Applied Physics Letters

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Cite as: Appl. Phys. Lett. **76**, 1101 (2000); https://doi.org/10.1063/1.125951
Submitted: 17 August 1999 • Accepted: 29 December 1999 • Published Online: 18 February 2000

R. Rudolph, Y. Tomm, C. Pettenkofer, et al.

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Van der Waals xenotaxy: Oriented growth of hexagonal GaSe(001) on rectangular GaAs(110)

R. Rudolph, Y. Tomm, and C. Pettenkofer
Department of Physical Chemistry, Hahn-Meitner Institut, D-14109 Berlin, Germany

A. Klein and W. Jaegermann[a)]
Department of Materials Science, Technische Universität Darmstadt, D-64287 Darmstadt, Germany

(Received 17 August 1999; accepted for publication 29 December 1999)

The growth of the layered chalcogenide GaSe on cleaved GaAs(110) surfaces was investigated with photoemission and low-energy electron diffraction (LEED). GaSe films grow with their *c* axis perpendicular to the GaAs(110) surface. LEED patterns after initial film growth are a superposition of rectangular GaAs:Se spots and two hexagonal domains rotated by $\pm 5°$ with respect to the GaAs $\langle 001 \rangle$ axis. At higher film thickness a hexagonal LEED pattern with GaSe $\langle 120 \rangle \parallel$ GaAs $\langle 001 \rangle$ is obtained. © *2000 American Institute of Physics.* [S0003-6951(00)00709-9]

Molecular beam epitaxy (MBE) is a powerful tool for semiconductor device fabrication. If the crystal lattices of the substrate and overlayer match, semiconductors can be grown on each other with a high degree of perfection. The limitation for material combinations is a mismatch exceeding 1%. Beyond this limit the stress or strain in the overlayer may lead to defect formation. This explains the great interest in buffer layers which can improve the quality of the grown films. The layered chalcogenides are promising materials to be used for this purpose.[1–3] Layered chalcogenides have a distinct two-dimensional structure in common. They consist of predominantly covalent bonded slabs held together by van der Waals-type forces. One slab of GaSe, for example, consists of the sequence Se–Ga–Ga–Se. The epitaxy of layered materials on each other is called van der Waals epitaxy (vdWe),[4] or quasi-van der Waals epitaxy (qvdWe) if the substrate or film has no layered crystal structure. Heterostructures with lattice mismatch of up to 60% can be grown by vdWe. Equality of surface symmetry is the generally accepted requirement for epitaxy.

There are several known cases where an overlayer changes the symmetry of rotation at the interface. Examples are Ag(111)/Si(001) (Ref. 5) and CdTe(111)/GaAs(001).[6] Monolayers of the layered material graphite were grown on various substrates such as NbC(001).[7] It was also attempted to grow single-crystalline layers of GaSe on GaAs(100) surfaces.[8–11] Abe *et al.*[11] reported a sixfold symmetry in reflection high-energy electron diffraction (RHEED) and Dai and co-workers[8,9] show high-resolution transmission electron microscope (HRTEM) images, proving the success of their MBE growth process. The results of Dai and co-workers[8,9] show that a thin reaction layer of Ga_2Se_3 is formed at the interface between the substrate and the film.

Selenium reacts with GaAs forming a terminating layer which passivates surface states and, therefore, improves its electronic properties.[12–14] A large number of publications on various interfaces of the ZnSe/GaAs and other selenium-containing heterosystems agree that an interface layer of Ga_2Se_3 is formed.[15–18]

The crystal structure of β-Ga_2Se_3 is a zinc-blende superstructure with structural vacancies and 4% lattice mismatch with the zinc-blende compound GaAs.[19] Tu and Kahn[15] stated that postgrowth annealing of a 30 Å ZnSe film on a rectangular GaAs(110) surface results in a loss of Zn and a hexagonal surface structure. They suggested that the hexagonal (001) surface of a Ga_2Se_3 crystal overlayer in a wurtzite modification was formed. This rarely mentioned phase is described by Wyckoff[20] as a high-temperature modification of Ga_2S_3.

In this letter we report on the growth of (001)-oriented films of GaSe on GaAs(110) cleavage planes. The (110) cleavage plane was chosen to demonstrate the versatility of the approach of vdWe. In addition, it is better defined in its structural properties as compared to the previously studied (100) plane[8–11] for which different surface reconstructions exist.[21] The formation of the film and its structural properties were investigated by synchroton-induced photoemission (SXPS) and low-energy electron diffraction (LEED). The experiments were performed in a coupled ultra-high-vacuum (UHV) analysis and growth chamber in a pressure range of 10^{-9} mbar or better. Crushed GaSe was evaporated from a single molecular-beam source with an open conic crucible. An additional selenium source was also available in the growth chamber. The growth rate was estimated by a quartz microbalance moved to the sample position before the growth process started. The substrate was clamped onto the sample holder and cleaved in UHV. The substrate temperature was kept at 450 °C during growth. The growth was interrupted and the sample allowed to cool down to room temperature to take SXPS data and LEED pictures at different coverages.

The series of LEED patterns obtained after different steps of the growth sequence are shown in Fig. 1. The cleaved GaAs surface shows the well-known unreconstructed 1×1 pattern [Fig. 1(a)]. Prior to the growth of GaSe, the GaAs surface was exposed 30 s to a Se beam with a rate of a few monolayers/minute at the growth temperature of 450 °C. This treatment leads to the well-known 1×2 recon-

[a)]Author to whom correspondence should be addressed; electronic mail: jaegerw@hrzpub.tu-darmstadt.de

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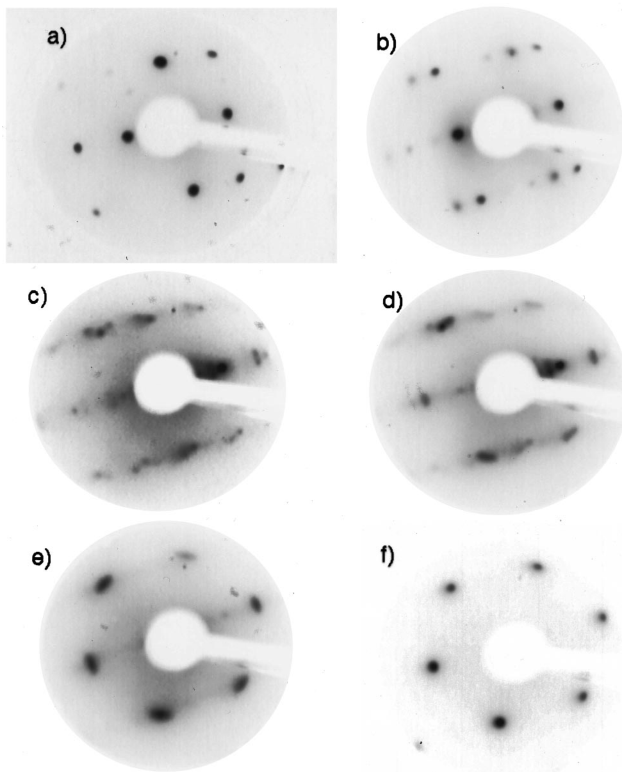

FIG. 1. Series of LEED patterns obtained during growth of GaSe on GaAs(110): (a) cleaved GaAs, (b) after Se exposure at 450 °C, (c) nominal 50 Å GaSe, (d) nominal 60 Å, (e) nominal 80 Å, and (f) nominal 1000 Å GaSe.

struction of the surface [Fig. 1(b)].[22] This Se-induced reconstruction is also evident from the changes in SXPS core-level and valence-band spectra (Fig. 2). The Se 3*d* signal shows two different emission lines. Their origin is discussed in detail in the literature.[13,16,23,24] Also, the valence-band features of the Se-covered GaAs(110) are in good agreement with those given by Schröter *et al.*[14]

After Se passivation, GaSe was sequentially deposited onto the substrate. The LEED pattern in Fig. 1(c) shows a

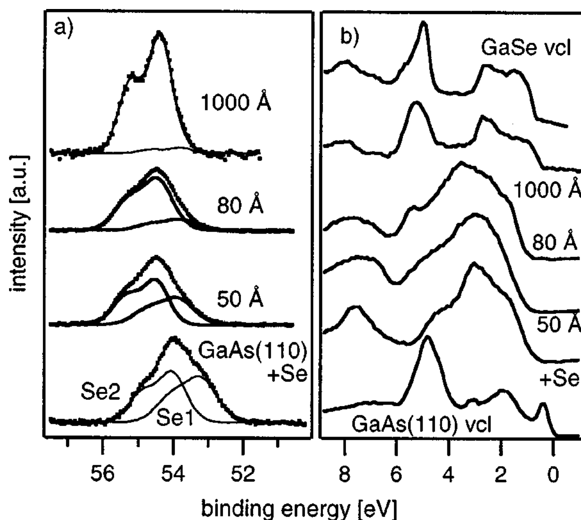

FIG. 2. Synchrotron-excited Se 3*d* (a) ($h\nu = 80$ eV) and valence-band (b) ($h\nu = 21$ eV) photoelectron spectra after different preparation steps. Spectra are measured in normal emission and coverages are given as nominal deposition thicknesses.

partially GaSe-covered GaAs(110) surface. Overlapping features of GaSe(001) and GaAs(110):Se are observed. It should be noted that the 1×2 reconstruction of the Se-passivated GaAs(110) is evidently lost again. With larger coverages up to 100 nm the typical hexagonal diffraction pattern of GaSe is built up [Figs. 1(c)–1(f)], exhibiting clearly increasing crystalline perfection. Also, the photoemission data (Fig. 2) indicate the growth of a GaSe overlayer as the spectral features approach the well-known spectra of crystalline GaSe(001). In the intermediate range, the transition of the GaAs:Se-termination layer to a Ga_2Se_3 interface layer is suggested by the observed changes in the Se 3*d* intensity ratios as well as in the valence-band spectra (Fig. 2). X-ray diffraction experiments of thicker films show only (00l) diffraction lines of GaSe. TEM indicates an intermediate reaction layer of ≈ 1.3 nm between the GaAs substrate and the GaSe overlayer.[25]

The experimental results show that crystalline films of hexagonal GaSe(001) are deposited in a defined structural relation to the rectangular GaAs(110) substrate. The hexagonal *c* axis of GaSe is parallel to the GaAs(110) surface normal. In addition, the overlayer films are azimuthally oriented to the substrate as is evidenced by LEED (Fig. 1).

The lattice parameter *a* of the grown film can be deduced from LEED and the *c* axis of the film was determined using x-ray diffraction. The results prove that the hexagonal overlayer grown at higher thicknesses consists of hexagonal GaSe rather than of Ga_2Se_3 because of their different lattice constants. The GaAs surface at high temperatures ($\geqslant 400$ °C) will most likely undergo a change to a Ga_2Se_3-like interface layer in the presence of elemental selenium or selenium compounds. A detailed analysis of the interface and of the epitaxy relations will be given in a subsequent paper.[25] On this passivating interlayer, GaSe grows as a crystalline film.

In summary, we have presented a LEED and SXPS study of the growth of GaSe(001) on GaAs(110) showing the change of rotational symmetry at the interface. We suggest this be termed van der Waals xenotaxy (composed of the greek expressions: xeno=alien; taxis=oriented). Hexagonal GaSe nucleates in two domains on the GaAs(110) surface. Further coverage leads to quasi-single-crystalline film without rotations. Evidently, it is possible, by using the concept of van der Waals epitaxy, to grow oriented films of dissimilar materials with different lattice constants and surface symmetry on substrates which are properly terminated by a van der Waals-type passivation layer. Thus, a wide range of novel semiconductor heterodevices may be feasible.

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