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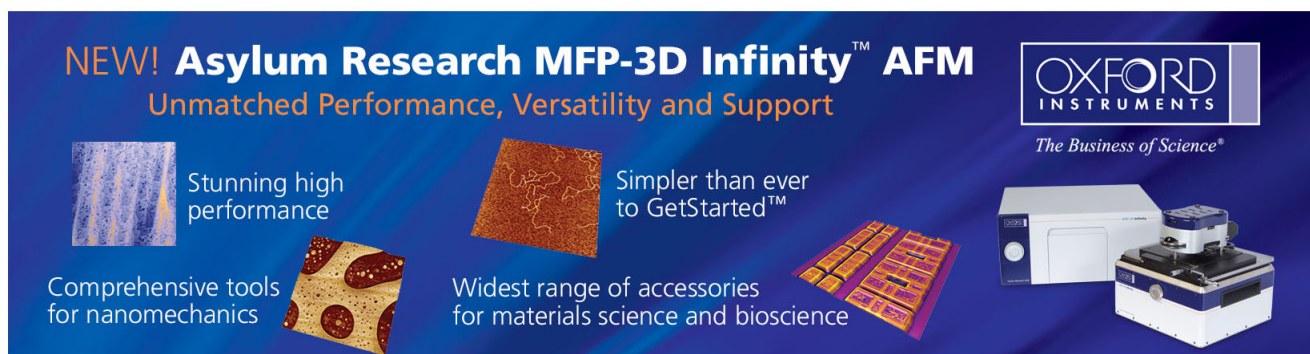J. Vac. Sci. Technol. B **29**, 032202 (2011); 10.1116/1.3574523

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Growth and stability of zinc blende MgS on GaAs, GaP, and InP substrates

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The molecular beam epitaxial growth of zinc blende (ZB) MgS on GaAs, GaP, and InP substrates has been investigated by X-ray diffraction and RHEED, with MgS layer strain varying between 3.1% compressive strain (GaP) and 4.4% tensile strain (InP). ZB MgS could be grown on all three substrates. X-ray diffraction showed substantial MgS relaxation during growth before conversion to the rock salt phase. Results are compared with predictions that stable growth on GaP is unlikely and relaxed ZB MgS does not grow in layers over a few Å thick. Our results imply growth of ZB MgS is truly metastable. © 2013 American Institute of Physics.
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It has long been recognized that a thin film can be grown in a crystal structure other than the one it would normally adopt by depositing it on a substrate with that crystal structure. One early study[1] suggested that a requirement for this to occur was a high supersaturation during growth. In addition, similar lattice constants for the substrate and metastable phase of the epilayer stabilize the metastable phase up to a certain critical size for the material deposit. In this model, the high surface area to volume ratio is a key parameter in the stabilization.

Subsequently, a different method was used to determine the stability of crystal structures when depositing rocksalt (RS) materials on zinc blende (ZB) substrates by Froyen, Wei, and Zunger (FWZ).[2] For each substrate and epitaxial film combination, the energy of both phases of the epitaxial layer can be plotted as a function of the lattice parameter. This is shown schematically in Figure 1. Here, the RS structure has an energy per formula unit (shown in blue) varying parabolically with lattice constant with a minimum at the equilibrium lattice constant a_{RS}. The corresponding ZB (red) curve minimum at a_{ZB} lies at an energy E_{ZB} above the RS minimum, meaning the ZB phase is metastable. Growth of thin films of either phase can occur on a substrate of different lattice constant a_{sub}. Pseudomorphic growth requires the epitaxial layer to be biaxially strained to the substrate lattice constant, and the energy curves have smaller curvatures than for hydrostatic strains (dashed lines in Figure 1). The ZB and RS curves intersect at some lattice constant a^*, and if $a_{sub} \geq a^*$ then the strained ZB phase has the lower energy and is stable. Effectively, the stability of the two phases is reversed due to the greater strain in the RS layer.

As the layer thickness, h, increases relaxation through the formation of strain relieving dislocations becomes possible. The relaxed RS phase with dislocations is shown schematically as point X in Figure 1 and has an energy greater than the perfect unstrained crystal of E_{Drs}. In this schematic, E_{Drs} is a function of h, reducing to zero as the layer becomes thicker. When $h = h_{cdrs}$, the energy falls below that for the strained layer, giving the critical thickness for dislocation formation in the RS phase. In contrast, a relaxed ZB phase, without conversion to RS, produces a layer at point Y in Figure 1 at a critical thickness $h = h_{cdzb}$. The FWZ model,

therefore, makes the following predictions about growth. First, the ZB phase grows initially only if $a_{sub} \geq a^*$ otherwise the RS phase forms. Second, as discussed below, typically $h = h_{cdrs} < h_{cdzb}$ then conversion from strained ZB to relaxed RS will occur at a minimum layer thickness $h = h_{cdrs}$. All ZB growth at $h < h_{cdrs}$ will be metastable.

A compound originally highlighted by FWZ was MgS, having a_{ZB} close to a_{sub} for GaAs and a small calculated E_{ZB}. The predicted a^* was 5.5 Å, so thin layers (≤ 1 nm) of the ZB phase grown on GaAs would be stable. This same model can also be used to determine the stability of other metastable thin film crystal structures including those where the stable structure is not cubic. In particular, it has been used to predict the stability of ZB epitaxial layers where the stable structure is nickel arsenide.[3] However, in this case, it has been suggested that interfacial energies may dominate in thin film growth.[4]

We have previously shown that ZB MgS grows on GaAs and under optimum conditions thicknesses over two orders of magnitude greater than h_{cdrs} are easily achievable.[5,6] In order to determine the influence of the substrate lattice constant on
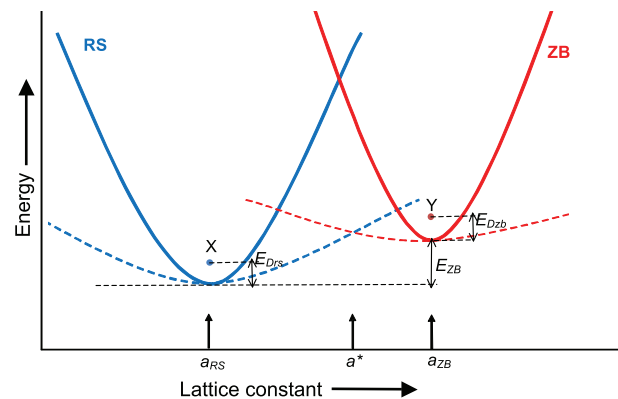
FIG. 1. Schematic diagram of crystal energy per formula unit as a function of lattice constant for both the rock salt (RS, blue curves) and zinc blende (ZB, red curves) phases with unstrained lattice constants a_{RS} and a_{ZB}, respectively. The solid curves are for bulk material, while thin biaxially strained layers are dashed curves crossing at a^*. The ZB phase is metastable with a minimum energy E_{ZB}. Points X and Y with energies E_{Drs} and E_{Dzb} are RS and ZB layers, respectively, that have relaxed by the introduction of dislocations.

growth mode, in this paper, we compare the growth of MgS on three different substrates (GaP, GaAs, and InP) with a wide range of lattice mismatches. All previous growths of ZB MgS by our group have occurred on thin ZnSe buffers deposited on GaAs substrates, and recently it was shown that an almost identical growth procedure to the one used by our group forms only RS MgS if deposited directly on GaAs substrates.[7] Here, it was suggested that other compounds which are not ZB are formed at the III-V/II-VI interface. Accordingly, to ensure that the ZB crystal structure is maintained across the interface we have grown MgS on II-VI buffers that are approximately lattice matched to the three III-V substrates. The combinations chosen and the MgS strains are given in Table I. Relaxation of the buffer layer is possible and the table also gives the strains between MgS and a relaxed buffer.

All layers were grown in a Vacuum Generators V80H MBE system as described previously.[5] The layers were grown on (100) oriented substrates, which were chemically etched prior to mounting on a holder using In. GaAs (100) substrates were etched using our standard procedure in a 2:2:20 $H_2O_2 : H_2O : H_2SO_4$ solution for 90 s, whereas GaP (100) substrates were etched in a 15:5:5 solution of HCl : H_2O : HNO_3 for 120 s.[10] All substrates were rinsed in deionized (DI) water after the etch. A two step chemical etching technique was adopted for InP cleaning. First, the substrate was etched for 120 s in a 4:1:100 $H_2SO_4 : H_2O_2 : H_2O$ solution to remove the native oxide and then a second etch in 1:1 $H_2SO_4 : H_2O$ solution for 30 s was used to remove the chemical oxide formed in the hydrogen peroxide solution.[11]

Samples were degassed in the preparation chamber, then transferred to the growth chamber for oxide layer desorption at $\sim 540\,^\circ\text{C}, \sim 520\,^\circ\text{C}$, and $\sim 300\,^\circ\text{C}$ for GaAs, GaP, and InP, respectively. Before depositing II-VI buffer layers, the substrates were cooled to $250\,^\circ\text{C}$ under a flux of Zn[12] for GaAs and GaP, while InP was cooled without any added flux to $170\,^\circ\text{C}$. Sharp 4×2, 2×4, and 2×1 RHEED patterns were always obtained from GaAs, GaP, and InP, respectively, following oxide removal and cooling indicating minimal sulfur contamination of the substrate surface.

After growth of the buffer layers, the MgS layer was deposited, followed by a capping layer to prevent oxidation. The MgS growth was monitored by RHEED, as the transition from ZB to RS is marked by sudden clear changes in the pattern.[5,6] Confirmation of the phase present was also obtained after growth using X-ray diffraction (XRD) as demonstrated previously for MgS on GaAs(100).[6]

Due to the near lattice match of MgS on GaAs, and our previous experience with ZB MgS growth, this substrate is used as a reference. On GaAs substrates, sample structures

TABLE I. Strains of MgS on different substrates and buffer layer combinations.

Heterostructure	Strain to ZB MgS (Ref. 8) $\epsilon_{substrate(buffer)}(\%)$	Strain to RS MgS (Ref. 9) $\epsilon_{substrate(buffer)}(\%)$
GaP/ZnS	−3.0 (−3.8)	4.8 (4.0)
GaAs/ZnSe	0.6 (0.8)	8.7 (9.0)
InP/Zn$_{0.6}$Cd$_{0.4}$Se	4.4 (3.7)	12.9 (12.1)

were GaAs(sub)/ZnSe(50 nm)/MgS(12 nm)/ZnSe(320 nm). A thicker ZnSe capping layer was grown than in previous studies to obtain a more intense X-ray signal for subsequent analysis. The ZnSe buffer layer shows a very sharp 2×1 RHEED pattern indicating a flat surface changing to a streaky $c(2 \times 2)$ pattern as soon as the MgS growth starts.[13] The 2×1 pattern reappears during the capping ZnSe layer. Throughout the growth, the RHEED patterns were compatible with growth of the ZB phase, and no features which could be assigned to RS growth were observed. Simulation of the X-ray data gave the sample thicknesses and a MgS growth rate of $\sim 0.38\,\text{Å/s}$.

Samples were grown on GaP substrates with ZnS buffers deposited at $170\,^\circ\text{C}$ before increasing the substrate temperature to $250\,^\circ\text{C}$. Within experimental error, the growth temperatures and fluxes for the MgS layers were identical with those used for growth on GaAs substrates. The first structures produced were GaP(sub)/ZnS(60 nm)/MgS(12 nm)/ZnS(320 nm) and for the ZnS capping layer, the substrate temperature was reduced to $170\,^\circ\text{C}$. The ZnS buffer layer shows a very faint $c(2 \times 2)$ RHEED pattern, which becomes stronger and streakier during MgS layer growth and does not change during the growth of the cap. Surprisingly, the RHEED patterns indicated that the MgS surface was very smooth and the ZnS capping layer was much smoother than the buffer layer. Again, there was no indication of RS conversion during growth. Subsequent samples were grown to determine the maximum ZB MgS thickness possible on a GaP substrate with structure GaP/ZnS (7 nm)/MgS (x nm)/ ZnS (7 nm). Here, the capping layer was only used to prevent oxidation of MgS. For up to $x \sim 40$ nm, RHEED showed a streaky $c(2 \times 2)$ pattern with no spots or diffuse features. With further growth, the RHEED streaks became spots and at $x \sim 70$ nm, the pattern became diffuse. Figure 2 shows the 004 x-ray rocking curves from (a) the 40 nm and (b) the 70 nm thick layers. The former shows a broad MgS epilayer peak at the correct position for a fully relaxed ZB layer and a subsidiary weaker peak, which is assigned to a ZnMgS mixing layers a few nm thick between the MgS and surrounding ZnS cladding. In contrast, the MgS signal is very weak or absent from all thicker samples, such as Fig. 2(b) confirming
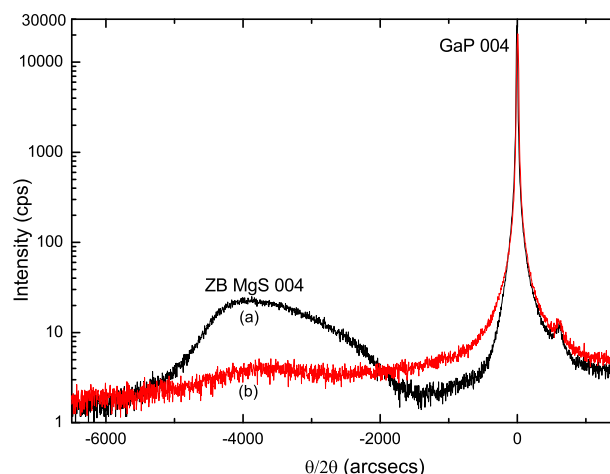

FIG. 2. 004 x-ray rocking curves from two GaP/ZnS (7 nm)/MgS (x nm)/ ZnS (7 nm) structures, where x is: (a) 40 nm, (b) 70 nm.

the phase conversion to RS of the underlying MgS. No attempt was made to maximize the MgS layer thickness by using a multilayer smoothing structure, as has been demonstrated previously on GaAs substrates.[6]

Samples were also grown on InP substrates with $Zn_{0.6}Cd_{0.4}Se$ buffer and capping layers. Samples had the structure, InP (sub)/$Zn_{0.6}Cd_{0.4}Se$ (80 nm)/MgS (12 nm)/$Zn_{0.6}Cd_{0.4}Se$ (320 nm). In this case, at the start of the buffer layer growth the RHEED patterns were spotty, but gradually improved to give a streaky 2×1 pattern and so a thicker buffer layer was used for a smoother ZnCdSe surface. The MgS layer was again flat with a sharp and streaky $c(2 \times 2)$ RHEED pattern and the $Zn_{0.6}Cd_{0.4}Se$ capping layer also showed a streaky RHEED pattern throughout growth.

Double crystal X-ray rocking curves were obtained from samples from all three substrates and examples are shown in Figure 3. The capping layers here are thick and are relaxed, giving broad peaks with no thickness fringes. For ZnSe capping layers grown on MgS on GaAs substrates, we have shown that the 400 X-ray peak is not visible after MgS conversion to RS.[6] Here, strong peaks from the capping layers are visible in all samples, confirming the RHEED observations that ZB is maintained throughout.

In thick relaxed semiconductor layers, the dislocation density can be measured and its anisotropy was determined by measuring the FWHM of the layer peak at different azimuthal angles.[14] Rocking curves were obtained from epitaxial layers thicker than 300 nm grown on all three substrates and their dislocation densities estimated for [110] and [1$\bar{1}$0] are listed in Table II. All are anisotropic with fewer dislocations along [110] than [1$\bar{1}$0]. Previously published results for epitaxial ZnSe layers on GaAs[14] show almost identical dislocation densities to the GaAs/ZnSe/MgS/ZnSe samples studied here.

This shows that ZB MgS can be grown on substrates with a wide range of tensile and compressive strains. The deposited layers are very similar on all three substrates and during growth it was noticed that it was impossible to tell from

the RHEED patterns alone which substrate was being used. This result was completely unexpected as we have previously found that growth of ZB MgS is very sensitive to growth conditions, in particular, substrate temperature and fluxes. However, if the growth conditions are optimized, then the choice of substrate appears far less critical. Irrespective of the epitaxial layer strain at the start of growth, relaxation occurs through mismatch dislocations. The capping layers grown on top of the MgS clearly relax and modeling of the X-ray data from the thickest ZB MgS layers indicates these also relax. This was previously observed with layers grown on GaAs substrates[6,8] and is now confirmed for GaP and InP. In all cases, the dislocation densities are anisotropic and presumably incomplete, at least along [110]. It also suggests that despite MgS having very different elastic constants to the surrounding layers,[2,8,15] the mismatch dislocations are probably the same type.

On the energy schematic in Figure 1, MgS evolves from some point on the strained ZB (red, dashed) curve to point Y before transferring subsequently to point X. This occurs for all three substrates, in particular, GaP. The lattice constant of GaP is 5.451 Å, which is smaller than a^* estimated by FWZ to be 5.5 Å. The energy diagram for the MgS ZB and RS phases was recently recalculated,[8] giving a_{MgS} much closer to the experimental value and additionally recalculating a^* to be ≈ 5.465 Å, still larger than a_{GaP}. There are potentially two large errors in calculating a^*. The first is the residual zinc level in the MgS, which is typically in the range 0.5%–3%. At the higher levels, this significantly increases the MgS elastic constants, raising a^* by ≈ 0.02 Å. The second source of error is the value of E_{ZB} used, which has not been experimentally determined. Both calculations[2,8] used 170 meV per formula unit. For $a^* < a_{GaP}$, then E_{ZB} must decrease by 80–100 meV, a significant reduction. It, therefore, appears that according to the FWZ model growth of ZB MgS on GaP is impossible, in direct contrast to our observations.

Growth of ZB MgS on GaAs and InP is allowed under the FWZ model, but the transformation from strained ZB (red curve) to relaxed ZB (point Y) to relaxed RS (point X) is not. FWZ estimated $h_{hdrs} = 5$ Å for RS MgS when the in-plane lattice constant was a_{ZB}. The critical thickness can be recalculated using different versions of Matthew's formula to allow for the anisotropy of the elastic constants,[16] but broadly similar results are obtained. Using the onset of dislocation formation given by Matthew's theory to indicate the transition point implies the phase transition is caused by the formation of the first few mismatch dislocations. It is possible that instead the transformation requires a much larger dislocation density. An upper bound for this can be found by determining the critical thickness for the generation of a

TABLE II. Dislocation densities calculated from two azimuths from capping layer FWHM.

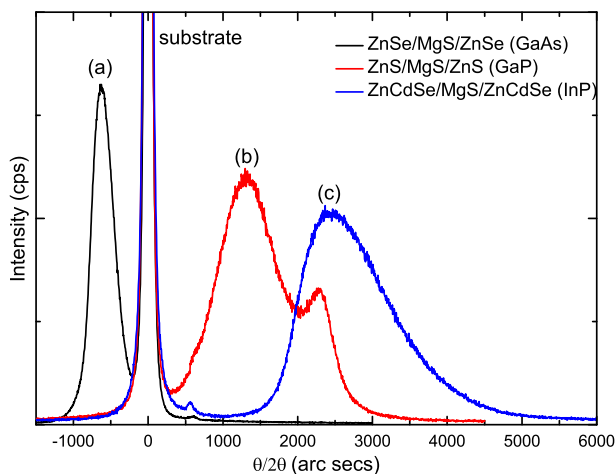| Heterostructure	Dislocation density (cm^{-2})	
	$D_{[110]}$	$D_{[1\bar{1}0]}$
GaAs/ZnSe/MgS/ZnSe	2.02×10^8	2.10×10^8
GaP/ZnS/MgS/ZnS	1.77×10^9	1.96×10^9
InP/ZnCdSe/MgS/ZnCdSe	1.42×10^9	1.43×10^9

FIG. 3. 004 x-ray rocking curves from samples with structures (a) GaAs (sub)/ZnSe (50 nm)/MgS (12 nm)/ZnSe (320 nm), (b) GaP (sub)/ZnS (60 nm)/MgS (12 nm)/ZnS (320 nm), (c) InP (sub)/$Zn_{0.6}Cd_{0.4}Se$ (80 nm)/MgS (12 nm)/$Zn_{0.6}Cd_{0.4}Se$ (320 nm). The curves are shown with the substrate peaks aligned at the origin. The broad peaks are from the capping layer. In (b), the subsidiary peak at larger angle arises from the strained ZnS buffer layer.

complete dislocation network for relaxation, but still gives very similar thicknesses of only a few Å. These small critical thicknesses arise from the elastic constants of RS MgS, where the bulk modulus is large and the shear modulus is small. Hence, any strain requires a large strain energy, while dislocations need little energy to form.

The relative magnitudes of the elastic constants give confidence that it is correct to assume that, in MgS, relaxation of RS is much easier than ZB, even though the predicted thicknesses are undoubtedly very inaccurate as they are all of similar magnitude to the Burgers vector. There are two key results. First, strained ZB MgS should always relax to RS MgS before relaxed ZB MgS ever forms, and second, all ZB MgS layers over 5 Å thick are unstable with respect to the RS phase. These conclusions are completely different to the observed behavior of MgS, which indicate that the growth of MgS in the ZB form is truly metastable, as it can be grown with a range of tensile and compressive strains, relaxing through the normal misfit mechanism back to its unstrained lattice constant. Under ideal conditions, it can grow very thick relaxed layers. To date, the thickest ZB layers deposited on GaAs are 200 nm thick,[17] which are completely relaxed.

Finally, for ZnSe growth on GaAs, there has been much work over many years to ensure the lowest possible dislocation density. One possibility (although unlikely) is that in GaAs/ZnSe (50 nm) buffer layers, the substrate threading dislocation density is so low that MgS is unable to relax and growth remains pseudomorphic. In this case, relaxation will only occur after MgS growth with dislocations from the relaxed capping layer. However, the threading dislocation density can be increased substantially by growing a relaxed 300 nm ZnSe buffer layer. Comparison of MgS layers deposited on 50 nm strained layers and 300 nm relaxed layers with different dislocation densities shows no change in RHEED or X-ray diffraction peaks indicating that threading dislocation densities are not important.

In conclusion, we have grown ZB MgS under both tensile and compressive strain on GaP, GaAs, and InP substrates. Both RHEED and X-ray diffraction measurements indicate that the ZB phase can be grown in layers at least 40 nm thick on all substrates. Conversion of ZB to RS MgS occurs only after the ZB phase has relaxed, in contrast to the theoretical predictions, which suggest that the relaxed ZB phase should not occur and that growth on GaP substrates is unlikely. The results suggest that epitaxial strain is not important in stabilizing the ZB phase and that the growth is truly metastable.

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