



Heriot-Watt University
Research Gateway

Molecular beam epitaxial growth of zinc blende MgS on GaAs (211)B substrates

Citation for published version:

Zhu, J, Eldose, NM, Mavridi, N, Prior, KA & Moug, RT 2018, 'Molecular beam epitaxial growth of zinc blende MgS on GaAs (211)B substrates', *Journal of Crystal Growth*, vol. 485, pp. 86-89.
<https://doi.org/10.1016/j.jcrysgr.2017.12.043>

Digital Object Identifier (DOI):

[10.1016/j.jcrysgr.2017.12.043](https://doi.org/10.1016/j.jcrysgr.2017.12.043)

Link:

[Link to publication record in Heriot-Watt Research Portal](#)

Document Version:

Publisher's PDF, also known as Version of record

Published In:

Journal of Crystal Growth

Publisher Rights Statement:

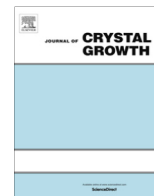
© 2018 The Authors. This is an open access article under the CC BY license (<http://creativecommons.org/licenses/by/4.0/>).

General rights

Copyright for the publications made accessible via Heriot-Watt Research Portal is retained by the author(s) and / or other copyright owners and it is a condition of accessing these publications that users recognise and abide by the legal requirements associated with these rights.

Take down policy

Heriot-Watt University has made every reasonable effort to ensure that the content in Heriot-Watt Research Portal complies with UK legislation. If you believe that the public display of this file breaches copyright please contact open.access@hw.ac.uk providing details, and we will remove access to the work immediately and investigate your claim.



Molecular beam epitaxial growth of zinc blende MgS on GaAs (2 1 1)B substrates



J. Zhu ^{*}, N.M. Eldose, N. Mavridi, K.A. Prior, R.T. Moug

School of Engineering and Physical Sciences, Heriot-Watt University, Edinburgh EH14 4AS, United Kingdom

ARTICLE INFO

Article history:

Received 20 December 2017

Accepted 28 December 2017

Available online 5 January 2018

Communicated by K.H. Ploog

Keywords:

A3. MBE

A1. Zinc blende

B1. MgS

A1. (2 1 1)B

A3. ELO

B2. II-VI

ABSTRACT

This paper reports the growth of zinc blende (ZB) MgS on GaAs (2 1 1)B substrates by molecular beam epitaxy. Initial growths of (2 1 1)B ZnSe were performed at 240 °C and showed to be of comparable quality to (1 0 0) ZnSe grown at the same temperature. Samples of MgS deposited on ZnSe buffers showed good quality 2D growth. Subsequently, multilayer structures of ZnSe and ZnCdSe were deposited on (2 1 1)B MgS layers for structural and optical examination before and after epitaxial lift off (ELO). Photoluminescence (PL) spectroscopy showed strong emission before and after ELO and X-ray spectra demonstrated the presence of a single continuous zinc blende phase.

© 2018 The Authors. Published by Elsevier B.V. This is an open access article under the CC BY license (<http://creativecommons.org/licenses/by/4.0/>).

1. Introduction

II-VI heteroepitaxial layers grown on GaAs (2 1 1)B substrates have been grown previously and have demonstrated properties which were exploited in various novel applications [1]. In particular, when strained layers are grown on low symmetry surfaces such as (2 1 1), there is a large polarization field due to the internal piezoelectric effect [2]. Also, there is a refractive index dependence for transmitted light related to the surface orientation of the epilayer which is the focus of the current work on (2 1 1) oriented layers. If an II-VI epitaxial layer can be removed from the GaAs (2 1 1) B substrate, by techniques such as epitaxial lift off (ELO), and stacked in different crystal orientations, then these (h11) oriented layers (or any surface other than (1 0 0)) allow devices to be constructed which optimize second harmonic generation [3].

ELO of heterostructures from their host substrates onto different materials has been investigated in both III-V and II-VI material systems. For GaAs/AlGaAs structures, AlAs is used as the sacrificial layer, while we have demonstrated ELO for II-VI layers deposited on GaAs (1 0 0) substrates [4]. ZnSe/ZnCdSe quantum well structures have been grown on GaAs (1 0 0) substrates and successfully lifted off by using MgS as the sacrificial layer, with an etching selectivity between ZnSe and MgS of approximately 10⁷:1 in 30% HCl [5].

Previously, our group demonstrated growth of zinc blende (ZB) ZnSe and Zn_{1-x}Cd_xSe ($x < 0.2$) epitaxial layers on GaAs (2 1 1)B substrates and monitored the surface roughness and reconstructions by reflection high energy electron diffraction (RHEED) [8]. The growth of ZB MgS and its subsequent use in ELO has been studied by our group on GaAs (1 0 0) substrates, but ZB MgS growth on GaAs (2 1 1)B has not been investigated and is key in transferring the ELO technique to GaAs (2 1 1)B substrates.

In this paper, we describe the conditions required for the growth of ZB MgS layers on GaAs (2 1 1)B substrates. Also, we demonstrate growth of ZnSe and ZnSe/ZnCdSe structures on MgS followed by ELO.

2. Experimental

In this study, samples were grown primarily on GaAs (2 1 1)B substrates, with similar growths on GaAs (1 0 0) substrates to allow a detailed comparison between both growth conditions and layer quality. All samples were grown using a V80H molecular beam epitaxy system, with 6N sources of elemental Zn, Se and Mg, together with a 6N compound ZnS source fitted with a LN₂ cooled shutter to reduce sulphur leakage into the chamber.

For all samples, the deoxidisation process was monitored in situ by RHEED. The surface reconstructions of both substrates were recorded along orthogonal azimuth directions. As expected, the oxide removal on (1 0 0) GaAs occurred at approximately 580 °C, while for the (2 1 1)B samples the deoxidisation occurred approx-

^{*} Corresponding author.

E-mail address: jz33@hw.ac.uk (J. Zhu).

imately 40 °C higher. De-oxidation was confirmed by the standard 4×2 RHEED pattern for (1 0 0) GaAs and for (2 1 1)B by short sharp streaks along $[0\ 1\ \bar{1}]$ and chevrons along $[\bar{1}\ 1\ 1]$. This pattern on (2 1 1)B implies the presence of an array of periodic steps along $[0\ 1\ \bar{1}]$ and facets along $[\bar{1}\ 1\ 1]$ [6].

The substrates were then cooled to the growth temperature under a Zn flux. Previously (2 1 1)B ZnSe was deposited at ~320–370 °C [6], but it has been shown that good MgS growth on (1 0 0) ZnSe buffer layers requires a lower substrate temperature [7] and so for this study we initially examined the growth of ZnSe on (2 1 1)B GaAs at 240 °C. 1 μm layers of (1 0 0) and (2 1 1)B ZnSe were grown at 240 °C. During (2 1 1)B growth that the patterns were comparable to previous studies with the typical short sharp streaks along $[0\ 1\ \bar{1}]$ and chevrons along $[\bar{1}\ 1\ 1]$. Subsequent high resolution double crystal X-ray diffraction (HRXRD) analysis of both (1 0 0) and (2 1 1)B samples showed FWHM of 315 and 392 arc seconds for the (1 0 0) and (2 1 1)B ZnSe peaks respectively. For the (1 0 0) sample a standard 400 scan was taken while for the (2 1 1)B sample, glancing exit 422 scans were taken. There are two possible explanations for the rise in FWHM in the (2 1 1)B sample: (1) there has been an increase in the dislocation density [8], or (2) it could be due to the relationship between the scattering vector $G(4\ 2\ 2)$ for the reflection and the burgers vectors of the dislocations, such that $G422.b > G400.b$. We quickly examined this by scanning the (1 0 0) ZnSe sample on a similar glancing exit 115 reflection. We observed a similar increase in the FWHM of the ZnSe peak with no change in the substrate. This suggests that 2 is the most likely contributor and therefore, for the purpose of this study, the (2 1 1)B samples can be regarded as having comparable quality to the (1 0 0) ZnSe, despite the lower growth temperature.

The growth modes of ZnSe and MgS are quite different. ZnSe, and ZnCdSe are typical of most II–VI compounds in that the growth is performed under slightly group VI rich conditions and this is reflected in the RHEED patterns. On (1 0 0) the typical Se-stabilised 2×1 surface is seen, while on (2 1 1)B, during ZnSe growth the RHEED pattern changed from chevrons along the $[\bar{1}\ 1\ 1]$ direction to short streaks, indicating a change from a faceted surface to a flat stepped one, as expected for a Se stabilised surface. The orthogonal direction stayed unchanged throughout growth.

In the case of (1 0 0) MgS, although the ZnS:Mg BEP ratio is approximately 500:1, the very low incorporation coefficient of S, compared to the near-unity coefficient for Mg, means that the surface is actually metal-rich. For (1 0 0) MgS the typical metal-rich $c(2 \times 2)$ RHEED pattern is observed. For (2 1 1)B MgS growth the RHEED pattern during optimized growth is unknown, but as growth occurs under identical conditions to that of (1 0 0) samples a metal stabilised surface should be visible. A metal stabilised ZnSe (2 1 1)B surface at the lower growth temperature was examined for comparison with MgS. During Zn only exposure, faint half order fractional order streaks in the $[\bar{1}\ 1\ 1]$ RHEED pattern were observed corresponding to a metal stabilised surface.

As the differences between the group VI and group II stabilised (2 1 1)B surface RHEED patterns are so small, all MgS structures were grown on both (1 0 0) and (2 1 1)B GaAs/ZnSe buffers to confirm growth conditions were optimized. At the start of growth, MgS grew well but showed no change in RHEED from the ZnSe buffer below. As the MgS layer thickness increased, there was no change in RHEED, and in particular, no formation of spots or inclined features indicative of 3D growth or phase transformation. This implies continuity of the ZB crystal structure throughout the growth.

MgS oxidises quickly in air and needs to be capped to study ex situ so new samples were designed for further characterisation. Two sets of samples were grown for this study, the first using our standard growth procedure on (1 0 0) GaAs, and the second

on (2 1 1)B GaAs. In both sets two samples were grown: first, a GaAs/ZnSe(15 nm)/MgS(6nm)/ZnSe(1 μm) layer for characterisation by HRXRD, and second, a quantum well sample of GaAs/ZnSe(15 nm)/MgS(6 nm)/ZnSe(70 nm)/ZnCdSe(8 nm)/ZnSe(70 nm) for PL. The purpose of these PL structures is to assess structural and optical quality. As such, the absolute concentration of Cd and well thickness are not required and due to differing incorporation rates for Zn and Cd on the two surfaces there may be some difference in well thickness and composition between the (2 1 1)B and (1 0 0) samples.

X-ray interference (XRI) has been previously used to study the quality and properties of MgS grown on GaAs (1 0 0) [9] but this method is inappropriate for (2 1 1)B substrates due to tilt introduced by the epitaxial layer strain. Therefore, an indirect measurement of the ZB MgS layer quality is required, and here we use the structural quality of the ZnSe layer grown on MgS, and the quality of the PL of a ZnSe/ZnCdSe QW grown on MgS. Quality can be compared both before and after ELO, and also to the samples grown on (1 0 0) GaAs.

3. Results

HRXRD scans were obtained on both (1 0 0) and (2 1 1)B samples of GaAs/ZnSe/MgS/ZnSe. A 1 μm ZnSe layer thickness was chosen for these samples so that the layers are fully relaxed. As the ZnSe buffer and MgS layer combined are below 20 nm thickness their contribution to the HRXRD spectrum is minimal compared to the layer above. Under non-optimal growth conditions there is a phase transition in MgS from the metastable ZB structure to the stable rocksalt [10] which leads to a mixed phase layer with domains of both ZB and RS material. When this occurs, any subsequent ZnSe growth becomes domain oriented and does not generate an XRD peak at the expected Bragg angle for ZB ZnSe. [11] In the (2 1 1)B samples the XRD peak expected for ZB ZnSe is observed, confirming both the presence of single crystal ZB ZnSe, and its continuity with the underlying ZB MgS layer.

Fig. 1 shows the experimental XRD 422 rocking curves for the (2 1 1)B sample. The ZnSe peak position is observed at 532 arc seconds relative to the GaAs reference peak, whilst the calculated

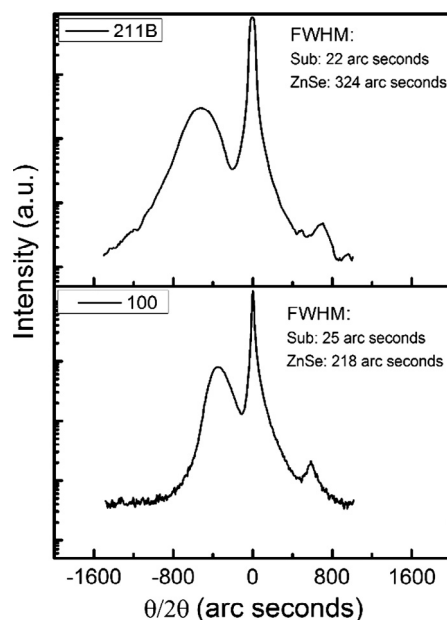


Fig. 1. HR-XRD rocking curves for 1 μm ZnSe grown on GaAs (2 1 1)B (Top) and GaAs (1 0 0) substrates (Bottom).



Fig. 2. Image of 5×5 mm ZnSe ELO layers transferred onto glass plates from (2 1 1) B substrate.

peak position for a completely relaxed ZnSe layer is at 534 arc seconds, well within experimental error. The FWHM of the (2 1 1)B ZnSe was compared to the (1 0 0) ZnSe sample. It was observed that, the FWHM of the (2 1 1)B ZnSe peak is larger at 324 arc seconds compared to the (1 0 0) ZnSe at 218. As before, this is likely due to the scattering vector for the dislocations on this reflection. This however would require further study to confirm. What is important to note is that both samples have narrower peak widths when grown on MgS surfaces. This further confirms that the (2 1 1) B MgS is of comparable quality to the (1 0 0), and has grown in the ZB structure.

ELO was then performed using our standard procedure, allowing the samples to be transferred to glass. Fig. 2 shows the ELO lifted-off layers from (2 1 1)B substrates transferred to glass plates. The lifted layers were crack free over square millimetre areas [12].

Figs. 3 and 4 show the typical PL spectra at 77 K of (1 0 0) and (2 1 1)B samples containing $1 \mu\text{m}$ thick ZnSe before and after lift-off and transfer to glass. Details of the PL spectra of the ZnSe/ZnCdSe/ZnSe QW and thick ZnSe layers grown on (1 0 0) and (2 1 1)B substrates are shown in Table 1.

The increase in the FWHM for the (2 1 1) QW structures compared to the (1 0 0) can arise from a number of differing effects such as fluctuations in well thickness arising from interlayer roughness, alloy broadening and the inbuilt piezo field in (2 1 1) layers.

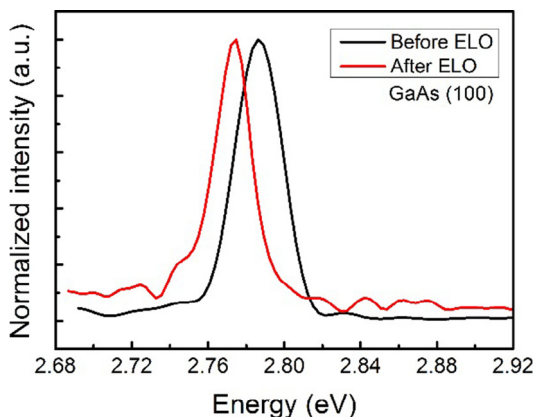


Fig. 3. Normalized PL intensity as a function of energy of a $1 \mu\text{m}$ ZnSe layer grown on GaAs (1 0 0) substrate at 77 K before and after ELO.

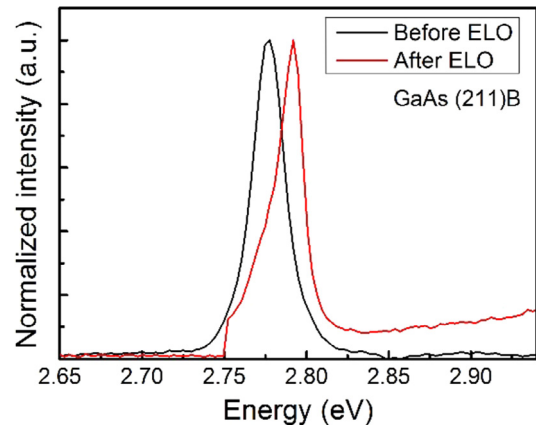


Fig. 4. Normalized PL intensity as a function of energy of a $1 \mu\text{m}$ ZnSe layer grown on GaAs (2 1 1)B substrate at 77 K before and after ELO.

Table 1

Summary of PL results for $1 \mu\text{m}$ ZnSe and single QW grown on GaAs (2 1 1)B and (1 0 0) substrates.

Sample	PL pre ELO (eV)	PL post ELO (eV)	FWHM pre ELO (meV)	FWHM post ELO (meV)
(1 0 0) QW	2.35	2.41	38	36
(2 1 1)B QW	2.46	2.49	64	100
(1 0 0) $1 \mu\text{m}$ ZnSe	2.79	2.77	18	27
(2 1 1)B $1 \mu\text{m}$ ZnSe	2.78	2.79	25	26

PL peak positions shift after lift-off, indicating a small change in strain within the layer, possibly caused by the wax used during the lift-off process or strain introduced during bonding, which requires further investigation. By measuring the QW emission peak shift that arises after lift-off we can estimate any change in strain attributed to the lift-off process. For the (1 0 0) sample we found the strain to be 2.2×10^{-2} after the sample was lifted, whilst for (2 1 1)B sample, the strain was 1.13×10^{-2} [13].

The broadening of FWHMs after ELO may arise from strains introduced during the ELO process. However, the FWHMs for (1 0 0) and (2 1 1)B ZnSe thick layers are comparable to each other which suggests no obvious degradation in optical quality after ELO.

The emission intensity from the (2 1 1)B samples were an order of magnitude lower than for the 100 samples, however these layers are not intended for light emission, so photon generation or recombination is not a crucial issue, while being single crystal ZB is the aim. The large increase in FWHM in the (2 1 1)B QW sample between the un-lifted and lifted layers is most likely due to an increase in dislocation density after lifting. It is seen that there is less strain after ELO of (2 1 1)B compared to 100 for identical systems this would imply that the strain energy has gone into generating more dislocations. This however would require further study to determine and is out with the scope of the paper.

4. Conclusion

In conclusion, we have demonstrated for the first time that ZB MgS layers can be grown on GaAs (2 1 1)B substrates and integrated into heterostructures with ZnSe and (Zn,Cd)Se. Characterisation by RHEED, HRXRD and PL indicates good quality II-VI

layers grown on the (2 1 1)B MgS surface. The crystal structure of the MgS grown was demonstrated to be ZB from the RHEED patterns observed during growth and from the HRXRD peak of the ZnSe capping layer. ELO was used for the first time on II-VI layers grown on GaAs (2 1 1)B substrates by etching the ZB MgS and releasing the II-VI layer, which showed good optical quality by PL.

Acknowledgements

The authors would like to acknowledge the support of EPSRC grant (EP/L025396/1).

References

- [1] S.Y. Wang, P.J. Thompson, G. Horsburgh, T.A. Steele, G.D. Brownlie, K.A. Prior, B.C. Cavenett, Piezoelectric effect in ZnSe/ZnCdSe quantum wells grown on (2 1 1) B GaAs, *J. Cryst. Growth* 159 (1996) 459–462.
- [2] J.S. Milnes, C. Morhain, S.A. Telfer, W. Meridith, T.A. Steele, K.A. Prior, B.C. Cavenett, A spectroscopic study of the piezoelectric effect in ZnSe/ZnCdSe single quantum wells grown on (2 1 1) B GaAs, *J. Cryst. Growth* (1998).
- [3] R. Haidar, P. Kupecek, E. Rosencher, R. Triboulet, P. Lemasson, New mid-infrared optical sources based on isotropic semiconductors (zinc selenide and gallium arsenide) using total internal reflection quasi-phase-matching, *Optoelectron. Rev.* 11 (2) (2003) 155–160.
- [4] A. Balocchi, A. Curran, T.C. Graham, C. Bradford, K.A. Prior, R.J. Warburton, Epitaxial lift off of ZnSe-based heterostructures using a II-VI release layer, *Appl. Phys. Lett.* 86 (2005) 011915.
- [5] R.T. Moug, C. Bradford, F. Izdebski, A. Curran, J. Warburton, K.A. Prior, A. Aouni, F.M. Morales, S.I. Molina, A comparison of ZnMgSSe and MgS wide bandgap semiconductors used as barriers: growth, structure and luminescence properties, *J. Cryst. Growth Vols. F. M. Morales, S. I. Molina* (2009) 2099–2101.
- [6] S.A. Telfer, G. Horsburgh, J.S. Milnes, C. Morhain, P.J. Thompson, K.A. Prior, B.C. Cavenett, Growth of ZnSe and ZnCdSe on (211)B GaAs substrates, *J. Cryst. Growth* 184 (185) (1998) 51–56.
- [7] A. Rajan, R.T. Moug, K.A. Prior, Epitaxial growth of zinc blende MgS directly on GaAs (0 0 1) substrates, *Semicond. Sci. Technol.* 29 (2014).
- [8] B. Yarlagadda, A. Rodriguez, P. Li, R. Velampati, J.F. Ocampo, E.N. Suarez, P.B. Rago, D. Shah, J.E. Ayers, F.C. Jain, X-ray characterization of dislocation density asymmetries in heteroepitaxial semiconductors, *Appl. Phys. Lett.* 92 (2008) 202103.
- [9] K.A. Prior, X. Tang, C. O'Donnell, C. Bradford, L. David, B.C. Cavenett, Characterisation of MBE grown II-VI semiconductor thin layers by X-Ray interference, *J. Cryst. Growth* 251 (2003) 565–570.
- [10] A. Rajan, R.T. Moug, K.A. Prior, Growth and stability of zinc blende MgS on GaAs, GaP, and InP substrates, *Appl. Phys. Lett.* 102 (2013) 032102.
- [11] C. Bradford, C.B. O'Donnell, B. Urbaszek, A. Balocchi, C. Morhain, K.A. Prior, B.C. Cavenett, Growth of zinc blende MgS/ZnSe single quantum wells by molecular beam epitaxy using ZnS as a sulphur source, *Appl. Phys. Lett.* 76 (2000) 3929–3931.
- [12] A. Rajan, A.I. Davidson, T.R. Moug, A.K. Prior, Epitaxial lift-off of II-VI semiconductors from III-V substrates using a MgS release layer, *J. Appl. Phys.* 114 (2013) 243510.
- [13] K. Ohkawa, T. Mitsuyu, O. Yamazaki, Effect of biaxial strain on exciton luminescence of heteroepitaxial ZnSe layers, vol. 38, p. 12465, 1988.