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High quality large area MoSe$_2$ and MoSe$_2$/Bi$_2$Se$_3$ heterostructures on AlN(0001)/Si(111) substrates by molecular beam epitaxy

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Atomically thin inherently 2D semiconductors offer thickness scaling of nanoelectronic devices and excellent response to light for low power versatile applications. Using small exfoliated flakes, advanced devices and integrated circuits have already been realized showing their great potential to impact nanoelectronics. Here, high quality single crystal MoSe$_2$ is grown by molecular beam epitaxy on AlN(0001)/Si(111) showing the potential for scaling up growth to low cost, large area substrates for mass production. The MoSe$_2$ layers are epitaxially aligned with the aluminum nitride (AlN) lattice showing uniform, smooth surface and interfaces with no reaction or intermixing and with sufficiently high band offsets. High quality single layer MoSe$_2$ are obtained with a direct gap evidenced by angle resolved photoemission spectroscopy and further confirmed by Raman and intense room temperature photoluminescence. Successful growth of high quality MoSe$_2$/Bi$_2$Se$_3$ multilayers on AlN shows promise for novel devices exploiting the non-trivial topological properties of Bi$_2$Se$_3$.

Using TMDs, mainly MoS$_2$, advanced field effect transistors$^{9,11}$ and generic integrated circuits (e.g. inverters, ring oscillators, SRAM, NOR gates$^{12,13}$) have been demonstrated, showing this material’s potential to impact nanoelectronics. So far, most of the research device work$^{9,12}$ has been performed on small (micron-sized) exfoliated flakes, while for mass production, large area synthesis of TMDs on insulating substrates is required to ensure reproducibility, high crystalline quality and homogeneity and ease of device fabrication. Most attempts to synthesize TMDs are based on CVD-like methods used first for the growth of MoS$_2^{14}$ and then applied to MoSe$_2$ growth.$^{15,17}$ These methods produce single crystals with sizes up to a few hundred microns, however, polycrystallinity, incomplete coverage and thickness uniformity are important issues.

Molecular Beam Epitaxy (MBE) of MoSe$_2$ on suitable crystalline substrates is expected to give highly oriented single crystals over the entire wafer. Apart from early pioneering work$^{18}$ there is a very recent report on the MBE growth of atomically thin epitaxial MoSe$_2$ on graphene-terminated 6H-SiC (0001) substrates$^{19}$ mainly focusing on the electronic band structure by angle resolved photoelectron spectroscopy (ARPES). There is little information about the structural quality, the band alignment and the optical emission properties

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**Introduction**

The isolation of various 2D layered transition-metal dichalcogenides (TMDs) in recent years, gave a large boost in the research for designing Van der Waals 2D structures with tailored properties depending on the material and the layer thickness.$^{1,3}$ TMDs with the general chemical formula MX$_2$ (M=Mo, W; X= S, Se, Te) are indirect semiconductors exhibiting an indirect to direct band gap crossover when thickness reduces from few layers to a single layer. The direct band gap in single layers results in intense room temperature photoluminescence (PL)$^4$ and more generally yields excellent response to light in the visible and near IR region of the solar spectrum, enabling a wide range of applications from optoelectronics$^{5-8}$ to energy conversion.$^8$ Owing to their strong covalent bonds within the MX$_2$ molecule, these materials exhibit high mechanical strength and since they can be grown few atom-thick, they are stretchable and bendable so they could be used for flexible transparent displays and a number of low power versatile applications.$^1$ Besides, the low dielectric constant (~4) and the ability to reduce the channel to a single layer of atoms without severely degrading mobility offer excellent electrostatic control allowing for aggressive lateral scaling beyond that presently achieved using silicon or other conventional semiconductors.

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of epitaxial single and few-layer MoSe$_2$ grown by MBE on alternative insulating substrates.

In this work, we demonstrate high quality few layer (1-6 ML) MoSe$_2$ which are grown epitaxially on AlN(0001)/Si(111) substrates by MBE with or without a buffer layer. We show that using AlN crystalline templates it is possible to obtain highly oriented single crystals of single- or few-layer MoSe$_2$ over the entire wafer (up to two inches) exhibiting high quality, very good uniformity and excellent stability in air, as verified by Raman characterization and room temperature photoluminescence. We also show that very good quality MoSe$_2$ can be grown on Bi$_2$Se$_3$ and that epitaxial Bi$_2$Se$_3$/MoSe$_2$ multilayers can be produced, thus creating the prospect for novel devices to exploit the non-trivial topological insulator properties$^{20}$ of Bi$_2$Se$_3$.

Experimental

Thin film growth and structural characterization

Films growth is carried out in an UHV-MBE system with base pressure in the $10^{-10}$ Torr range. All growth procedures are monitored by Reflection High Energy Electron Diffraction (RHEED) technique using a 15 keV e-gun. MoSe$_2$ is deposited either directly on 200nm AlN/Si(111) substrates or with a thin (3 or 5 quintuples (QL)) epitaxial Bi$_2$Se$_3$ buffer layer.

The 200 nm Al-face AlN(0001) layers are epitaxially grown by MOCVD on B-doped p-type 1150 µm Si(111) substrates, with a resistivity $> 1$ Ohm-cm. AlN is unintentionally n-type doped, typical for MOCVD grown AlN layers. The AlN substrates received both $ex situ$ and $in situ$ cleaning in the MBE chamber, following the procedure described in Ref. 20.

High purity Mo (99.95%) and Se (99.999%) are evaporated from an electron-gun evaporator and an effusion cell respectively, under Se-rich conditions with Mo/Se flux ratio of $\sim$1:10 and a MoSe$_2$ growth rate of 3 ML/min. Bi$_2$Se$_3$ buffer layer growth on 200nm AlN(0001)/Si(111) substrate is performed by evaporating Bi (99.997%) and Se (99.999%) both from effusion cells with a Bi/Se flux ratio of $\sim$1:20 and a growth rate of 1.5QL/min. After MoSe$_2$/AlN layers deposition, samples are transferred in the STM chamber attached to the MBE growth chamber for in situ STM characterization. STM topographies were obtained in UHV (base pressure of low $\times 10^{-9}$ mbar) at RT using an Omicron Large Sample SPM microscope with a Pt/Ir tip.

For the HRTEM characterization, cross-section TEM specimens are prepared by the sandwich technique. Mechanical grinding followed by focused Ar$^+$ ion milling in the GATAN PIPS is used to thin the specimens to electron transparency. HRTEM observations are performed using a 200 kV JEOL 2011 microscope, spherical aberration coefficient Cs=0.5 mm and point resolution 0.192 nm. Thickness-defocus HRTEM image maps are simulated using the EMS$^{21}$ software package and are associated to the HRTEM experimental images.

Physical and chemical characterization

In situ ARPES is conducted at RT in a µ-metal analytical chamber equipped with a 100 mm hemispherical electron analyzer (SPECXS PHOIBOS100) and a 2D CCD detector. The energy resolution of the detection system is better than 40meV, while the total experimental energy resolution is $\sim$100meV$^{22,23}$ dominated by the thermal broadening at RT. The excitation source is a He discharge lamp (SPECXS UV533/10) with He I (He II) radiation at 21.22 eV (40.814 eV). Photoelectrons emitted by the samples are measured in the energy distribution curve (EDC) mode. $In situ$ x-ray photoelectron spectroscopy (XPS) is performed with excitation by Mg-K$_x$ radiation (1253.6 eV) using a SPECS XR50 source, at take-off angle of 52$^\circ$.

For Raman spectroscopy a 532 nm laser beam is used with a power of $\sim$2mW on the sample surface. Spectra are resolved by a spectrometer using a grating of 1800 l/mm and acquired by an EMCCD detector. A 100x objective lens is used and the FWHM of the laser beam intensity at the sample surface is $\sim$1 µm. For the photoluminescence (PL) spectroscopy measurements, a 100x objective lens is used in combination with a grating of 600 l/mm. Both Raman and PL measurements are performed at RT.

Electronic structure calculations

The calculations are performed within the density functional theory (DFT) framework by using the Vienna ab initio simulation package. The Perdew-Burke-Ernzerhof with dispersion (PBE-D) exchange-correlation functional is engaged for our calculations. Spin-orbit effects are treated self-consistently. All atoms are allowed to relax until the force and the energy is converged to $10^{-2}$ eV/Å and $10^{-4}$ eV, respectively.

Results and discussion

MoSe$_2$ growth on AlN and on Bi$_2$Se$_3$ buffer layer

MoSe$_2$ is grown using a two-step process. Initially, MoSe$_2$ is deposited on AlN/Si(111) substrates at the relative low temperature of 350 °C, where a blurred RHEED pattern is observed indicating poor crystalline quality. In the second step, a post-deposition annealing in UHV is performed at 690 °C. The result is that the crystallinity is substantially improved as evidenced by the RHEED streaky pattern in (Figs. 1g, h) although a slightly disordered surface may not be excluded considering that the streaks are not as sharp as in the case of clean AlN surface (Fig. 1a, b). The streaky RHEED pattern in both [11-20] and [1-100] azimuths of a 1ML MoSe$_2$ in Figs. 1g and 1h respectively, indicates that the two hexagonal unit cells are perfectly aligned such that [11-20]MoSe$_2$//[11-20]AlN and [1-100]MoSe$_2$//[1-100]AlN in the plane. It is worth noting that the RHEED beam covers an area of a few mm at least, which is a significant portion of the cm-scale wafer. The absence of additional streaks indicates also the absence of rotated 30 or 90 deg domains meaning that the layers are highly oriented single crystals extended over large part, if not the entire wafer. The small, almost undetectable difference in the relative positions of the streaks (Fig. 1a, g) reflects the rather small lattice mismatch of $\sim$6% between the MoSe$_2$ and AlN (a$_{AlN}$=3.11Å, a$_{MoSe2}$=3.299Å) at room temperature; the latter nearly matched condition may be the reason for the perfect orientation of MoSe$_2$ crystal relative to the substrate.

Recently, our group reported$^{20}$ the high quality epitaxial growth of Bi$_2$Se$_3$ thin films on AlN(0001) substrates, which motivated us to use 5 quintuple layers (QL) of Bi$_2$Se$_3$ as a buffer layer for 2ML MoSe$_2$ overgrowth. The results in Fig. 1i-n show that both Bi$_2$Se$_3$ and MoSe$_2$ layers are epitaxial and perfectly oriented with the AlN substrate such that [11-20]MoSe$_2$//[11-20]AlN and [1-100]MoSe$_2$//[1-100]AlN. It is remarkable that MoSe$_2$ is grown highly oriented on Bi$_2$Se$_3$ despite the large mismatch of about 20% between the two materials. The growth of MoSe$_2$ is constrained to low temperatures due to the limited thermal stability of the underlying Bi$_2$Se$_3$ buffer which decomposes in vacuum at
temperatures higher than 300 °C. Nevertheless, the presence of the Bi$_2$Se$_3$ buffer layer promotes the growth of MoSe$_2$ at much lower substrate temperatures (300 °C) compared to the direct deposition on AlN(0001) substrate (690 °C) without reduction in epitaxial quality. The ability to lower the growth temperature of such 2D materials could be advantageous for large scale device manufacturing especially for applications where heterogeneous integration with Si devices is required.

![Image of RHEED patterns](Fig. 1)

**Fig. 1** RHEED patterns of: (a-h) 1ML MoSe$_2$ deposited on AlN(0001) with the 2 step-process and (i-n) 2ML MoSe$_2$ deposited on 5QL Bi$_2$Se$_3$ buffer layer epitaxial grown on AlN(0001). (a, i) show bare AlN(0001) pattern along [11-20] azimuth and (b, j) bare AlN(0001) along [1-100] azimuth. (c, d) are recordings at 350 °C after the deposition of MoSe$_2$, (e, f) are recordings at 690 °C, after the post-deposition annealing step while (g, h) present the MoSe$_2$ film on AlN after final cooling down to RT. (e, f) MoSe$_2$ becomes high crystalline with the respective crystal orientations aligned to those of AlN which is clearly observed after cooling down in (g, h). (k, l) 5QL Bi$_2$Se$_3$ buffer layer grows epitaxial on AlN(0001) at 300 °C with high crystalline quality, (m, n) MoSe$_2$ deposited on Bi$_2$Se$_3$ buffer layer at 300 °C grows epitaxial with [11-20]$_{\text{MoSe}_2}$//[11-20]$_{\text{Bi}_2\text{Se}_3}$ and [1-100]$_{\text{MoSe}_2}$/[1-100]$_{\text{Bi}_2\text{Se}_3}$. Blue and yellow downward arrows show AlN and Bi$_2$Se$_3$ streaks respectively. Red upward arrows show MoSe$_2$ streaks.

**Film structural characterization**

The surface structure of a 3 ML MoSe$_2$ sample is imaged in situ by UHV-STM as depicted in Fig. 2. The high resolution image (Fig. 2a) shows the hexagonal symmetry of the lattice. The brighter spots in Fig. 2a represent Se atoms located in the three corners of the top hexagon (Fig. 2b) separated by a distance of 3.3 Å as shown in the line scan 1 of Fig 2c. This is in good agreement with the theoretical value of the lattice constant $a_{\text{MoSe}_2}=3.299$ Å. The Mo atoms are located in the three corners of the hexagon located 1.67 Å below the top one (see also ESI†, Fig. S1a). This picture is further supported by the line scan 2 in Fig. 2d showing that Mo atoms are in a lower position and have a distance of ~ 2 Å from neighboring Se atoms, close to the theoretical value of 1.9 Å. STM performed in a larger scale (see ESI†, Fig. S2a, b), reveals that at the low deposition temperature the sample has root-mean-square (RMS) surface roughness value of 1.25 nm which however significantly improves after post-deposition annealing (see ESI†, Fig. S2c, d) yielding an RMS roughness of 0.62 nm, over a scanned areas of (5x5) µm$^2$. The annealed sample shows a continuous film with smooth surface morphology.

![Image of STM image](Fig. 2)

**Fig. 2** (a) Room temperature high resolution STM image of 3ML MoSe$_2$ on AlN(0001) (Ubias=0.7 V, I= 0.9 nA) showing a honeycomb structure. The bright corners in the honeycomb configuration are attributed to Se atoms occupying the three corners of the topmost hexagon. (b) Stick and ball model of MoSe$_2$ honeycomb structure along the [0001]$_{\text{MoSe}_2}$ axis showing the Se and Mo atoms positions. Se atoms reside on the three corners of the top hexagon while Mo occupies the three corners of the hexagon located 1.67 Å from the top one. (c) Profile along line 1 in image (a) showing the estimated distance of 3.3 Å between Se-Se atoms, in good agreement with the MoSe$_2$ lattice constant $a_{\text{MoSe}_2}=3.299$ Å. (d) Profile along line 2 in image (a) showing the buckling between Se-Mo atoms and their estimated lateral distance of 2 Å, close to the theoretical value of 1.9 Å.

Additionally large area optical images of samples with different size and parts of a sample inspected by SEM, (see ESI†, Fig. S3) indicate a uniform, homogeneous film over the entire substrate.

The films microstructure is examined by High Resolution Transmission Electron Microscopy (HRTEM) (Fig. 3). A low magnification cross section TEM image is presented in Fig. 3a, showing a 3 ML MoSe$_2$ film of uniform thickness and smooth surface and interface with AlN substrate, as also verified by large area STM images (see also ESI†, Fig. S2).
The HRTEM image of Fig. 3b shows 3 layers of MoSe₂ imaged along the [11-20]_{AlN} zone axis. The corresponding simulated image (thickness 15 nm along the electron beam, defocus -70 nm) superimposed on the right side confirms that the [11-20] directions of AlN and MoSe₂ lattices are aligned in agreement with the RHEED data in Fig. 1. The intense bright rows correspond to space between MoSe₂ layers (Se atoms appear dark) whilst Mo atoms relate to the bright dotted rows in between (see also ESI†, Fig. S1b). Fig. 3c shows the same sample imaged along the [1-100]_{AlN} zone axis. Similarly, dark rows correspond to the MoSe₂ layers and bright areas to the space between them. Because of the dense atom configuration along this direction (see also ESI†, Fig. S1c), no atoms are resolved in the dark areas in contrast to Fig. 3b. Figs. 3d and 3e show 2 ML of MoSe₂ grown on top of 5QL epitaxial Bi₂Se₃ buffer and 2ML of MoSe₂ sandwiched between two Bi₂Se₃ layers, 3QL-thick each, respectively. The corresponding image simulation is shown as inset in Fig. 3e (thickness 8.5 nm, defocus -70 nm) in which bright dotted rows correspond to Mo atoms. In summary, the data in Fig. 3 (combined with the RHEED data) show that high quality epitaxial MoSe₂ and MoSe₂/Bi₂Se₃ multilayers can be grown on AlN substrates with flat surface morphology and clean, crystalline interfaces.

A small distortion of AlN just underneath MoSe₂ can be seen in Figs. 3b and 3c. The appearance of an interlayer in the TEM pictures in a first approach could be attributed to an artifact. Ion milling certainly affects this interface preferentially, given the weakness of the van der Waals bonding and the fact that AlN is easily amorphized under the ion beam. In this regard, some interfacial damage is expected during sample preparation. The brighter contrast of the AlN lattice fringes at the interface could be attributed to the locally smaller thickness of the foil due to the preferential thinning mentioned above. Therefore, the interfacial region is not amorphous in the as-grown sample and any amorphization is induced by the ion milling during TEM specimen preparation.

In a closer examination of the interface, we have undertaken detailed measurements of lattice fringe spacings from cross sectional HRTEM images in Fig. 3c. Our measurements, supported by the absorption contrast profile, showed a gradual increase of the (0002) d-spacing between the top 3 or 4 AlN lattice fringes as shown in Fig. 3c. Furthermore, a strain mapping performed using geometrical phase analysis (GPA) (see also ESI†, Fig. S4), showed an increase of up to 20% in the spacing of these fringes. The local increase of the lattice constant could be attributed either to a change in chemical composition, or to elastic strain, or to both. Elastic strain, if present, could even promote the local amorphization of these top layers under ion beam milling. A possible cause for the increase of the d-spacing is the modification of the top 3-4 AlN layers through the incorporation of molybdenum atoms. Mo has a higher electron affinity than Al, and a larger atomic radius. The absorption contrast profile in Fig. 3c shows an increase of the lattice parameter by up to ~20% prior to the MoSe₂ film. Hexagonal molybdenum nitride has a 13% larger lattice constant than AlN.
MoSe along the growth direction, denote the conduction and valence band offsets, respectively. eV/0.1 eV for the MoSe deposited on 3QL Bi analysis. In situ X-ray photoelectron Spectroscopy is applied to both MoSe/AlN and MoSe/BiSe/AlN heterostructures. The binding energies of Mo3d_{5/2} and Se3d_{5/2} core levels for 1ML MoSe deposited directly on AlN(0001) (Fig. 4a, b) are 228.89 eV and 54.51 eV respectively. These values are in good agreement with other reported 18 on thin film and bulk single crystal MoSe. The core level peaks positions and lineshapes indicate that only Mo-Se bonds exist. Therefore, within the detection limit of our XPS it can be inferred that MoSe does not react with the AlN substrate in large quantities. A limited incorporation of Mo in the top 3 layers of AlN may not be excluded though taking into consideration the HRTEM analysis of the image in Fig. 3c as described in the previous section. Similarly, in the case of 1ML MoSe deposited on 3QL BiSe buffer layer on AlN at 300 °C (Fig. 4c, d) the Mo3d_{5/2} peak position at 229.12 eV indicates Mo-Se bond and agrees well with MoSe formation while the Se3d peak is attributed to two contributions, one to Se-Mo bonds and one to Se-Bi bonds. The Bi4f_{7/2} core level binding energy of 158.52 eV (not shown here), indicates that Bi is bonded only with Se and no reaction at BiSe/AlN interface occurs. In addition, using tabulated sensitivity factors the Se/Mo ratios are found to be in the range of (1.9-2.05) indicating that the layers have stoichiometry close to the ideal one that is Se/Mo=2/1.

The band offsets of the MoSe/AlN and MoSe/BiSe/AlN heterostructures were derived from XPS measurements (Fig. 4e, f). In particular, the valence band offsets (VBO) have been determined using Kraut’s method 28 to be 2.84 eV and 2.87 eV/0.1 eV for the MoSe/AlN and Bi2Se3/AlN systems, respectively (see also ESI†). Accordingly, the conduction band offsets (CBO) have been calculated to be 1.81 eV and 2.86 eV/0.98 eV for the MoSe/AlN and Bi2Se3/AlN systems, respectively, using band gap values (see also ESI†) taken from the literature. The estimated CBO and VBO between the MoSe2 and AlN indicate sufficiently high transport barrier for both electrons and holes perpendicular to the layers, implying that the AlN layer could provide sufficient insulation for the operation of MoSe2-based electronic devices with minimum leakage through the substrate. It is worth noting that the XPS reconstructed band alignments are consistent with electron affinity values (see Fig. 4e, f) reported in the literature for AlN, MoSe2, and Bi2Se3 materials 29-31 and the position of the Fermi level E_F with respect to the CB and VB of the layers in the stack, suggesting that there is no band bending or charge transfer at the interfaces.

Electronic band structure of MoSe2 films

Fig. 5 shows the valence band structure of 1 to 6 ML MoSe2 films grown on AlN(0001) substrates as imaged by ARPES in the ΓK plane of the 1st BZ of MoSe2 22,32 using He I (21.22 eV) and He II (40.814 eV) excitation energies. Except for the spin-splitting of the band near K which is not resolved because of limited resolution (~110 meV) at room temperature, in the monolayer limit, the observed band dispersion along Γ-K (Fig. 5a, d) agrees quite well with the theoretical calculations (Fig. 5g). The VB maximum is located at the K-point with a binding energy E_B=1 eV, about (150-200) meV higher in energy than at the Γ point. Comparison with first principles calculations (Fig. 5g), which predict a conduction band minimum also at the K point, indicates that our nominal single layer MoSe2 films have a direct band gap. 9,33,34 As thickness increases to 3ML (Fig. 5b, e) and 6 ML (Fig. 5c, f) the VB maximum switches to the ΓA-point, due to a shift of the topmost valence band to lower binding energies (closer to E_F) around ΓA-point, while its
The small difference between He I and He II data is due to a weak dispersion \( E(\vec{k}_z) \) around the zone center\(^{22,32} \) which is picked up by the different photon excitation energies. As thickness increases, mainly \( Mo \) 4\( d \)\(_2\) orbitals\(^{22,23,32-34} \) contribute to the VBM around the \( \Gamma \)-point through the vdw-interlayer-interaction\(^{33} \) showing its bulk character. On the other hand the topmost VB around \( K \)-point shows negligible thickness dependence due to the \( Mo \) 4\( d \)\(_2\)\( _\perp \)\(_2\) origin.\(^{22,23,32-34} \) The data in Fig. 5 present well resolved spectra characteristic of energy dispersion along the \( \Gamma \)K crystallographic direction in \( k \)-space in agreement with theory. This supports our claim made on the basis of RHEED in Fig. 1 that the films are highly oriented essentially forming a single crystal. If several orientation domains existed, then a more complex and fuzzy dispersion would have been observed in Fig. 5, characteristic of a mixture of dispersions along different crystallographic orientations, which is not the case here.

**Film quality and thickness uniformity by Raman and PL.**

The vibrational modes of the prepared monolayer MoSe\(_2\) film on 200nm AlN(0001)/Si(111) is investigated by Raman spectroscopy. The group theory analysis for bulk TMDs which are members of \( D_{6h} \) point group symmetry,\(^{35} \) predicts four Raman active and two Raman inactive modes. From the active modes only the in plane mode \( E_{2g}^1 \) and the out-of-plane mode \( A_{1g} \) are accessible under the experimental conditions. Additionally, one Raman mode that is inactive in bulk crystals, becomes optically active when the number of layers decreases due to the breakdown of translation symmetry.\(^{15,33} \) This is an interlayer vibrational mode \( B_{2g}^1 \) characterized as breathing mode and is present only in few-layer material and absent in a single layer MoSe\(_2\).

The typical Raman spectrum of single layer MoSe\(_2\) on AlN shown in Fig. 6a, has two intense sharp Raman peaks. One is attributed to the MoSe\(_2\) out-of-plane vibrational mode \( A_{1g} \) at 240.8cm\(^{-1}\) and one to the crystalline Si\(^{35} \) substrate at 521 cm\(^{-1}\). The in-plane \( E_{2g}^1 \) mode of MoSe\(_2\) is located at 288.5 cm\(^{-1}\) (clearly shown in the expanded Raman spectrum in the region of (200-400) cm\(^{-1}\) in Fig. 6d). There is no evidence of the breathing mode \( B_{2g}^2 \) peak around 352 cm\(^{-1}\), an area of the spectrum which is dominated by weak background signals. The bands centered at 303 cm\(^{-1}\) and 960 cm\(^{-1}\) (Fig. 6a) are associated with the 2TA and 2TO modes of crystalline Si.\(^{36} \)

From the peak positions of the Raman shifts and their intensities it is difficult to distinguish between monolayer and bilayer MoSe\(_2\). However, most of the evidence in this work is in favor of monolayer MoSe\(_2\) and it is in good agreement with published data of monolayer MoSe\(_2\) either transferred\(^{15,37} \) or grown\(^{5,17,38} \) on SiO\(_2\)/Si substrates. The intensity ratio between out-of-plane \( A_{1g} \) and in-plane \( E_{2g}^1 \) modes (\( A_{1g} / E_{2g}^1 \)) is found to be ~ 23, in agreement with published values for exfoliated single layer MoSe\(_2\).\(^{37,39} \) In addition, the weak or totally absent breathing mode (Fig. 6d) points to single layer MoSe\(_2\) material.

Fig. 5 Valence band structure imaging by ARPES of (1 to 6ML) MoSe\(_2\) layers grown on AlN(0001) substrates along the \( \Gamma \)/A-K/H direction of the 1\(^{st} \) BZ of MoSe\(_2\). Measurements made at RT, using (a-c) He I (21.22 eV) and (d-f) He II (40.814 eV) resonance radiations. The images in (a-f) show the binding energy as a function of the wavevector component \( k_{\perp} \) parallel to the surface. In the monolayer limit (a, d) the VBM is located at the \( K \)-point at \( E_\beta=1 \) eV indicating a direct band gap. In thicker films, at 3ML (b, e) and 6ML (c, f) the VBM is located at the \( \Gamma \)-point which is consistent with an indirect band gap. Among He I and He II data at 3ML (b, e) and 6ML (c, f) films, small differences in the band structure around the \( \Gamma \)-point are observed. This is attributed to a small \( E(\vec{k}_z) \) dispersion around the \( \Gamma \)-point. Red solid lines indicate the \( E_\beta \) level position, while orange dashed lines indicate the position of VBM at \( K \)/A point. (g) First principle calculated band structure of 1ML. The red arrow indicate the direct band gap position, (h) the first Brillouin zone of 2H structure of MoSe\(_2\).
Fig. 6 (a-c) Characterization of nominally single layer MoSe$_2$ on AlN(0001) (a) Raman spectrum showing the $A_{1g}$ peak at 240.8 cm$^{-1}$ associated with MoSe$_2$. (b) Photoluminescence spectrum showing the presence of two excitonic peaks at 1.55 eV and 1.75 eV (c) schematic detail of theoretical band structure around the K-point of 1 ML MoSe$_2$, indicating the two excitonic transitions A and B with 190meV energy difference due to spin-orbit splitting. The theoretically predicted energy difference is in good agreement with the measured PL peaks energy difference in (b). (d-f) Large scale uniformity investigation of (2x2) cm$^2$ sample of the same MoSe$_2$ sample on AlN(0001). (d) Raman spectra and (e) photoluminescence spectra measured at variable distances from sample edge. (f) Correlation of Raman and PL peaks intensities measured at variable distances from sample edge. On large scale area two different behaviors are observed. The high Raman signal of $A_{1g}$ peak is correlated to the low PL intensity of exciton A and vice versa.

Photoluminescence spectroscopy was used to investigate optical emission properties of monolayer MoSe$_2$ grown on AlN with the main aim to probe the quality of the layer and verify that the material has a direct band gap as indicated by in-situ ARPES. The epitaxially-grown single-layer MoSe$_2$ on AlN presents strong PL emission at room temperature, as shown in Fig. 6b, with a dominant peak at 1.55 eV and a weaker peak at 1.75 eV, attributed to direct excitonic transitions A and B, respectively, corresponding to the transitions schematically shown in Fig. 6c. Due to loss of inversion symmetry in monolayer MoSe$_2$, the VB degeneracy is lifted$^{19,40}$ under the influence of strong spin-orbit interaction resulting in the VB splitting near the K-point as predicted by DFT (Fig. 6c) and probed by PL (Fig. 6b). The measured energy difference of ~200meV between the two PL signals, agree very well with the calculated spin-orbit splitting of ~190 meV in Fig. 6c as well as with published experimental$^{15}$ and theoretical values.$^{40}$ The strong PL signal in Fig. 6b indicates direct gap material in accordance with the nominally 1 ML thickness of the grown MoSe$_2$, although the possibility to obtain similar double peak PL at the same energy from a bilayer MoSe$_2$ cannot be excluded.

To extract information about uniformity in terms of structural and optical properties, the sample is probed over the entire 2 cm square substrates. At short scale, in an area of (40 x 40) µm$^2$, a highly uniform layer in terms of Raman $A_{1g}$ peak intensity, width and position is revealed (see also ESI†, Fig. S5). In general, Raman selection rule does not exclude a dependence of the Raman peak intensities on the crystal orientation which should reflect in the polarization of the scattered light. However, the Raman experimental set-up used here does not have an analyzer so the detection system lacks sensitivity with respect to the polarization of the scattered radiation from the sample. Therefore, the peak intensities do not depend on the crystal orientation as verified by arbitrarily rotating the sample (not shown here). Given the insensitivity of the different Raman peaks to crystal orientation, the intensity ratio between $A_{1g}$ and $E_{2g}^1$ is an appropriate parameter for an accurate uniformity assessment of the MoSe$_2$ film. Since the $E_{2g}^1$ peak is small and overlaps with a nearby Si peak, both peaks are fitted simultaneously and the height of the $E_{2g}^1$ peak is extracted. An example of a $E_{2g}^1$ fitting result is given in Fig. S5. It is clear that the $A_{1g} / E_{2g}^1$ Raman mapping (see also ESI†, Fig. S5) indicates a uniform MoSe$_2$ layer over a 40 x40 µm$^2$ area with an average value of $A_{1g} / E_{2g}^1$ ratio of ~23, indicative of monolayer MoSe$_2$.$^{37}$

On a larger scale, the sample is probed along a line which runs across the substrate from one edge to the other with 200 µm steps and the results are summarized in Figs 6d, e. Although the sample is very uniform over large areas, the data show a remarkable “digital” behavior mainly revealed in the Raman
spectra (Fig. 6d). The Raman $A_{1g}$ mode acquires either low or high values but no values in between. The PL (Fig. 6e) follows a similar behavior although with a larger dispersion in intensity. However, correlation with the Raman peak is observed: the PL intensity is high where the Raman intensity of $A_{1g}$ is low and vice versa (Fig. 6f), a behavior which is not fully understood. Based on previous PL work on MoS$_2$ 
and Bi$_2$Se$_3$ it is tempting to associate the low Raman/high PL behavior with the presence of single layer MoSe$_2$ areas and the high Raman/low PL one with bi-layer MoSe$_2$ in other areas on the same wafer. This has to be treated with caution though given that an abnormally high PL at room temperature has been reported in few-layer MoSe$_2$. Finally it is worth noting that uncapped single and bi-layer MoSe$_2$ have been examined by Raman and PL over a period of time and they have been found to be very stable over at least two weeks while exposed to air (see also ESI†, Fig. S6).

Critical assessment of microstructure and uniformity

The characterization of large area MoSe$_2$ films is very challenging because most of the techniques which are sensitive to microstructure such as HRTEM are sampling techniques probing only a limited area of the order of (80-100) nm in length. In such length scale, the single crystal quality and thickness uniformity is unambiguously confirmed (Fig. 3) in several sampled areas on the wafer. Low magnification TEM can provide information about thickness uniformity in the few hundred nm scale as for example the TEM image in Fig. S7 (ESI†) which shows a very good thickness uniformity of MoSe$_2$ over a region that exceeds 250 nm in length. Other techniques, such as STXM or SEM probe larger areas in the few tens of a micron- or mm- scale and by using these techniques (see also ESI†, Figs. S2 and S3) we conclude that the films are continuous with full coverage over the entire 2 inch diagonal substrates and that there are no major thickness variations across the wafer. However these techniques are less sensitive to thickness variations at the level of a single atomic layer and to the existence of microstructure such as grains.

Orientational grain boundaries (GB) retain a crystalline structure and may be of high or low angle. In this case, the pertinent high angle GBs are the orientation twins that have not been identified in our films by RHEED as already discussed above in connection to Fig. 1. The cross sectional HRTEM observations are also consistent, i.e. no twin boundaries were observed.

Regarding low-angle GBs, plan view TEM observations are required. The preparation of such TEM specimens is difficult due to the AlN substrate which renders useless the currently available approaches. Although it was not possible to account for such GBs from plan view TEM, we argue that, if they are present to any significant extent, such GBs would consist of dislocations parallel to the growth direction. In our cross section observations we did not observe any appreciable density of such defects.

The characterization and uniformity assessment of ultrathin (a few ML) MoSe$_2$ films remain big challenges. In fact, most of the techniques, including XRD, are not sensitive when applied to atomic scale materials. Raman is a technique which has sufficient sensitivity for single layer crystals and is extensively use for graphene and 2D MX$_2$-type semiconductors. This provides a rough estimate about thickness and physical properties with micron resolution probing uniformity over a (10-100) µm scale at least. The MoSe$_2$ films mapped by Raman over such a range were found to have excellent uniformity, while the same tests repeated in several parts of the wafer yield similar excellent uniformity results.

In summary, despite the difficulties in the characterization of ultrathin films on a large area of the substrate, our investigation using a variety of techniques provide evidence that the films are continuous, covering the entire substrate and that they do not have gross non-uniformities with respect to the thickness and the surface roughness. Moreover, electron diffraction (RHEED) and HRTEM show no evidence for randomly oriented grains or for high (twin) or low angle orientational grains suggesting highly oriented single crystal films epitaxially grown on cm-scale AlN substrates.

Conclusions

In summary, we demonstrate the molecular beam epitaxial growth of large area, highly oriented single crystals of controllable single to few- layer MoSe$_2$ films on AlN/Si(0001)/Si substrates. We show by HRTEM that MoSe$_2$ films on AlN/Si(0001) have high structural quality and surface and interface morphology confirmed also by XPS data showing stoichiometric MoSe$_2$ with no reaction at the interface with AlN. In addition, very good uniformity and excellent stability in air is evidenced by room temperature Raman and photoluminescence. We also show that MoSe$_2$ can grow with very good quality on Bi$_2$Se$_3$ buffer layers and that epitaxial Bi$_2$Se$_3$/MoSe$_2$ multilayers can be produced. As a final remark, it is emphasized here the important role of the substrate. Since AlN is a wide band gap material, it offers the benefits of MoSe$_2$ semiconductor-on-insulator integration scheme creating the prospect for low leakage through the substrate and improved electrostatic control. This is further supported by XPS analysis which indicates sufficiently high CBO and VBO acting as barriers for charge transport through the substrate. Moreover, AlN/Si(111) large area (200 mm and 300 mm) wafers are readily available as they have been developed for several years in the context of III-nitride power and lighting devices. Once high quality epitaxial MoSe$_2$ is prepared on 300 mm AlN/Si wafers, devices and circuits can be realized on the same wafers, or the MoSe$_2$ layer can be transferred onto other optimal large area substrates of choice, including flexible or transparent substrates for further device processing. Therefore AlN/Si creates the prospect for low cost wafer-scale manufacturing of MoSe$_2$-based devices and circuits when TMD technology becomes mature enough for volume production.

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Notes and references

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