Standard Project

Experimental Report

Proposal title: Structural properties of MoSe2/WSe2 layers on sapphire: effect of post-growth annealing **Structural properties of the van der Waals heterostructure $MoSe_2$-graphene**		**Proposal number:** 20160498
Beamline: BM32	**Date(s) of experiment:** from: 25/01/2017 to: 31/01/2017	**Date of report:** 14/02/2017
Shifts:	**Local contact(s):** Gilles Renaud	*Date of submission:* 15/02/2017

Objective & expected results (less than 10 lines):

The initial objective of the proposal was to study the effect of post-growth annealing on structural properties of transition metal dichalcogenides (TMDs) $MoSe_2$/WSe_2 grown on sapphire substrate. During the first shifts of the beam time, we found that the TMDs grew in an inhomogenous manner on the substrate without any preferential crystallographic orientations and the post-anneal did not help to rearrange the domains. The study with synchrotron diffraction was meaningless on this system. For this reason, we have dedicated the rest of our time shifts to study vertically 2D heterostructure based on TMDs and graphene, which is also an attractive structure for exloring new physics in the 2D system. We aimed to characterize the structural properties of the top layer $MoSe_2$ and to unveil the van der Waals epitaxial registry between the TMDs layer and graphene-SiC, which has been so far not reported yet. In the main part of the present report, we focus, therefore, only on the results obtained with the heterostructure $MoSe_2$/Graphene-SiC.

Results and the conclusions of the study (main part):

Three samples have been characterized, of $MoSe_2$ thicknesses of ~0.7 ML, ~1 ML and 3.5 ML on multilayer graphene on SiC(0001).

Figure 1 shows an in-plane reciprocal space map (rsm) measured on the 3.5 ML sample, covering one sixth of the ℓ=0 reciprocal plane, and indexed using the SiC(0001) reciprocal lattice units. The map measured on the 0.75 ML and 1 ML samples are very similar, with weaker intensities. In addition to the reciprocal space map, very precise radial scans were performed along the high symmetry directions (*h*00) (Fig. 2a) and (*hh*0) (Fig. 2b), as well as precise rocking scans (see e.g. Fig. 2c), and measurements as a function of ℓ along the rods of scattering on all measurable Bragg peaks/rings (see e.g. Fig. 2d). ℓ was varied by increasing the exit angle with respect to the surface while keeping the incident angle fixed.

The diffraction from three hexagonal lattices is clearly visible on the in-plane rsm: the hardly visible peaks of the SiC(0001) substrate; the peaks from the multilayer graphene grown on it also hardly visible, and finally and those of the $MoSe_2$ thin layer, in the form of wide, in-plane textured, rings of scattering. No other feature is visible.

The position of these peaks (together with out-off plane ones, not shown), yields the following epitaxial relationships: SiC[10-10](0001)//Gr[1-100](0001)//$MoSe_2$[1-100](0001). This finding indicates that the in-plane lattices of graphene and MoSe2 commensurately align to each other, whereas the SiC substrate lattice rotates an angle of 30° with respect to the two adjacent overlayers.

The exact lattice parameters of the multilayer graphene and of $MoSe_2$ were deduced by fitting the positions of the corresponding Bragg peaks along radial scans. The widths of these peaks were also used to estimate the in-plane domain size according to:

$(\Delta Q)^2 = (2\pi/D)^2 + Q^2 (\Delta a/a)^2$,

Where ΔQ is the peaks Full Width at Half Maximum FWHM in nm^{-1}: D is the domain size (nm), Q the reciprocal space location (or momentum transfer (nm^{-1}) and $\Delta a/a$ the FWHM of a possible inhomogeneous distribution of in-plane lattice parameter. A linear evolution of the $MoSe_2$ peak width with Q was indeed found, revealing a distribution of in-plane lattice parameter, *i.e.* some inhomogeneous strain.

The in-plane mosaic spreads were deduced from rocking scan measurements across the graphene and $MoSe_2$ peaks. No evolutions were found with varying momentum transfer Q, thus showing the peak widths are completely dominated by in-plane mosaic spread.

The out-off plane thickness and structure, and in particular the stacking sequence, were determined by simulating the rods of scattering by the $MoSe_2$ layer. The position of the out-off plane allowed and forbidden Bragg peaks allowed to unambiguously demonstrated that the $MoSe_2$ layer is of 1H (2H) structure. Note that these fits yield a 3 to 4 % expansion of the $MoSe_2$ inter-plane distances perpendicular to the surface.

The structural parameters deduced from the different X-ray measurements are summarized in Table 1.

From this study, it was found that crystallographic directions of the $MoSe_2$ lattice align perfectly along the ones of the graphene lattice, resulting in only one commensurate configuration. This reveals a novel feature of the vdW epitaxy where the vdW interaction between the two layers was revised. The latter guides all domains of the $MoSe_2$ layer orienting along the graphene. This finding suggests the unique configuration of epitaxial registry between $MoSe_2$ and graphene which enables for orientation-independent investigation of heterostructure properties without anisotropic effect.

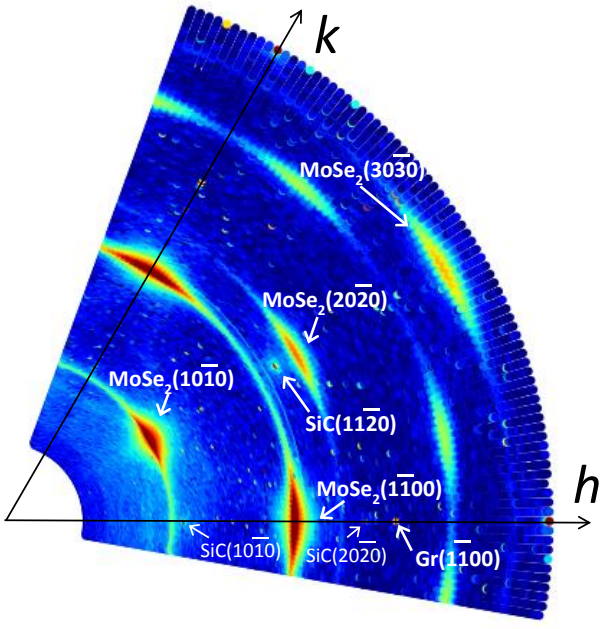

Figure 1. In-plane reciprocal space map (rsm) of the 3.5ML–thick $MoSe_2$ sample (right), measured by rocking the sample over 80° at increasing values of the in-plane SiC(0001) reciprocal lattice units h and k with increments of 0.01. The Si(0001) unit cell, is hexagonal with 3.079 Å and 10.05 Å lengths, respectively in-plane and out-off plane lattice parameters. The out-off plane ℓ value is close to zero; the intensity being integrated over $\Delta\ell$ = 0.1. Note that a 3D measurement is actually performed thanks to the 5° long detector perpendicular to the surface, covering an ℓ-range between 0 and 0.75. The color scale is logarithmic, the highest (red) intensity being 10^6 ph/seconds and the background ~80 ph/s.

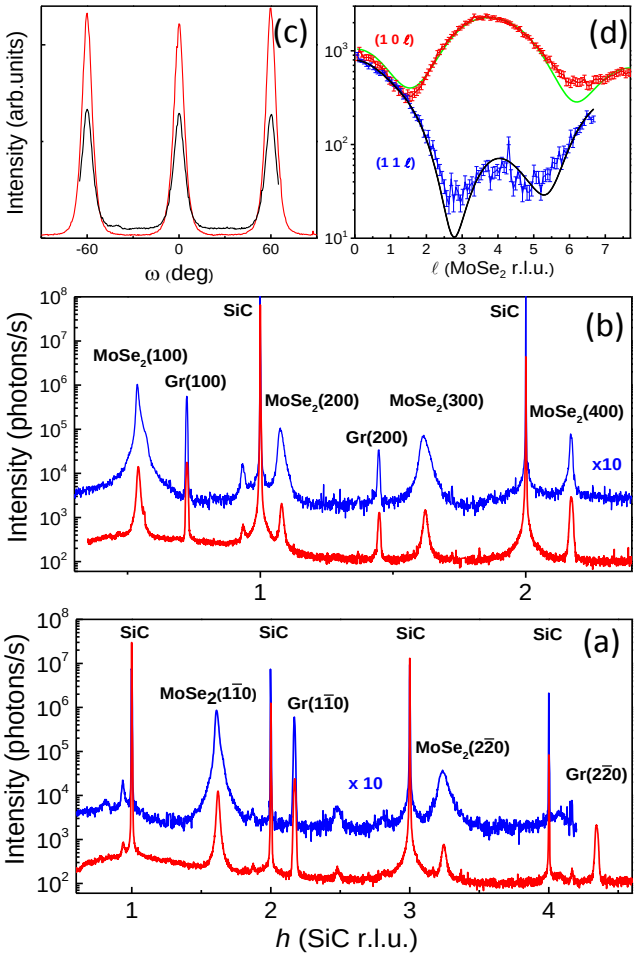

Figure 2: (a) Radial scan along the in-plane (*h*00) direction for the 1 ML (red) and 3.5 ML (blue, multiplied by 10) $MoSe_2$-thick samples, crossing the following Bragg peaks, in order of increasing *h* : $MoSe_2(1\bar{1}00)$, $Gr(1\bar{1}00)$, $MoSe_2(2\,\bar{2}\,00)$, and $Gr(2\,\bar{2}\,00)$. (b) Radial scan along the in-plane (*hh*0) direction for the 1 ML (red) and 3.5 ML (blue, multiplied by 10) $MoSe_2$-thick samples, crossing the following Bragg peaks, in order of increasing *h=k* : $MoSe_2$(H0-H0), Gr(H0-H0),with H=1,2,3 and 4. (c) Azimuthal rocking scans across the $MoSe_2(10\bar{1}0)$ reflection, for 3.5ML (red) and 1 ML (black). (d) Measured intensity along the 10ℓ (red) and $1\bar{1}\ell$ (blue) rods of $MoSe_2$ for the 1 ML-thick sample together with simulated rods (green and black lines, respectively) for a perfectly 1ML-thick $MoSe_2$ layer of H-type structure. On the figure, the standard 3 index notation (hkl) is used. The four hexagonal four index notation is (hk*i*l) with *i*=-(h+k).

Sample nominal thickness	0.7 ML	1 ML	3.5 ML
In-plane SiC lattice parameter	3.079 ±0.001 Å	3.079 ±0.001 Å	3.080 ±0.001 Å
SiC in-plane mosaic spread		0.008°	0.008°
ML graphene in-plane lattice parameter	2.454 ± 0.001 Å	2.456 ± 0.001 Å	2.457 ± 0.001 Å
ML graphene in-plane mosaic spread	0.44° ± 0.03°	0.52° ± 0.04°	0.43°± 0.03°
ML graphene thickness	18 nm	20 nm	23.5 nm
FWHM of graphene relative $a_{//}$ distribution		$4 \times 10^{-3} \pm 1 \times 10^{-3}$	$4 \times 10^{-3} \pm 1 \times 10^{-3}$
ML graphene in-plane domain size		~25 ± 3 nm	~39 ± 3 nm
In-plane $MoSe_2$ lattice parameter	3.287 ± 0.001 Å	3.289 ± 0.001 Å	3.299 ± 0.002 Å
FWHM of $MoSe_2$ relative $a_{//}$ distribution	$4 \times 10^{-3} \pm 2 \times 10^{-3}$	$8 \times 10^{-3} \pm 2 \times 10^{-3}$	$6 \times 10^{-2} \pm 2 \times 10^{-2}$
$MoSe_2$ in-plane mosaic spread	8.3 ± 0.2°	7.8 ± 0.2°	8° ± 0.2°
$MoSe_2$ in-plane domain size	~25 ± 10 nm	~18 ± 10 nm	~30 ± 10 nm
$MoSe_2$ thickness *t*	0.67 ML	0.95 ML	1.9 ML

Table 1. Structural parameters deduced for the three samples on nominal thicknesses 0.7; 1 and 3.5 ML. The SiC(0001) substrates in-plane lattice parameter, of 3.079 Å is the tabulated one for all samples. The in-plane mosaic spread, of 0.008°, is very small. The MoSe2 characteristics are similar for the 0.7 and 1 ML samples: and average in-plane lattice parameter of 3.288 ± 0.001 Å with some inhomogeneous strain of FWHM between 0.013 and 0.026 Å, an in-plane mosaic spread of 8 ± 0.2° and an average domain size ~20 nm. The thickness deduced from the fits of out-of plan rods is almost nominal. The thicker (3.5 ML) sample yields different results, though. The average in-plane lattice parameter is much larger, as is its distribution, about 10 times larger. The mosaic spread and domain size are comparable, but the fitted thickness is smaller than the nominal

Justification and comments about the use of beam time (5 lines max.):

Publication(s):

M. T. Dau et al., Commensurability in vertical two-dimensional heterostructure: a comprehensive study of structure and electronic properties with gap opening in MoSe2-graphene, *to be summited*