualized at 2733 cm$^{-1}$. This peak can be fitted to a single Lorentzian (see the inset in figure 3) indicating the monolayer nature of the sample.$^{38}$ The WS$_2$ growth is inferred by a slight attenuation of the SiC Raman features and of the graphene 2D peak as well as by the appearance of the two WS$_2$ characteristic peaks at 355 and 417 cm$^{-1}$. The former is $E_{2g}^{1}$ mode, which involves the in-plane displacement of W and S atoms, and the latter is $A_{1g}$ mode, which involves the out-of-plane displacement of S atoms.$^{39}$ The decrease in intensity of the SiC and graphene Raman features is attributed to interference effects and absorption of WS$_2$.$^{32}$ Noteworthy, the spectrum shape does not change (except for the signal attenuation) in the region around 1350 cm$^{-1}$ where the graphene D peak is expected. This demonstrates that the growth process does not affect the graphene structural quality, since the occurrence of any damaging would increase the intensity of the D peak.

Raman analysis can also be used to identify and quantify the interfacial strain on the fabricated TMDC/G heterostructures.$^{32}$ The following equation correlates the graphene strain ($\varepsilon$) induced by the WS$_2$ deposition to the shift in wavenumber of the 2D Raman mode ($\omega-\omega_0$, where $\omega_0$ is the initial wavenumber):

$$\varepsilon=(\omega-\omega_0)/2\gamma \omega_0$$

where $\gamma$ is the Gruneisen parameter, which uniquely depends on the material. Considering a 2D shift of 3 cm$^{-1}$, an initial position of 2733 cm$^{-1}$, and $\gamma$ of 2.6,$^{32}$ we have estimated a negligible compressive strain of about 0.02%. This result

![Fig. 2 SE spectra of the real ($\varepsilon_1$) and imaginary ($\varepsilon_2$) parts of the pseudodielectric function ($\varepsilon = \varepsilon_1 + i\varepsilon_2$) of WS$_2$ grown on epi-G/SiC (deposition time of 10 min).](image1)

![Fig. 3 Raman spectra of epi-G on SiC before and after WS$_2$ growth (10 min of deposition time). Inset shows a magnification of the 2D peak of epi-G.](image2)
confirms the potential of van der Waals epitaxy in relaxing the interface between two materials.

The morphologies of WS$_2$ film grown on epi-G for deposition times of 5, 10, 15 and 20 min are shown on the SEM images reported in fig. 4 (a, b, c and d-e, respectively). For a deposition time of 5 min (fig. 4a), the sample still shows the terraces due to the miscut of the silicon carbide wafer which characterizes the morphology of an epi-G sample (see fig. S1 in electronic supplementary information, ESI). No substantial differences can be found in the morphology of the substrate before and after WS$_2$ growth except for the presence of nanometer sized clusters which are arranged in triangular geometries. These have been identified as sulfur condensed at the surface of triangular-shaped crystals of WS$_2$ whose presence is attested by both Raman and PL measurements (black spectra in figures 4f and 4g).

For longer deposition times, the complete coalescence of WS$_2$ crystals into a continuous film occurs and the epi-G substrate loses its characteristic SiC terraced morphology (fig. 4b). Over this continuous film, we can notice isolated triangles supporting further WS$_2$ crystals which have nucleated in the proximity of their centers. Moreover, SEM images acquired by a second electron detector at the initial stage of WS$_2$ growth (see figure S2a and S2b) indicate that the formation of such

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Fig. 4 (a-e) SEM images of WS$_2$ films grown on epi-G/SiC substrate for 5 (a), 10 (b), 15 (c), and 20 min (d, e) of deposition times (scale bars are 200 nm). (f) Raman and (g) photoluminescence spectra of WS$_2$ samples grown for different deposition times (legend in g). PL spectra are normalized to the intensity of the 2LA(M) Raman mode.
WS₂ new layers starts before the complete coverage of the substrate by a monolayer. Specifically, the growth starts with WS₂ monolayer with hundred nanometer size. For longer growing times (> 10 min), the continuous nucleation of new WS₂ layers gives rise to the formation of multilayered pyramids touching each other (fig. 4c) and evolving in a textured surface morphology (see background of fig. 4d and 4e). The last also promotes a totally different WS₂ growth mode leading to the formation of triangular quantum dots and nanowires (fig. 4d and 4e). Such transition to a quasi-unidimensional growth is indicative of a Stranski-Krastanov growth mode as reported also for the epitaxial growth of MoS₂ on mica.⁴¹ The Stranski-Krastanov growth arises because strain energy in the deposited layers increases as the thickness increases, which is reflected by an increase in the interface energy between preformed and new WS₂ layer. Beyond a critical layer thickness, this leads to a switch in the growth mode that continues through the nucleation of new WS₂ layer rather than the lateral growth of preformed ones.

Raman and photoluminescence, PL, spectra provided by the different WS₂ morphologies are reported in figures 4f and 4g. When a WS₂ film is excited at 532 nm (almost in resonance with the B exciton transition), the Raman spectrum reveals a series of overtone and combination peaks not visible with a 473 nm laser source (see figure 3). The 2LA(M)−2E₂g(Γ) mode appears at lower wavenumber (297 cm⁻¹), while the Raman feature around 350 cm⁻¹ is the convolution of four peaks including the 2LA(M)−E₂g(Γ), E₁g(M), 2LA(M) and E₂g(Γ) modes, which are pointed at 325, 345, 352 and 356 cm⁻¹, respectively (values derived for the spectrum of the WS₂ sample grown with a deposition time of 5 min). Similar to the case of MoS₂, the Raman modes of WS₂ exhibit a thickness dependence. Upon increasing the WS₂ thickness from monolayer to bulk, several authors reported a gradual increase in the frequency difference between the A₁g mode and the E₂g(Γ) (or 2LA(M)), which stiffens and softens, respectively. ¹⁰, ²⁰, ³⁵, ⁴²-⁴⁴ When a 532 nm laser source is used, the 2LA(M) results more prominent than the E₂g(Γ) and, hence, the WS₂ thickness is typically correlated to its frequency. Despite the consistent differences between the morphologies of WS₂ films grown for 5 and 10 min (fig. 4a and b), their Raman spectra are almost identical (black and red lines in fig. 4f) with a 2LA(M) and A₁g modes at 352 and 420 cm⁻¹, respectively, and a frequency difference of 68 cm⁻¹ that is consistent with the values previously reported for 2 layers of WS₂. ⁴², ⁴³ For longer deposition times, the WS₂ Raman spectra present several changes. The increasing thickness is reflected by a gradual increase in intensity of the A₁g peak ⁴³, ⁴⁴ that also blue-shifts to 422 and 423 cm⁻¹ for 15 and 20 min of deposition times, respectively, while the 2LA(M) modes are found at 352 and 350 cm⁻¹, respectively. Thus, we find values of frequency differences of 70 and 73 cm⁻¹ which have previously been reported for 3-4 layers of WS₂ and WS₂ bulk, respectively. ⁴³ A stronger dependence is found between the morphologies of WS₂ films and their PL responses reported in fig. 4g. The samples present a single PL peak originating from the exciton transition A whose intensity decreases with the increasing of growing times, up to the complete disappearance (as expected for WS₂ bulk). The isolated WS₂ triangles in fig. 4a present a PL peak located at 623 nm (1.99 eV) and a narrow fwhm of 27 meV. When the coalescence of WS₂ crystals in a continuous film occurs (growing time of 10 min, SEM image in fig. 4b), the sample shows a PL peak (red spectrum) slightly shifted toward longer wavelengths (625 nm at maximum) with an increased fwhm of 33 meV. The PL mapping of this sample (fig. S3 in supporting information) has also demonstrated an almost constant PL response over an area of 20 x 20 μm². PL wavelength at maximum of 625 ± 1 nm and a relative standard deviation below 20% on the PL intensity. For longer deposition time, the WS₂ pyramidal textures on fig. 4c and 4d-e present, respectively, a broad PL peak centered at 630 nm and the complete absence of PL signal. It is probable that the PL signal collected by the laser spot size (~700 nm in diameter) is the contribution of different WS₂ domains. Anyway, the PL analysis demonstrates that this growth methodology can lead to WS₂ continuous film with homogeneous PL response as required by applications based on van der Waals heterostructures.

The use of CVD graphene supported on Si/SiO₂ as WS₂ substrate allows a better understanding of the sulfide growth mode. Since SEM analysis on SiO₂ substrate results in a better colour contrast for WS₂ rather than that observed on epi-G, the study of the WS₂ deposition also at the early stage of its growth is possible. SEM image in fig. 5a shows that the distribution density of WS₂ crystals after 5 min of growth is not homogeneous over the substrate surface. Specifically, the density of WS₂ crystals at graphene grain boundaries appears much higher than that inside the grains. This makes the polycrystalline structure of CVD graphene clearly visible. Such favoured WS₂ nucleation derives from the higher concentration of structural defects at graphene grain boundaries. Vacancies and Stone-Wales defects are formed between two coalesced graphene grains in order to accomplish their in plane misorientations. ⁴⁵ These locally alter the chemical reactivity of graphene and, in our case, it results in a reduction of the WS₂ nucleation energy barrier. A denser distribution of WS₂ crystals is also found in presence of graphene bilayer. The two specular regions in the center of fig. 5a correspond to bare SiO₂ (on the left side) and twisted bilayer graphene, TBG (on the right side) which derive from the detachment and folding of the graphene film. The absence of graphene prevents the WS₂ growth on bare SiO₂. Conversely, WS₂ nucleation results strongly promoted on TBG as well as on Bernal-stacked bilayer graphene (BBG) islands. ⁴⁶ These appear as darker grey regions inside graphene grains and derive from the nucleation and growth of a second graphene layer next to the substrate. ⁴⁶ Magnification in fig. 5b shows that isolated WS₂ triangles are not randomly oriented on the graphene surface. Inside a single graphene grain, we can distinguish equilateral triangles with only two different orientations related to each other by a rotation of 60°. Such non random distribution of WS₂ triangles is indicative of distinct crystallographic orientations between deposited TMDC and the substrate as previously demonstrated by diffraction techniques for the epitaxial
growth of MoS$_2$ on graphene$^{30}$ or sapphire,$^{47}$ WSe$_2$ on graphene,$^{26}$ and WS$_2$ on hBN.$^{27}$ Specifically, these works show how the orientation of TMDCs crystals with perfect triangular shape, as defined uniquely by a zigzag sulfur edge structure, can be univocally identified with their lattice orientation. Thus, we can attest for an epitaxial relation also for WS$_2$ on graphene and for the existence of substantial WS$_2$/graphene interactions which can affect the growth of WS$_2$ triangular crystals in order to find energetically favoured orientations.

Under continued growth, triangular crystals can merge to form a continuous WS$_2$ layer. However, the properties of the resulting WS$_2$ film will be strongly affected by its polycrystalline nature. The detrimental effects of grain boundaries on the optical and electrical properties of the film depend on the specific atomic structure of grain boundaries.$^{47-49}$ The last is strictly correlated to the relative in-plane crystallographic orientations of two merging TMDCs crystals.$^{47-49}$ Previous studies on the large area growth of MoS$_2$ film have demonstrated that two TMDCs triangles sharing the same in-plane orientation and, hence, crystalline orientation can join without the appearance of any grain boundaries.$^{47,48}$ Thus, the growth of WS$_2$ triangles with only two distinctive in-plane orientations offers a great potential for the deposition of polycrystalline large area film with reduced density of grain boundaries. Conversely, if TMDCs merging triangles are misaligned, the strong directional dependence of surface energies of their edges$^{48}$ can result into strongly faceted grain boundaries (“tilted” grain boundaries) or into overlapping regions.$^{47,49}$ Indeed, TMDCs triangles with a relative in-plane rotation of 60° (as shown in figure 5b) provide the perfect alignment of their zigzag sulfur edges which results into a specific grain boundary atomic structure named as “mirror twin”.$^{47,48}$ In contrast to “tilted” grain boundaries, the “mirror twin” ones have been experimentally demonstrated not to degrade the electrical properties of a polycrystalline TMDC film.$^{47,48}$ However, the possibility of depositing WS$_2$ continuous film with reduced density of grain boundaries and with the favoured formation of “mirror twin” boundaries is confined to a single graphene grain. For larger areas, the polycrystalline nature of the substrate will be also reflected in the WS$_2$ film.

The SEM image reported in fig. 5c shows a detail of the edges alignment between two tilted merging triangles. The same image has been acquired also by using a secondary electron,
SE2, detector (fig. 5d) since it provides a sharper thickness-dependent contrast for 2D materials on insulating substrates. The image attests for the absence of an overlapped junction between merging WS$_2$ triangles and highlights the presence of supplementary WS$_2$ triangular layers already formed over them. Thus, when WS$_2$ nuclei are formed, their lateral growth is in competition with the growth of new WS$_2$ layers starting from the same nucleation seeds. Such growth mode is consistent with a Volmer–Weber one and leads to the formation of multilayered WS$_2$ islands rather than a continuous film with uniform thickness as desired for applications in devices based on van der Waals heterostructures. Considering only thermodynamic criteria, the Volmer-Weber growth is indicative of a weaker interaction between WS$_2$ and graphene than between WS$_2$ layers. In terms of surface energies ($\gamma$), the islands growth mode occurs when $\gamma_{WS2} > \gamma_{Graphene} > \gamma^*$, where $\gamma^*$ is the graphene/WS$_2$ interface energy. The main issue relies on the extremely low surface energy of monolayer CVD graphene ($\gamma_{Graphene} \approx 70$ mJ/m$^2$) in comparison to the WS$_2$ one ($\gamma_{WS2} \approx 260$ mJ/m$^2$).\textsuperscript{51} This limits the WS$_2$ nucleation as well as the attachment of sulfur and tungsten adatoms to the edges of WS$_2$ monolayer.

Conversely, the favoured WS$_2$ nucleation on TBG and BBG (fig. 4a) derives from the (25%) higher surface energy value of bilayer graphene compared to that of monolayer one.\textsuperscript{52} Fig. 6 demonstrates that the high density of nucleation sites on BBG can provide the localized deposition of a WS$_2$ film on the bilayer graphene island without almost no sulfide deposition inside monolayer graphene grains. The high structural quality and few layer nature of WS$_2$ film grown on BBG is attested by a frequency difference between 2LA(M) and $A_{1g}$ Raman modes of 66 cm$^{-1}$ and a PL peak with a maximum at 610 nm (2.03 eV) and an intensity five times higher than the Raman features at $\approx 350$ cm$^{-1}$.

Conclusions

We have reported the successful van der Waals epitaxy of WS$_2$ on epi-G and CVD-G by direct CVD growth with W(CO)$_6$ and elemental sulfur as precursors. The Raman analysis on WS$_2$/epi-G has highlighted the absence of strain at the heterostucture interface as well as the absence of graphene defects induced by the deposition process. The PL analysis has demonstrated that this synthetic route can provide continuous WS$_2$ films with homogeneous PL response. Moreover, SEM analysis has shown the occurrence of an epitaxial growth leading to specific in plane orientations which provides a great potential for the growth of large area continuous film. Finally, the possibility of tuning the WS$_2$ growth dynamic and localizing WS$_2$ deposition by tailoring the graphene surface energy has been demonstrated. The proposed growth methodology opens the way towards the direct bottom up fabrication of a huge variety of TMDCs/graphene devices that are based on van der Waals heterostructures integrating 2D materials.

Experimental

The epi-G substrates were fabricated by thermal annealing of hydrogen-plasma cleaned 6H-SiC substrates at 1500°C for 2 min at 10$^{-8}$ mbar. CVD-G was grown on 25 μm thick copper foils at 1000 °C using CH$_4$/H$_2$ as precursors. The prepared graphene was then transferred onto 300 nm SiO$_2$/Si substrates by using a thermal release tape and a water solution of ammonium persulfate (0.1 M) as copper etchant. The methodology for the growth of WS$_2$ is reported in the main text.

WS$_2$ Raman and PL spectra were collected using a LabRAM HR Horiba-JobinYvon spectrometer with a 473 and 532 nm excitation laser sources, and a 100X objective. Ellipsometric spectra were acquired using a phase-modulated spectroscopic ellipsometer (UVISEL, Horiba JobinYvon) in the 1.5–3.25 eV spectral range with 0.01 eV resolution.
The sample morphology was studied through field emission scanning electron microscopy (FE-SEM) observations, using a Carl Zeiss Sigma microscope, equipped with a high resolution FE-SEM Gemini electron column, an in-lens detector (SE) placed inside the electron column, and an external Everhart-Thornley detector (SE2) placed outside the column. A primary electron beam acceleration voltage ranging between 1 and 5 kV and a working distance of around 3 mm were employed.

Acknowledgements

The authors acknowledge funding from the National Laboratory Sens&Micro Lab Project (POFESR 2007–2013, code number 15) funded by Apulia Region. The authors wish to acknowledge F. Marzo for FE-SEM observations.

References

Direct epitaxial growth of WS2 isolated crystals and WS2 continuous films providing homogeneous and narrow PL peak onto epitaxial- and CVD-graphene.