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In a previous experiment (see Report 32-03-741), we have realized the formation and the quantitative structure determination by SXRD of a single layer of $PtSe_2$ obtained by selenization of Pt(111). The $PtSe_2$ layer is perfectly epitaxial and aligned with the underlying Pt(111). It is slightly compressively strained by 0.7% so as to create a very well ordered superstructure lattice corresponding to three $PtSe_2$ in-plane unit cells in coincidence with four Pt(111) ones. Displacements in the substrate are strong, and at least 3 Pt(111) layers have to be taken into account in the SXRD structure determination. This later is almost finished, and a publication is in preparation (1). We also found that this structure is stable until 400°C, temperature above which the diffraction by the superstructure vanishes and is replaced by diffuse scattering due to Se vacancies and mobile adatoms. The pristine $PtSe_2$ structure is recovered by cooling down to RT; hence, a reversible path can be followed from dissolution to recrystallization of $PtSe_2$ upon cycles of annealing and cooling. At this point, we wondered whether, after degradation of the $PtSe_2$, one could follow a new cooling path in the presence of a sulphur precursor, leading to an ordered chalcogen alloyed SL TMDC, *via* substitution of some Se atoms by S ones, thanks to the higher stability of Pt-S bonds compared to Pt-Se ones. To test this proposal, we supplied sulphur in the form of gaseous H_2S, which is known to decompose on noble metal surfaces.

We prepared a first sample called SPtSe by pre-annealing it in UHV a few tens of degrees above 400°C in order to create Se vacancies in the topmost chalcogen layer. Then, a 10^{-4} mbar H_2S partial pressure was introduced and maintained for five hours at a slightly lower temperature. We monitored the sulphurization process by GIXRD to track possible structural changes due to the chalcogen substitution in the $PtSe_2$ lattice, *e.g.* strain, loss of the superstructure order, surface disorder, new phases with different lattice parameters, or additional/suppressed peaks corresponding to different crystal symmetries. In Figure 1a, the radial scans of as-grown $PtSe_2$ and sulphurized $PtSe_2$ are compared. After H_2S treatment, the intensity loss (-58%) of the (600) $PtSe_2$ Bragg peak (the h index is multiplied by 4 with because of the Pt(111) 4x4 coincidence surstructure lattice) and the broader tail in the low h values of the Pt(400) and (800) Crystal Truncation Rod peaks suggest an increased surface disorder. Except for that, the spectra are remarkably similar to those of pristine $PtSe_2$/Pt(111), the (3×3)$PtSe_2$-on-(4×4)Pt(111) coincidence being exactly maintained. The chemical composition of this SPtSe sample was probed by a quantitative Angular Resolved XPS study, from which we confirmed that we formed a Janus SPtSe layer, in which the top Se layer has been fully substituted by S while the amount of S in the bottom Se layer is negligible.

We also achieve full sulphurization of a second sample (called PtS_x) by exposing $PtSe_2$ to H_2S partial pressure for longer time at higher temperature. Similarly to Fig. 1a, Fig. 1b shows two radial scans along the h direction taken before (black) and after (red) the sulphurization process. Here, the peak intensity at $h = 6$ (previously $PtSe_2$ reflection) is severely damped to about one tenth of the pristine intensity, and the intensity at the Pt CTRs tails (on the low-h sides of the $h = 4$ and $h = 8$ peaks) is higher, which suggests disorder in the surface layer. The $PtSe_2$ overlayer is very likely degraded due to the higher temperature used and to the longer exposure to H_2S. A residual ordered superstructure is still preserved, which

however can be hardly associated to any pure $PtSe_2$ or SPtSe alloy because of the lack of selenium determined by XPS. As shown in the map (Fig. 1c), no other diffraction signals were found which could be attributed to a relaxed platinum disulfide (PtS_2) or other phases. Note that for PtS_2 to be in a 4:3 ratio with Pt(111), conditions required by the superstructure, it should stretch its lattice parameter by 4.6 %. In general, according the largely different lattice parameters of 1T PtSe2 (3.7 Å) and PtS2 (3.54Å) structures, one would expect extra reflections or intensity bumps or diffuse intensity between $h = 6.00$ and $h = 6.28$ for the PtS_2 phase. The only new detectable signatures are some peak shoulders, suggesting non identified sulphide phases of slightly shorter lattice parameter than $PtSe_2$ coexisting with the pristine superstructure or some significant contribution to the scattering by defects. A plausible hypothesis is that the provided sulphur has in this case replaced most of the pristine selenium. No substantial modifications of the pristine diffraction pattern were observed by GIXRD in the small map of Fig. 1c. The only significant changes are the clear elongation of most of the superstructure peaks toward the (440) $PtSe_2$ main reflection. These elongations might arise from specific defects that would need a very extensive investigation, which is beyond the scope of the present study. Some rods of scattering by the superstructure were also measured on both sulfurized samples (Fig. 1d). Except for their lower intensity and faster decrease with l, they show qualitatively exactly the same features as the original $PtSe_2$ ones. This indicates that in both cases, even for the fully sulfurized sample, the original $PtSe_2$ structure is preserved. We thus conclude that the recrystallization occurring during thermal annealing in H_2S does not relax the elastic deformation in the $PtSe_2$/Pt(111) structure, but the atoms are instead *pinned* at the initial positions. Both the strong interaction between Pt and $PtSe_2$ and the fortunate 4 to 3 coincidence of the in-plane lattice parameters are believed to lead to this *pinning*. This conclusion is a further evidence that the epitaxy in this system, rather than being of vdW type, is governed by more covalent interface interactions leading to distortions in both the overlayer and the substrate. These interactions probably explain why the $PtSe_2$ crystal retains its crystal integrity upon sulphurization.
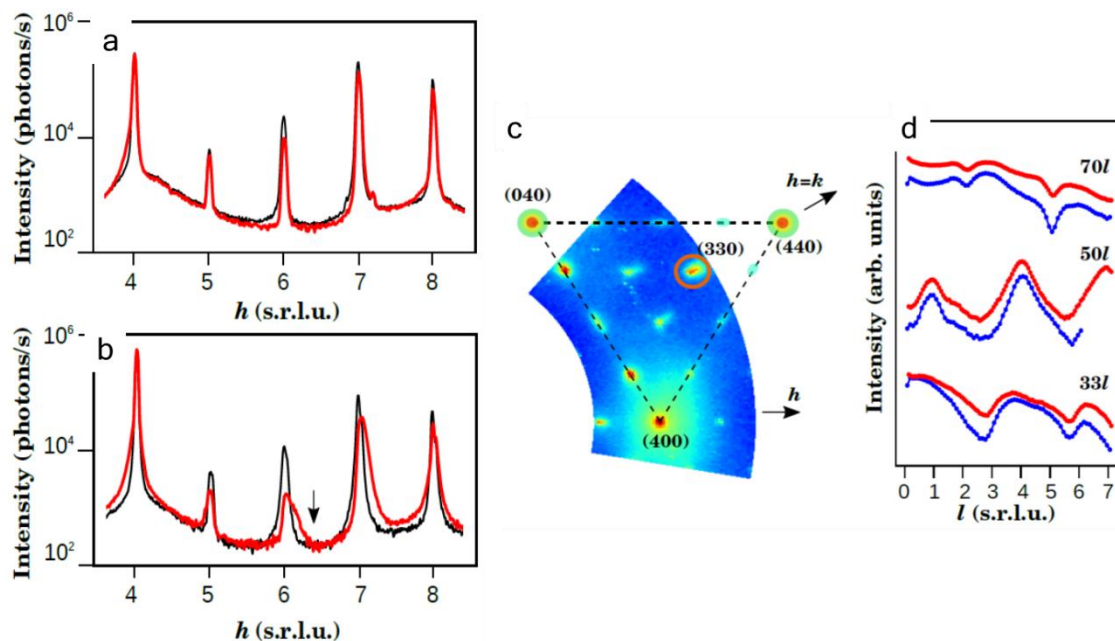

Figure 1: a) Radial scan along the h axis, *before* (black) and *after* (red) the partial sulphurization leading to a Janus SPtSe layer b), The same *before* (black) and *after* (red) the full sulphurization. The arrow indicates the expected position for a freestanding PtS_2 reflection. c) In-plane reciprocal space map corresponding of the fully sulphurized PtS_x sample. It shows that the main features of the diffraction pattern remains unaltered, although chalcogen substitution is demonstrated by photoemission spectroscopy, but the shape of some of the peaks has changed, displaying a strong diffuse scattering toward the $PtSe_2$(440) reflection. This scattering is the signature of defects. d) Rod of scattering as a function of the out-of plane coordinate ℓ, for the initial $PtSe_2$ structure (blue) and after sulphurization (red). The identical features call for very similar structures.

References
(1) Sant et al., *Synthesis of epitaxial monolayer Janus SPtSe*, npj 2D Materials and Applications (2020) 4:41 ; https://doi.org/10.1038/s41699-020-00175-z and R. Sant, PhD-Thesis, Univ. Gre. Alpes, 2019.