Structural properties of ZnSe/InSe/ZnSe heterostructures grown by molecular beam epitaxy on GaAs(001) substrates

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Abstract. The paper reports on molecular beam epitaxy of ZnSe/InSe/ZnSe quantum well (QW) heterostructures grown on GaAs(001) substrates as well as studies of their structural properties. The structures were characterized by reflection high energy electron diffraction, scanning electron microscopy, and high-resolution transmission electron microscopy techniques. The evolution of surface morphology of QW heterostructures as a function of the InSe thickness has been studied. The quasi van der Waals growth of ZnSe on the InSe(0001) surface has been demonstrated, with the ZnSe(111) plane being oriented parallel to the (0001) plane of InSe because of a small lattice mismatch between InSe and ZnSe(111).

1. Introduction

2D semiconductor materials are of great interest for the fabrication of new devices due to their unique electronic and optical properties [1]. The use of a combination of conventional and two-dimensional semiconductors in a single heterostructure allows expanding the range of potential applications. In part, the InSe/ZnSe is a promising heteropair for potential applications in the field of photonics and electronics, especially taking into account that the band-line-up for the InSe/ZnSe interface has been reported to be of strong type I [2] as well as the existence of matured molecular beam epitaxy (MBE) technology of ZnSe/GaAs(001) [3].

Bulk InSe crystals consist of vertically ordered ~0.83 nm-thick layers which are bonded together by weak van der Waals (vdW) forces, and each InSe layer contains four covalently-bonded Se-In-In-Se atomic sheets (so-called tetralayers (TLs)). InSe has a direct bandgap $E_g = 1.26$ eV and high electron mobility at room temperature [1,4]. Layered InSe like other 2D group-III metal chalcogenides have a number of polytypes ($\beta$, $\gamma$, and $\varepsilon$), which result from the different stacking sequence of the layers [1,5]. The MBE growth of 2D layered materials on standard 3D substrates is provided via vdW forces, and the lattice mismatch between the growing layer and the substrate can be as high as to 30% [6]. This paper reports on the MBE growth of InSe/ZnSe and ZnSe/InSe/ZnSe quantum well (QW) heterostructures grown on GaAs(001) substrates, as well as studies of their surface morphology and structural properties.

2. Experiment

The InSe/ZnSe and ZnSe/InSe/ZnSe QW heterostructures were grown on undoped GaAs(001) substrates with a 200 nm-thick GaAs buffer layer by using a double-chamber MBE setup (SemiTEq, Russia). Standard In and Zn effusion cells as well as a Se valve cracking cell (Veeco, USA) with the cracking zone temperature $T_{Se,(cr)} = 500^\circ$C were used as molecular beam sources. The InSe growth temperature ($T_3$) was as high as $T_3 \sim 450^\circ$C. The details of the MBE growth of ZnSe/GaAs(001) were...
published elsewhere [3]. The Se/In flux ratio was controlled by measuring the Se and In beam equivalent pressures (BEPs) at the substrate position by using a Bayard-Alpert ion gauge before each growth run. The In beam flux was \( \sim 1.2 \times 10^{-7} \) Torr (BEP), which corresponds to an average InSe growth rate \( \sim 1.2-1.3 \) nm/min. The Se flux was kept constant throughout the growth. The samples were characterized by high-resolution transmission electron microscopy (HRTEM) (Jeol JEM 2100F microscope) and scanning electron microscopy (SEM) (CamScan microscope) techniques.

3. Results and discussion

One of the main problems in MBE growth of InSe layers is associated with the formation of numerous In\(_5\)Se\(_3\)-type phases. In part, it is difficult to control the stoichiometric composition of InSe films on the GaAs(001) surface. Both X-ray diffraction and Raman spectroscopy studies confirmed the existence of “parasitic” In\(_5\)Se\(_3\) phases (mainly In\(_4\)Se\(_3\)) in InSe/GaAs(001) layers grown in a wide range of growth temperatures \( T_S = 350-500^\circ C \) using standard In and Se effusion cells as molecular beam sources [7]. It has been suggested that the double-domain structure in InSe is probably due to the coexistence of the In\(_4\)Se\(_3\) phase in the grown films. The task of growing “pure” InSe films in the case of using Se valve cracking cell seems even more complicated. For example, the inclusions of the Ga\(_2\)Se\(_3\) “parasitic” phase were observed in GaSe/GaAs(001) layers grown using a Se valve cracking cell with a high cracking zone temperature \( T_{cr}(cr) = 950^\circ C \) not only at high Se/Ga flux ratios, but also in near stoichiometric conditions [8]. So, when using the Se cracking cell as a Se source, one can expect the similar situation for the MBE growth of InSe/GaAs(001) and InSe/ZnSe(001) layers. Indeed, the X-ray diffraction measurements (not shown here) of a 1 \( \mu \)m-thick InSe/GaAs(001) layer grown in this study using a Se valve cracking cell with \( T_{cr}(cr) = 500^\circ C \) confirm the existence of In\(_4\)Se\(_3\) phase inclusions. The substrate temperature of \( T_S = 450^\circ C \) was chosen for the MBE growth of InSe both to avoid the film re-evaporation, and to provide simultaneously the maximum structural quality of the growing film. Suggesting the similar dependence of the stoichiometric VI/III flux ratio on the Se cracking zone temperature as in the case of GaSe [9], the near stoichiometric InSe/GaAs(001) MBE growth conditions at \( T_S = 450^\circ C \) should correspond to the Se/In (BEP) \( \sim 2.5-3 \) flux ratio. The same growth conditions were used also for the epitaxial growth of InSe on the ZnSe(001) surface.

![Image](a) ![Image](b) ![Image](c)

**Figure 1.** The evolution of RHEED images at MBE of the ZnSe/5 TLs InSe/ZnSe QW structure. (a) the (2x1) ZnSe(001) surface before InSe deposition \( (T_S = 450^\circ C) \); (b) after the deposition of 1 TL of InSe; (c) after 1 min. of ZnSe growth on the InSe surface at \( T_S = 300^\circ C \).

The nominal thickness of the InSe layer in the ZnSe/InSe/ZnSe QW heterostructures ranged from 2 to 7 TLs. The thicknesses of the ZnSe bottom and top layers were within 80-160 nm and 20-40 nm ranges, respectively. Additionally, a 130-nm thick InSe/ZnSe(001) layer was grown for the surface morphology measurements.
The InSe growth was initiated by the opening of the In flux on the Se-exposed (2x1) ZnSe(001) surface and monitored in situ by using the reflection high energy electron diffraction (RHEED) technique. The RHEED images of the (2x1) ZnSe(001) surface before InSe deposition and after the growth of 1 TL of InSe are presented in figure 1 (a),(b). After the opening of the In shutter, the RHEED pattern quickly changes to that corresponding to InSe. The RHEED pattern remains streaky during the growth of the first few tetralayers of InSe, which indicates a fairly smooth surface of the growing InSe film. However, as the thickness of the InSe layer increases, the surface becomes rougher due to the formation of domain boundaries. The brightness of the RHEED pattern decreases, which is also accompanied by the appearance of concentric rings and spots typical for the growth of polycrystalline films.

![Figure 2](image_url) The plan-view SEM images of the ZnSe/InSe/ZnSe QW heterostructure with different InSe thickness: (a) 2 TLs, (b) 5 TLs.

The plan-view SEM images of the ZnSe/InSe/ZnSe QW heterostructures with an InSe thickness of 2 and 5 TLs are presented in figure 2. One can see that the structure with 2 TLs of InSe has a rather smooth surface (figure 2 (a)) with a number of selenium drops typical for the ZnSe surface exposed to atmosphere [10]. With an increase in the thickness of InSe up to 5 TLs, the roughness of the surface also increases (figure 2 (b)). The growth of the top ZnSe layer on the InSe surface was carried out at $T_S = 300^\circ$C. After the opening of the Zn shutter, the RHEED pattern gradually changed from the streaky to spotty one (figure 1 (c)). The RHEED pattern transformation is an indirect indication of the microstructure changes in the InSe layer.

![Figure 3](image_url) Cross-section HRTEM images of the ZnSe/InSe/ZnSe QW heterostructure with an InSe nominal thickness of 7 TLs: the whole structure (a) and the InSe QW region (b). The selective area electron diffraction image of the ZnSe/InSe/ZnSe QW heterostructures is shown in fig. 3(a). The reflexes from the top ZnSe layer are marked with an asterisk, and the growth direction is indicated by the arrow.
formation of ZnSe clusters due to a weak interaction of ZnSe with the underlying layered InSe. It should be noted that the tendency of II-VI materials (CdTe, ZnSe, etc.) to form clusters on the low energy vdW surfaces was reported earlier [2,11,12]. Based on the fact that the cluster size and shape vary depending on the combination of ZnSe and layered chalcogenide compounds, it was suggested that this variation is due to the difference in the interface energy, which, in turn, influences the surface diffusion length [12].

Rough estimates of the thickness of top ZnSe layers in QW structures, based on the analysis of cross-sectional SEM images showed that the average growth rate of the top ZnSe layer is about 20% lower than that of the bottom one. It can be assumed, that the lack of dangling bonds on the vdW InSe surface hinders the process of ZnSe nucleation. Our data agree well with the previous works on 3D/2D MBE growth, where it was shown that the sticking coefficient of the 3D material on the van der Waals plane is rather low and in some cases could be even close to zero [12].

Figure 3 demonstrates the cross-sectional TEM images of the ZnSe/InSe/ZnSe QW structure with a 7 TLs-thick InSe layer; the thicknesses of the bottom and top ZnSe layers were 160 nm and 40 nm, respectively. The TEM data confirm the multi-domain character of InSe/ZnSe(001) nucleation. At the growth temperature used, the e axis of InSe is directed normally to the growth surface (Figure 3 (b)). The TEM data also confirm the (111)-oriented ZnSe growth on the InSe(0001) surface, as was previously reported in ref. [10]. However, it should be noted that the orientation of the ZnSe layer does not change in the parts of the structure where there are no InSe islands. The existence of the (111)-oriented ZnSe in the structure has also been confirmed by selective area electron diffraction (SAED) measurements (see inset to figure 3 (a)). One can suppose that the growth of ZnSe with a (111) orientation onto the (0001) van der Waals surfaces is caused by the proximity of the InSe and ZnSe(111) lattice parameters (Δa/a ~ 1% or less, a(InSe)=4.002Å, a(3D-InSe)=4.05Å [5]). The InSe vdW surface provides a defined epitaxial orientation of the top ZnSe layer, despite the weak interaction between them. Moreover, in this case, the cluster-like growth of ZnSe(111) can be explained in terms of minimizing the elastic energy of the growing layer.

4. Conclusions

The structural properties of InSe/ZnSe and ZnSe/InSe/ZnSe QW heterostructures grown by MBE on GaAs(001) substrates have been studied using a number of characterization techniques. The gradual transformation of the RHEED pattern with increasing InSe thickness confirms the growth of polycrystalline InSe/ZnSe(001) films. The cross-sectional TEM images of the QW structures indicate the (111)-oriented ZnSe growth on the InSe(0001) surface. The optical properties of ZnSe/InSe/ZnSe QW heterostructures will be studied and reported in a separate paper.

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