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Highly oriented layers of the three-dimensional semiconductor CdTe on the two-dimensional layered semiconductors MoTe₂ and WSe₂

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The II–VI semiconductor CdTe was sequentially deposited onto the (0001) van der Waals surfaces of the layered compound semiconductors MoTe₂ and WSe₂ by molecular beam epitaxy. Growth could only be achieved after deposition of a nucleation layer of CdTe at room temperature. After nucleation subsequent deposition steps followed at increased substrate temperatures ($T=170\text{--}370\text{ }^\circ\text{C}$) in order to increase the crystalline quality of the films. The deposited films were investigated after each growth step by low energy electron diffraction and photoelectron spectroscopy. The diffraction pattern indicates a faceting of the (111) oriented film surfaces. From photoemission data we exclude interface reactions between substrate and film material. Transmission electron microscopy was used to examine the film morphology after the UHV experiments. The mean diameter of the film crystallites is 200–400 Å. © 1996 American Institute of Physics. [S0021-8979(96)02422-X]

I. INTRODUCTION

In recent years considerable efforts have been devoted to the growth of dissimilar materials one on another. In semiconductor technology this is stimulated by the promising properties of novel heterojunction devices.¹ Electronic properties of the devices strongly depend on the atomic and structural arrangement at the interface. Chemically reacted phases, dangling bonds, and structural defects may considerably deviate the properties of the real device from those which had been expected from the ideal interface. Such interface problems are the limiting factors for a large number of principally interesting material combinations.² Only recently a novel concept called van der Waals epitaxy (vdWE) emerged, which may help to overcome the intricate structural problems of mismatched heterointerfaces. The initial idea of Koma and co-workers^{3–6} was later taken up by other groups.^{7–13}

The concept of vdWE is based on the preparation of heterointerfaces which are interconnected with at least one van der Waals surface present at the interface. van der Waals surfaces are naturally exhibited by materials with layered crystal structure (i.e., pronounced two-dimensional, therefore referred to as 2D), as mica, graphite, and a number of transition metal dichalcogenides; they are chemical inert and free of dangling bonds. Therefore no strong structural coupling is mediated across the interface, and it could be shown that epitaxial films without interface strain can be grown even with mismatches up to 50%. However, until recently the reported experiments on the growth of heterojunctions by vdWE were confined to the growth of a layered material on top of other layered materials or on hexagonally close packed (111) surfaces of Si and GaAs. Deposition of three-dimensional (3D) materials onto layered substrates was carried out only in few experiments so far.^{14,15} But for a pos-

sible use of vdWE buffer layers between mismatched heterointerfaces of 3D semiconductors, the epitaxial growth of 3D material on a layered substrate must be achieved.

In the experiment to be reported here CdTe was deposited on the layered compounds MoTe₂ and WSe₂. Lattice parameters are compiled in Table I. With the expression $m=(a_f-a_s)/a_s$ for the lattice mismatch we derive for the interface between the (0001) layered compound and (111) zinc blende in-plane mismatches of $m=30\%$ and 40% for CdTe/MoTe₂ and CdTe/WSe₂, respectively. The growth of the CdTe layer and structural properties of the film was *in situ* studied by low energy electron diffraction and photoelectron spectroscopy. The structural studies were completed by *ex situ* transmission electron microscopy results.

II. EXPERIMENT

The experiments were performed in a commercial ultrahigh-vacuum chamber (UHV, base pressure 3×10^{-11} mbar) equipped with an angular resolving hemispherical photoelectron spectrometer (VG ADES 500) and a three grid low energy electron diffraction optic (VG). The chamber was connected to the TGM 7 beamline at the electron storage ring BESSY in Berlin. Photon energies between 15 and 120 eV were available as the excitation source. The combined resolution of the monochromator and the analyzer has been determined from gaussian broadening of a metallic Fermi edge to be 420 meV at 80 eV excitation energy.

The substrates MoTe₂ and WSe₂ were grown by chemical vapor transport, with Cl₂ and Br₂ as transport agents. The samples were cleaved in air, clamped to the Cu-sample holder with a tantalum mask and via a fast entry lock transferred into the vacuum chamber. In UHV the samples were heated to 470 °C for 5 min in order to remove residual surfaces contamination. During the cleaning cycle the chamber pressure was below 1×10^{-8} mbar. The soft x-ray photoemission spectra (SXPS) and electron diffraction pattern [low energy electron diffraction (LEED)] of the cleaved surface

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TABLE I. Compilation of structural data of the layered substrate materials MoTe₂ and WSe₂ and the film material CdTe.

	MoTe ₂	WSe ₂	CdTe
Structure	P6 ₃ /mmc	P6 ₃ /mmc	F43m
a[Å]	3.522	3.286	6.482
c[Å]	2×6.984	2×6.488	

agree to those obtained from cleaved surfaces of such crystals. CdTe was sublimated from a home made evaporation cell, which was charged with ultraclean CdTe powder. The nominal CdTe fluxes were monitored with a water cooled quartz microbalance.

After finishing the UHV experiments the films were examined *ex situ* with a high resolution transmission electron microscope (TEM, Phillips CM 12, acceleration voltage 120 kV). Pictures were digitally recorded with a VME200A Slow Scan charge coupled device camera (1024×1024 pixels).

III. RESULTS

A. Film growth

Prior to deposition the substrates were investigated by SXPS. They showed the well known valence band and core level emission features from clean and high quality surfaces of WSe₂ and MoTe₂. The substrate LEED pattern is a hexagonally ordered array of sharp spots.

First deposition steps were attempted under growth conditions known to yield high quality epitaxial films of CdTe,¹⁶ i.e., substrate temperatures between 200 and 300 °C at deposition rates of about 10 Å/min. Even after extended exposure of CdTe, i.e., nominal deposit above several hundred Å, we could not detect the characteristic CdTe photoemission lines on the (0001) surfaces of the layered compounds. Evidently the sticking coefficient of the 3D material on the van der Waals plane is close to zero due to the weak substrate/adsorbate interaction. This finding is in qualitative agreement with other adsorbates as certain metals and molecular adsorbates.¹⁷

1. Low temperature deposition step of CdTe on the layered substrates

Adsorption of Cd and Te could only be achieved on substrates held at room temperature, with a particle flux still of 10 Å/min. The characteristic emission lines were then monitored by SXPS; see Figs. 1 and 2. An estimate of the sticking coefficient from the relative film and substrate core level intensities and the known particle flux gives a value of ≈0.1–0.3.

In all further experiments, therefore, a deposition step of a few Å of CdTe was carried out on substrates held at room temperature. The total amount of the offered film material was adjusted such that substrate core level emissions were only slightly reduced, i.e., the deposited film was not closed. On the other hand, enough film material had to be deposited in order to allow for subsequent film growth at higher temperatures. If too low an amount had been deposited in this step the film growth proceeded extremely slowly by subsequent deposition at increased substrate temperatures; see be-

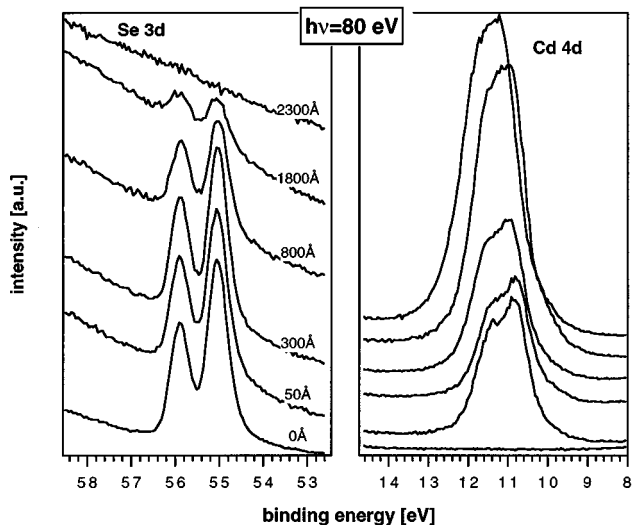


FIG. 1. CdTe/WSe₂ photoemission core level spectra of Se 3d substrate and Cd 4d film taken at an excitation energy of 80 eV. Spectra are normalized with respect to the incoming photon flux. The thickness tags at the spectra refer to the flux the surface had been exposed to. No evidence for chemical interface reactions are observed.

low. Complete film growth at room temperature was not undertaken because the crystalline quality of such a film is expected to be poor.

2. Subsequent deposition at elevated substrate temperatures

In order to obtain CdTe films with good structural quality the subsequent growth was continued at substrate temperatures between 170 and 350 °C. Upon heating the CdTe covered surfaces to temperatures above 250 °C the core level photoemission intensities of the film material was reduced,

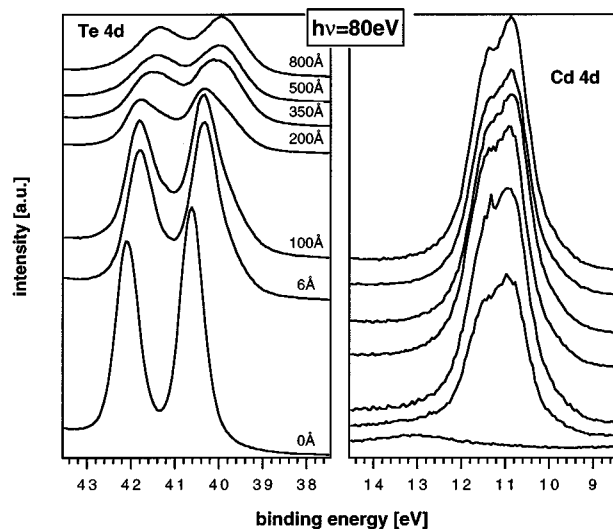


FIG. 2. CdTe/MoTe₂ photoemission core level spectra of substrate and film at an excitation energy of 80 eV. Spectra are normalized with respect to the incoming photon flux. The sharp Te 4d emission line from the MoTe₂ substrate becomes gradually exchanged by the slightly broader Te 4d line from the CdTe film. Deconvolution of the spectra, as well as the spectral shape of the Cd 4d line, gives no evidence for chemical interface reactions.

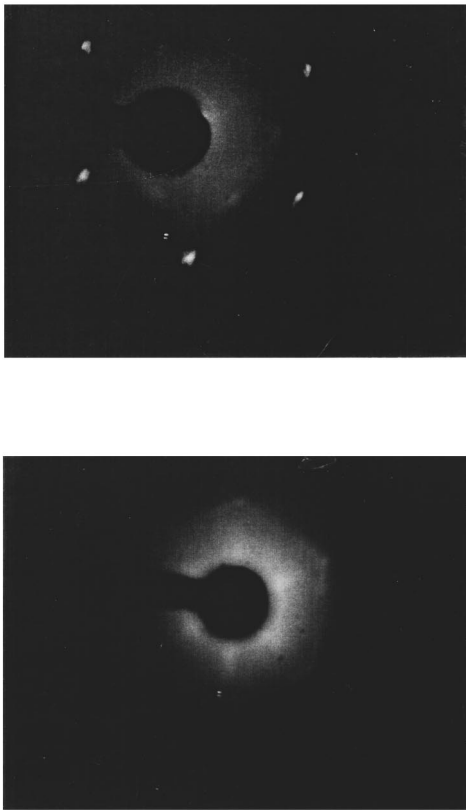


FIG. 3. LEED pattern obtained from the system CdTe/WSe₂ at (a) low nominal surface coverage (≈ 600 Å) and (b) from the closed CdTe film (≈ 2000 Å).

indicating either a desorption or clustering of the surface adlayer. In these cases the amount of film material to be deposited until the substrate core level emission lines were completely attenuated, i.e., until the film is completely closed, had to be increased drastically (up to several thousand Å). To obtain films at a reasonable growth rate we carried out most of our experiments at substrate temperatures of about 170 °C.

B. Film surface structure

We shall only give a schematic description of the film surface structure since the electron diffraction patterns obtained are rather poor. Two LEED patterns of CdTe on WSe₂ are depicted in Fig. 3. In Fig. 3(a) the sharp outermost spots are from the substrate due to partly uncovered substrate areas. Faint extra spots caused by the CdTe overlayer are observable. The overlayer pattern reproduces the hexagonal array of the substrate pattern indicating thereby a (111) orientation of the film surface. At this stage of the film formation most of the substrate is still not covered by the CdTe. Upon further film growth the substrate pattern gets attenuated and finally vanishes completely. The residual diffraction pattern exclusively stems from the CdTe film.

The surface mesh of the overlayer main diffraction spots exhibits a ratio of $\approx 38\%$ to the substrate mesh. This value is in good correspondence to the expected ratio of 40% given by the a axis of the substrate and $\langle 011 \rangle$ axis of the CdTe

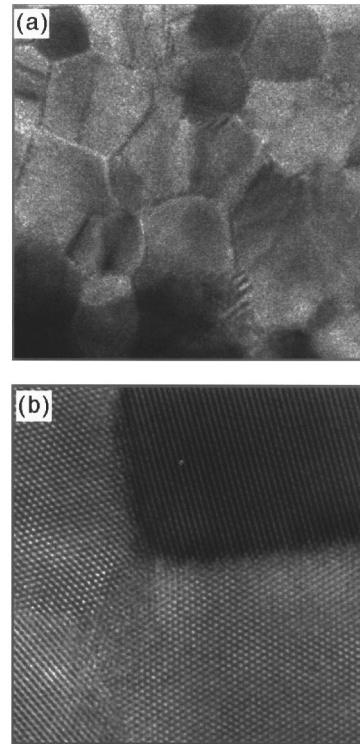


FIG. 4. TEM micrograph obtained from a CdTe film drawn from a WSe₂ surface. (a) A multitude of straight edged crystallites is observed. The mean diameter of the crystallites is around 200 Å. (b) Single atomic rows are resolved, reproducing the hexagonal order of the (111) surface.

overlayer. In addition, weak half-order spots of the CdTe film can be identified. The resulting (2×2) superstructure is well known for the polar (111) surfaces of zinc blende type semiconductors.¹⁸ It is formed to reduce the dipolar charging of the polar surfaces. We are not able to conclude from the LEED data the orientation of the overlayer film. A detailed analysis of the band lineup and the sample work function, which will be published elsewhere,¹⁹ suggests that the CdTe film grows with the Cd layer oriented to the substrate and the Te layer towards the vacuum. The diffraction spots are rather streaky. By changing the electron energy the streaks shift between the cornerpoints of the hexagonally ordered pattern thus indicating a faceting of the film surface.

On MoTe₂ substrates the films behave in a qualitatively similar manner. However, the obtained LEED diffraction spots of the CdTe are clearly observable but less defined on an increased diffuse background.

C. Film morphology by TEM

After the UHV experiments the films were torn off from the layered substrates and deposited without further treatment on a C-grid sample holder of the TEM. This preparation allows only for an observation of the films perpendicular to the film plane. Morphology and crystallite sizes of the films were investigated. In Fig. 4(a) TEM micrograph is depicted as obtained from a CdTe film grown on WSe₂. The CdTe film consists of a polycrystalline layer. The average shape of the crystallites is close to a honey comb with a mean diameter of 200 Å. In most cases the grain boundaries

are line segments enclosing 120° angles. In a higher resolution micrograph Fig. 4(b) single atomic rows are observed. The hexagonal order of the atomic rows as well as the diffraction pattern refer to the $\langle 111 \rangle$ orientation of the films.

IV. DISCUSSION

The adsorption behavior of CdTe on the layered surfaces corresponds to that of CdS on the same materials investigated earlier.²⁰ Deposition of the II–VI material on the layered substrates is not possible at temperatures known to yield epilayers of these materials in conventional epitaxy, i.e., epitaxy on 3D substrate crystals. Our observations indicate that a deposition on layered substrates is hindered by the fail of nucleation on the van der Waals surfaces with deposition conditions known from conventional epitaxy.

As van der Waals surfaces do not exhibit dangling bonds at their surfaces, only weak bonding interaction of the incoming film material is expected. Therefore most of the film material is assumed to desorb from the surface before assembling to the critical growth nuclei of sufficient size.²¹ Furthermore van der Waals surfaces do not exhibit a high concentration of steps, thereby contrasting also the surfaces of three-dimensional materials used in conventional epitaxy. Their substrate surfaces always exhibit steps and kinks which are predominant adsorption centers for incoming deposit material. Once a step is decorated with incoming particles there is a new step and so on. This case is therefore referred to as “step flow.”²² This condition can obviously not hold for the growth on single crystal van der Waals surfaces since they are atomically flat over mesoscopic regions.

The nucleation problem might be overcome by drastically increasing the deposition rates in order to increase the supersaturation on the surface. However, film thickness control would be lost by this procedure and interface formation could not be monitored by surface sensitive techniques. We therefore refrained from this procedure. Alternatively, the substrate temperature was lowered in order to allow the nucleation of the incident particles and to deposit a layer of nucleation centers on the substrate surface. From these nucleation centers the film growth may proceed upon subsequent deposition. For the deposition of the CdS nucleation layer a temperature of -100°C was required; for CdTe it was sufficient to deposit at room temperature. However, at this temperature the actual deposit is still below the nominal deposition, i.e., the sticking coefficient is still estimated to be well below unity (0.1–0.3). Also, the intensity observed from the substrate emissions indicates that the overlayer consists of CdTe islands which leave most of the substrate surface uncovered.

Subsequent deposition was performed at elevated substrate temperatures. Growth conditions on already grown islands of CdTe should be close to those known from conventional epitaxy in order to obtain good structural quality. We cannot conclude so far whether the stable critical nuclei move in a sufficient way on the surface to allow for optimized film crystallinity. We have tried to trade off between the extremely low sticking of incident particles on van der Waals surfaces and the (homoepitaxial) growth conditions for CdTe.

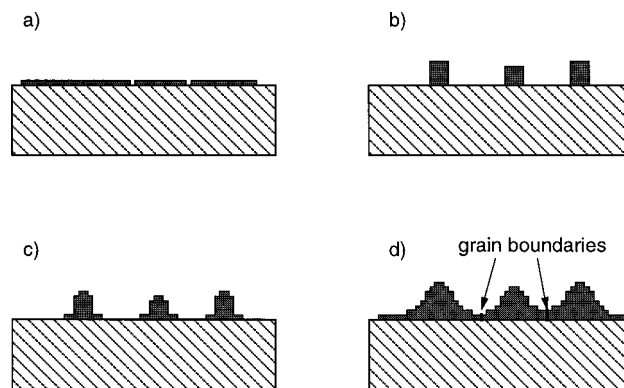


FIG. 5. Summary of the growth of CdTe film on layered substrates MoTe₂ and WSe₂ following the growth protocol described in the text: (a) nucleation layer formed at room temperature; (b) formation of three-dimensional islands during heating to subsequent growth temperature (170°C); (c) initial growth at $T=170^\circ\text{C}$; (d) continued growth at $T=170^\circ\text{C}$.

Part of the deposit from the first step was desorbed upon heating the nucleation layer above 150°C . With further increasing temperature the nucleation centers are considered to assemble to larger 3D clusters uncovering more of the substrate surface and reducing nucleus density. However, to get reasonable growth rates the density of nucleation centers should be kept high enough.

The film morphology is obviously a consequence of the above discussed growth behavior. Growth proceeds from the initially deposited nucleation centers which are randomly distributed over the substrate surface. From their rather even distribution and number we conclude that nucleation does not occur at steps and/or cleavage defects but on two-dimensional terraces as also observed in conventional van der Waals epitaxy (2D on 2D).^{8,23,24} Complete coverage of the substrate is reached when the crystallites meet each other. Since the sticking coefficient of the incident particles can readily be assumed to be much higher on the CdTe islands than on the van der Waals surfaces the film will grow in a simultaneous multilayer mode.²⁵ A sketch of the complete growth procedure is depicted in Fig. 5. The formation of facets on the CdTe surfaces may be recognized as a consequence of this growth mode resulting in pyramidal three-dimensional crystallites. A high texturization in $\langle 111 \rangle$ direction is also observed for CdTe deposition on glass substrates.²⁶ The additional preferential azimuthal orientation, observed in our experiments on van der Waals planes, must be related to a directional interaction with the underlying substrate. In 2D/2D van der Waals epitaxy a corrugation of ultrathin overlayer films has been proven by scanning tunneling microscopy^{8,23} and by LEED²⁴ experiments. This corrugation would lead to “locked” (in registry) and “unlocked” (out of registry) areas across the heterointerface. Whether a similar mechanism is valid also for 3D/2D interfaces has to be checked by further experiments on the initial nucleation steps and resulting overlayer morphologies. We expect that with such experiments the crystallinity and the morphology of the film can further be optimized by changing the deposition parameters and geometry.

V. CONCLUSION

CdTe was grown on the van der Waals surfaces of the layered compounds MoTe_2 and WSe_2 . To achieve film growth the deposition of an initial nucleation layer was necessary. The deposited films are polycrystalline with crystallites of mean diameter 200 Å, which are oriented with the (111) crystal direction parallel to the (0001) direction of the substrate surfaces. Diffraction pattern indicate faceted surfaces. The growth procedure remains to be further optimized for the use of 2D layered materials as buffer layers to overcome the lattice mismatch problems of dissimilar 3D materials.

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