Electronic structure of quasi free 2 dimensional HfS$_2$ clusters

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Cluster research so far only dealt with either 3D free clusters or clusters on substrates with strong electronic coupling at the interface. Preparation of free and orientated 2D clusters is usually not possible because one of these conditions generally excludes the other. We demonstrate a new way to grow 2D clusters of transition metal dichalcogenides which are only weakly bound to the substrate, i.e. quasi free, but all show the same orientation thus allowing angle resolved photoemission experiments. In combination with scanning tunneling microscopy this provides for the first time the possibility to investigate the correlation between the size of quasi free 2D clusters and its associated electronic structure. For 2D HfS$_2$ clusters grown by van der Waals epitaxy we demonstrate that $k_{\parallel}$–dispersion of electronic states already occurs for cluster diameters above $\sim$100 nm.

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In the last decade there was a growing interest in the geometric and electronic properties of clusters. Especially, fundamental properties as band gaps or melting points depend strongly on the cluster size. According to Alivisatos in the course of growing cluster size first the formation of the centers of the electronic bands can be observed which coincide with the corresponding atomic levels and afterwards the development of the band edges. With further increasing cluster size the investigation of the formation of the momentum-resolved electronic structure of intrinsic clusters is challenged. Employing angle resolved photoemission spectroscopy two conditions need to be satisfied: (i) The clusters must be quasi free and independent of the substrate to retain their intrinsic properties and (ii) because of spatial averaging they have to have the same orientation to allow momentum-resolved measurements. In general one of these conditions excludes the other and vice versa. So far free clusters could only be prepared in three or zero dimensions. Flying "disks" (2D) or "wires" (1D) have not been reported. Oriented clusters of such dimension have been prepared on surfaces of a number of preferably covalently bonded bulk crystalline materials (see e.g. ref. 3). However, strong bonding between cluster and substrate together with additional dangling bond surface states on the cluster surface complicate the investigation of intrinsic properties of the cluster itself.

In this paper we utilize the extremely weak van der Waals forces between sandwiches of quasi two dimensional layered transition metal dichalcogenides (TMDC) to prepare quasi free 2D HfS$_2$ clusters. Extremely flat WSe$_2$ surfaces serve as ideal substrates to study intrinsic properties of the clusters independent of the underlying material. Crystal structures of layered TMDC’s are characterized by hexagonal metal layers sandwiched between chalcogen sheets. While inside one sandwich layer strong ionic and covalent bonding predominates, weak van der Waals forces act between the layers allowing heteroepitaxy of layered materials almost independently of the actual lattice mismatch. In addition, no dangling bond type surface states have been observed on these surfaces. The weak interaction between the sandwich layers is responsible for the small dispersion of the electronic states in normal direction of layered materials. Van der Waals epitaxy (vdWE) is applied here to grow HfS$_2$ clusters on WSe$_2$. Employing angle resolved photoemission spectroscopy in combination with scanning tunneling microscopy we focus on the development of the dispersion $E(k_{\parallel})$ of electronic states parallel to the surface with increasing cluster size.

All experiments were carried out in an ultrahigh vacuum (UHV) system (base pressure $10^{-10}$ mbar) consisting of chambers for (i) van der Waals epitaxy (vdWE), (ii) angle resolved photoemission spectroscopy (ARPES), (iii) scanning tunneling microscopy (STM), and (iv) low energy electron diffraction (LEED), all connected by an UHV transfer system.

HfS$_2$ clusters were grown by coevaporation of hafnium and sulfur from different sources. The hafnium beam was generated by an electron beam evaporator with an integrated flux monitor permitting direct control of the hafnium flux during epitaxy. Sulfur was evaporated from a Knudsen cell by heating pyrite (FeS$_2$) to about 400$^\circ$C. The corresponding partial pressure of sulfur was $p_{\text{S}} = 1 \times 10^{-9}$ mbar. Substrate temperatures $T_S$ were chosen between 300 and 400$^\circ$C. The 2H–WSe$_2$ substrates and 1T–HfS$_2$ crystals used as substrate and reference material, respectively, were grown by chemical vapor transport using iodine as transport agent. All substrates were air cleaved and annealed at 450$^\circ$C for two hours to obtain smooth and clean surfaces.

Angle resolved photoemission spectra were taken with a Helium discharge lamp ($\text{HeI, radiation, } h\nu = 21.22$ eV). Electrons were detected by a 180$^\circ$ spherical analyzer (energy resolution $\Delta E = 65$ meV) mounted on a two axes goniometer (angle resolution $\Delta \vartheta < 0.25^\circ$). The STM consists of a single tube scanner system mounted on a self developed vibration damping with an eddy current attenuation. Coverages were determined by count-
ing the pixels in STM images that belong to either HfS$_2$ clusters or the substrate.

In fig. 1 we show a series of combined normal emission photoelectron and scanning tunneling microscopy data in different phases of HfS$_2$ growth on bulk WSe$_2$. (The middle panel shows difference spectra obtained by subtracting a normalized clean WSe$_2$ spectrum from data shown in the left panel. For comparison the differences are hatched in the left panel.) At the bottom a normal emission photoelectron spectrum of the cleaved WSe$_2$ substrate exhibiting the characteristic valence band emission peaks and the corresponding STM image and LEED pattern are plotted. Upon initial stages of growth the STM image for a coverage of 52% of a monolayer (ML) HfS$_2$ reveals small irregularly shaped clusters with typical diameters of about 50 nm. The corresponding photoemission spectrum is still being mainly attributable to emissions of the WSe$_2$ substrate. With increasing cluster size up to a coverage of 87% the upper valence band peak A corresponding to WSe$_2$ is still visible while peak B is covered by a new structure which can be related to the HfS$_2$ emission feature R (compare top panel). At 92% coverage with respect to the first monolayer peak A still appears as a weak shoulder. For coverages beyond one monolayer (STM image at the top) the photoemission spectrum reveals the significant structures of pure HfS$_2$. For comparison see the spectrum of a cleaved HfS$_2$ crystal shown at the top. In the spectra the peaks of the WSe$_2$ substrate are broadened in the course of the epitaxial growth. Especially, WSe$_2$ emission A shows this behavior.

Just like the photoemission spectrum at 80% coverage in the first monolayer the corresponding LEED image consists of a composition of both HfS$_2$ and WSe$_2$ contributions: Two hexagonal patterns are superimposed with the outer pattern belonging to WSe$_2$ because of its smaller lattice parameter (a$_{WSe_2}$ = 3.286 Å, a$_{HfS_2}$ = 3.635 Å). It should be noted that the 2D clusters grow with the same lattice parameters parallel to the surface as bulk HfS$_2$. The alignment of the HfS$_2$ with the WSe$_2$ pattern demonstrates that the HfS$_2$ clusters have the same crystallographic orientation as the substrate lattice. This has also been observed for several other heterojunctions (e.g. GaSe growth on WSe$_2$ and InSe(GaSe) growth on GaSe(InSe)). The alignment offers the possibility to examine the k$_z$-dispersion of the electronic structure of quasi free 2D HfS$_2$ clusters as will be discussed later.

Note that in the submonolayer regime the photoelectron spectra of the HfS$_2$ clusters are superimposed by WSe$_2$ substrate contributions and, especially, at small coverages are hardly noticeable. In order to examine the electronic structure of the HfS$_2$ clusters in more detail, the HfS$_2$ overlayer spectrum has to be separated from the substrate features. Since the HfS$_2$ clusters are only bound by weak van der Waals forces they may be viewed as nearly independent of the substrate. This justifies subtractions of the pure WSe$_2$ spectrum to separate spectral contributions of clusters and substrate.

WSe$_2$ emission A ($\vartheta = 0^\circ$) is located in the band gap of HfS$_2$ and is only weakened by the HfS$_2$ clusters but not superimposed by HfS$_2$ emissions. Consequently, it remains discernable up to coverages of more than one monolayer. This provides the possibility to estimate the contribution of the WSe$_2$ substrate to the photoelectron spectra of both, clusters and substrates. For each coverage we compared the area under peak A before and after deposition of the HfS$_2$ clusters and thus considered relative height and broadening of the substrate spectrum to obtain a normalized WSe$_2$ spectrum. Subtracting this normalized spectrum from the combined HfS$_2$/WSe$_2$ spectra results in the difference spectra shown in fig. 1 (middle panel). This analysis yields further details on the electronic structure of the clusters. While the HfS$_2$/WSe$_2$ spectrum at 72% coverage is dominated by substrate contributions, the difference spectrum already reveals the weak contributions of the HfS$_2$ clusters. For higher coverages the difference spectrum resembles the HfS$_2$ bulk spectrum more clearly than the HfS$_2$/WSe$_2$ spectrum.

Following the combined characterization of the geometric and electronic features of the HfS$_2$ clusters we will now investigate the electronic structure of the clusters parallel to the surface. Fig. 2(a) and (b) show the change of the photoemission spectra with increasing cluster sizes and final formation of a complete monolayer at two off normal emission angles ($\vartheta = 20^\circ$, $\vartheta = 38^\circ$) along the ΓK(AH) direction of the Brillouin zone (left panels). As in fig. 1 the corresponding difference spectra are plotted in the right panels.

In line with the results in normal direction at 72% coverage (650 K substrate temperature) corresponding to cluster diameters of approximately 100 nm (see fig. 1) new structural features appear which in the case of $\vartheta = 38^\circ$ can be attributed to the HfS$_2$ emission feature S. This is further corroborated for cluster formation at 600 K substrate temperature. At a coverage of 80% typical cluster sizes are comparable to those observed for 72% coverage at 650 K while shapes of the latter are smoother because of the higher substrate temperature. The photoemission ratio clusters to substrate is higher in this case because of the higher coverage and spectral features corresponding to the clusters can be separated more clearly. At 80% coverage the characteristic emission features of HfS$_2$ R,S,T,U, and V emerge and a distinct change in the density of states for the three polar angles $\vartheta$ is observable (see fig. 2). Fig. 2(a) shows the photoemission spectra of cleaved bulk HfS$_2$ in ΓK(AH) direction where the spectra for $\vartheta = 0^\circ$, $\vartheta = 20^\circ$, and $\vartheta = 38^\circ$ are replaced by the difference spectra of van der Waals epitaxially grown HfS$_2$ at 80% coverage. They qualitatively well describe the band dispersion along ΓK(AH). This demonstrates that the main HfS$_2$ spectral features are developed revealing k$_z$-dispersion of the electronic states even for cluster diameters of about 100 nm.
Although the photoelectron spectra of the van der Waals epitaxially grown films resemble those of bulk HfS$_2$ well, slight but intriguing differences exist. At $\vartheta = 38^\circ$ especially emission S is shifted towards lower binding energies demonstrating less pronounced $k_\parallel$-dispersion of the bandstructure in clusters as compared to bulk HfS$_2$. Further differences between epitaxially grown and cleaved bulk HfS$_2$ become obvious by comparing relative peak positions in normal emission photoelectron spectra. Fig. 3(b) shows photoemission spectra of bulk HfS$_2$ and 3 monolayers HfS$_2$ on WSe$_2$. The epitaxial HfS$_2$ emission features are broadened and, in particular, a distinct deviation in the relative energy position of the peaks occurs (fig. 3(b)). Peak R of 3 monolayers HfS$_2$ shows almost the same binding energy as the corresponding peak R of bulk HfS$_2$. However, emissions U and T of the epilayer spectrum are shifted by 350 meV towards lower binding energies with respect to the bulk crystal.

This modified electronic structure may be caused by the spatial restriction of the wave function of the 2D HfS$_2$ clusters. In parallel direction the wave functions are limited by the cluster boundaries. Dangling bonds at these boundaries may lead to additional edge derived electronic states. Perpendicular to the layers the thickness of 3 monolayers is still insufficient to build up a dispersive $k_\parallel$ band structure.

In conclusion, applying van der Waals epitaxial growth of layered transition metal dichalcogenides we prepared quasi free two dimensional clusters of HfS$_2$ on WSe$_2$ substrates. Weak van der Waals bonding between cluster and substrate allowed an investigation of the dispersion of electronic states with increasing cluster size independent of the substrate. At initial stages of growth the clusters are irregularly shaped rounding off with increasing cluster size and finally forming complete monolayers. Due to orientational order of the clusters in the submonolayer regime angle resolved photoemission experiments were possible. The spectra exhibit an onset of dispersion of electronic states already for typical cluster sizes of about 100 nm as characterized by STM. This highlights the necessity of orientating quasi free two dimensional clusters on van der Waals surfaces to properly perform $k$-resolved measurements of the electronic structure of two dimensional clusters as far as combined angle and spatial resolving instruments are not available.

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FIG. 1. Photoemission data (h\nu=21.22 eV, normal emission, k_\parallel = 0) (left panel), difference spectra obtained by subtracting a normalized clean WSe_2 spectrum (middle panel), and scanning tunneling microscopy data with LEED images as inset (E_{kin} =100–150 eV) (right panel) showing the transition from the clean WSe_2 substrate to the grown HfS_2 overlayer. Bottom: Photoemission spectrum of the substrate (cleaved and annealed WSe_2) and corresponding STM image (horizontal size 9 nm). Upward increasing coverage with HfS_2: photoemission spectra and STM images of the same samples (horizontal size 150 nm). Coverages are given with respect to one nominal monolayer (100%). Top: spectrum of cleaved HfS_2 for reference. Substrate temperatures were 650 K (52%,72%) and 600 K (80%–3ML), respectively.

FIG. 2. Photoelectron spectra of HfS_2/WSe_2 for increasing coverage at two different polar angles \vartheta in \Gamma K(AH) direction ((a) \vartheta = 20^\circ, (b) \vartheta = 38^\circ, left panel respectively) in comparison to the corresponding spectra of cleaved HfS_2 on top (h\nu = 21.22 eV, \Delta E = 65 meV). (a) and (b), right panels: difference spectra obtained by subtracting a normalized WSe_2 spectrum.

FIG. 3. (a) Photoelectron spectra (h\nu = 21.22 eV, \Delta E = 65 meV) in \Gamma K(AH) direction of cleaved bulk HfS_2 containing the difference spectra of quasi free 2D free HfS_2 clusters on WSe_2 (bold dots, marked by arrows). Typical cluster diameters are \sim 100 nm (80 % coverage) (b) photoemission spectra of cleaved bulk HfS_2 (top) and 3 monolayers HfS_2 on WSe_2 (bottom): relative peak positions are compared.
This figure "FIG1.JPG" is available in "JPG" format from:

http://arxiv.org/ps/cond-mat/9909411v1
