

Van der Waals Growth of 2D WS₂ Atomic Layers on CVD and Epitaxial Graphene

G. V. Bianco^{1*}, M. Losurdo¹, M. M. Giangregorio¹, A. Sacchetti¹, P. Capezzuto^{1,2}, P. Prete³, N. Lovergine⁴, and G. Bruno¹

¹ CNR-NANOTEC, Istituto di Nanotecnologia, via Orabona, 4, 70126, Bari, Italy

² Department of Chemistry, University of Bari, via Orabona, 4 70126 Bari, Italy

³ Institute for Microelectronic and Microsystems, National Research Council, UOS Lecce, Via Monteroni, I-73100 Lecce, Italy

⁴ Department of Innovation Engineering, University of Salento, Via Monteroni, I-73100 Lecce, Italy

^{1*} giuseppevalerio.bianco@cnr.it

Van der Waals heterostructures represent a promising technological perspective for exploiting bidimensional materials (graphene, hBN, WS₂, etc.) and their peculiar properties into innovative devices rather than as substitute of conventional bulk materials into well-established technologies.^[1] In particular, the integration of monolayers of transition metal dichalcogenides, TMDs, (MoS₂, WS₂, WSe₂, etc) and graphene can provide the synergic exploitation of the direct band gap (in the visible) of TMDs and the high transport properties of graphene into 2D innovative optoelectronic devices.^[2] The recent literature reports several examples of TMD/graphene heterostructures which are made by transferring and stacking different 2D crystals on top of each other.^[3] However, this fabrication approach often results in impurities trapped at the heterojunction interface which strongly affect the individual properties of the 2D building blocks as well as the charge transfer processes between them. Conversely, the direct growth of TMDs on graphene has been demonstrated effective for allowing atomic order thickness and very abrupt interfaces owing to the occurrence of a “Van der Waals epitaxy” growth mode.^[4]

Although previous works have demonstrated that high quality micrometer crystals of TMDs can be successfully grown on graphene, their controlled growth as continuous film with homogeneous optical properties, as required by applications based on 2D heterostructures, results still difficult. In this contribution, we report the successful direct synthesis by chemical vapor deposition, CVD, of continuous films of WS₂ on both epitaxial graphene (as obtained by Si sublimation from SiC substrates) and CVD graphene. In particular, we demonstrate the homogeneous photoluminescence response of WS₂ film as well as the possibility of localizing its deposition by tailoring the graphene surface energy.

References

- [1] A. K. Geim et al., *Nature* 499 (2013) 419.
- [2] L. Britnell et al, *Science* 340 (2013) 1311.
- [3] K. Zhou et al, *ACS Nano* 6 (2014) 9914.
- [4] A. Koma, *Thin Solid Films* 216 (1992) 72.
- [5] 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 (Department of Innovation Engineering, University of Salento, Lecce, Italy.) for FE-SEM observations.

The deposition of atomic layers of WS₂ is carried out by using elemental sulfur and tungsten hexacarbonyl (W(CO)₆) as precursor. Experimental parameters (partial pressure of precursors, deposition time and temperature) are controlled for tuning the WS₂ morphology from isolated triangular crystals to continuous film (SEM images in figure 1) and, then, for defining the WS₂ thickness (layers number). The dependence of WS₂ Raman spectrum on the layers number (figure 2a) is exploited for achieving a fast control (also on large area by Raman mapping) on both WS₂ thickness and thickness homogeneity. The last is very important for the fabrication of Van der Waals heterostructures since WS₂ optical properties strongly depends on its layers number (figure 2b). Moreover, we take advantage from the dependence of the WS₂ growth dynamics on the graphene surface energy for providing an additional degree of control on its growth. In particular, we demonstrate that graphene wettability to WS₂ can be improved by structural or chemical modifications in order to provide the spatial control on the WS₂ growth. Analyses based on Raman, photoluminescence and spectroscopic ellipsometry measurements demonstrate that this synthetic route can provide WS₂/graphene heterostructures characterized by the absence of interface defects and strain and with homogeneous PL response.^[5]

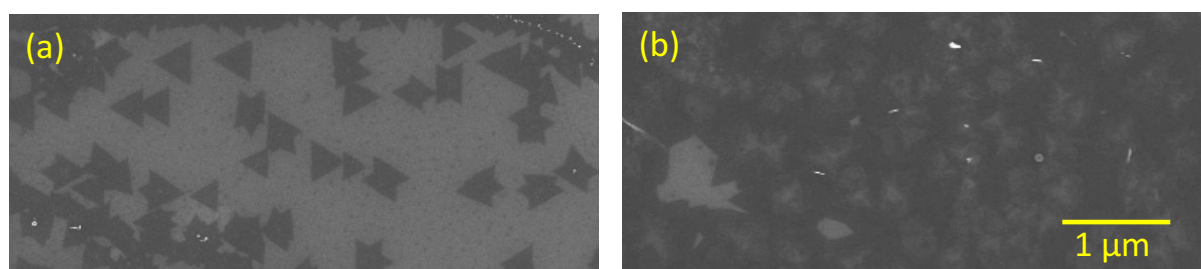


Figure 1: (a) Isolated triangular crystals and (b) continuous film of WS₂ grown on CVD graphene supported on Si/SiO₂ substrate.

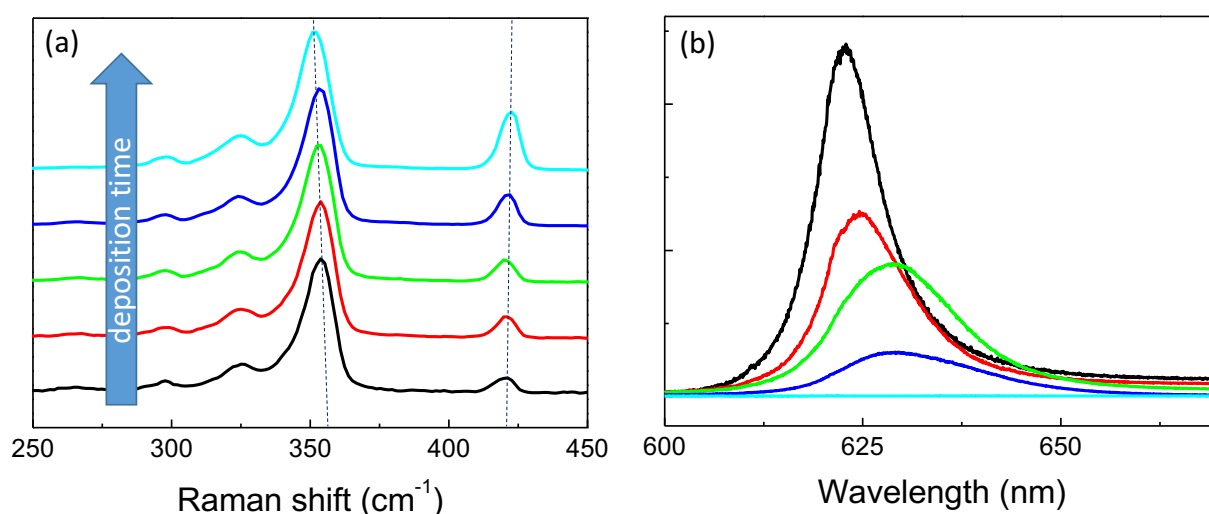


Figure 2: (a) Raman and (b) Photoluminescence spectra of WS₂ films grown on graphene with different deposition time.