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INVESTIGATIONS ON ZnSe/GaAs INTERFACE BY TREATMENT OF GaAs (2×4) SURFACE WITH Te AND Mg

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The heterovalent interface ZnSe/GaAs, despite the small lattice misfit, still poses certain problems. The condition of the substrate surface prior to growth start determines the initial growth conditions, which on the other hand are assumed to be responsible for defect densities. Since Zn, in contrast to Se, hardly binds to GaAs the initial surface during growth start is essentially Se terminated. Therefore the binding of Mg to Se terminated GaAs was investigated. The structural quality of 140 nm thick ZnSe layers on different MgSe coverages were compared to conventionally grown and Te initiated ZnSe epilayers of the same thickness.

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1. Introduction

Due to the small lattice mismatch between GaAs and ZnSe, GaAs is the dominant substrate material for MBE growth of blue-green optoelectronic II-VI devices. Nevertheless the heterovalent interface still remains a major problem.

The initial growth conditions determine the defect densities [1], which on the other hand are known to be responsible for the degradation of optoelectronic devices [2]. Therefore a precise control of the initial surface is of great importance. Since the sticking coefficient of Zn on GaAs is much smaller than that of Se, ZnSe growth starts on a Se terminated GaAs surface (Se/GaAs) if Zn and Se are offered simultaneously. This surface has been investigated [1] and is known to be almost inert [3]. Therefore ZnSe growth proceeds predominantly at defects, which results in an unfavorable island growth mode and high defect densities [4].

One obvious way to avoid the Se termination of GaAs is the exposure of the (2×4) GaAs surface to Zn prior to ZnSe growth. Compared to conventionally grown ZnSe the defect density is significantly reduced [5]. However, since Zn does not stick on (2×4) GaAs [6], this approach has the disadvantage to rely on the reaction dynamics. Recently we have demonstrated that similar improvement can

be obtained by a static approach, when ZnSe growth is started on a GaAs surface terminated with Te [6]. This procedure leads to a two-dimensional growth mode already during the first few monolayers, resulting in a generally improved layer quality and a significantly higher critical layer thickness [6].

In this paper we investigate an alternative static growth start, i.e. the nucleation of Mg on Se/GaAs. Since the bonding strength of Mg to Se is higher than Zn to Se, Mg should be able to bond to Se terminated GaAs. This surface as well as the ZnSe growth start on such Mg treated surfaces was studied by X-ray photoelectron spectroscopy (XPS) and reflection high energy electron diffraction (RHEED). The structural quality of ZnSe layers on Mg terminated Se/GaAs was controlled by high resolution X-ray diffraction (HRXRD).

2. Experimental set up

All samples were prepared on GaAs buffer layers which were grown in a III/V-growth chamber with a background pressure less than 2×10^{-10} mbar. The substrate temperature was controlled by a thermocouple. Standard effusion cells were used to evaporate Ga, As₄ and Si. The flux was determined by an ion gauge, measuring the beam equivalent pressure (BEP). The surface symmetry was observed by RHEED (12 kV acceleration voltage).

The samples were subsequently moved to the II/VI-growth chamber under UHV conditions (pressure smaller than 5×10^{-10} mbar). Standard effusion cells (Zn, Se, ZnCl, Mg and Te) were employed and the flux measurement was similar to that in the III/V-growth chamber. The surface reconstruction and topology was observed by RHEED (30 kV).

XPS measurements were performed in a separate surface analysis chamber which is also connected to the growth chambers via an UHV transfer module. X-rays were provided by an Al K_{α} (1486.6 eV) source. The resolution of the energy analyzer was 0.3 eV.

A high-resolution six crystal-diffractometer equipped with a laboratory X-ray source (Cu K_{α}) provided the information about the structural quality of the grown ZnSe layers. The photoluminescence measurements were performed in a helium bath cryostat at 2 K with a HeCd laser at a wavelength of 325 nm with an optical power of 3 mW.

3. Substrate and surface preparation

The substrates were first cleaned under nitrogen flow, then etched in a $\text{NH}_4/\text{H}_2\text{O}_2$ solution, rinsed with water and finally dried under nitrogen flow. They were glued to the molybdenum holders with indium.

The oxide layer of the GaAs substrate was desorbed under As-flux at 580°C. The 250 nm thick silicon doped GaAs buffer layers were grown at 600°C with a growth rate of 500 nm/h under As-rich conditions (As BEP $\approx 2.5 \times 10^{-5}$ mbar, Ga BEP $\approx 5.0 \times 10^{-7}$ mbar). The flux of the silicon oven at 1100°C provided a doping concentration of 5×10^{18} cm⁻³. The growth was stopped by leaving the samples under As flux for two minutes, subsequently closing the shutter and simultaneously turning off the substrate heater. This leads to a (2 × 4) symmetry as observed by RHEED.

This pattern was still observable after transfer at room temperature to the II/VI-growth chamber. The samples were again brought to a substrate temperature of 300°C. To obtain the initial interfaces, we exposed the specimens to Se (BEP 2.5×10^{-6} mbar) for two minutes. The appearing (2×1) reconstruction of Se terminated GaAs (Se/GaAs) is a relatively well-known surface [1]. It is generally assumed that half of the Se absorbed remains at the surface, whereas the other half is incorporated into underlying layers [3]. The Se/GaAs surface was then exposed to a Mg flux (BEP 1.0×10^{-8} mbar), which led to a (1×1) reconstruction pattern.

We investigated the nucleation of Mg on Se/GaAs as a function of the time of exposure. For this purpose the sample was exposed to a constant Mg flux (BEP 1.0×10^{-8} mbar). The various coverages were examined by XPS. Therefore, the samples had to be moved to the surface analysis chamber (background pressure smaller than 3×10^{-11} mbar) at room temperature for the measurement and afterwards back to the growth chamber, where they had to be brought to 300°C again. A special care was taken to avoid contamination between successive exposures. This included the observation of carbon and oxygen peaks at every measurement. None of the two was observed in a crucial amount.

We examined the low binding energy range of the concerned elements by XPS (Ga $3d$, Se $3d$, As $3d$ and Mg $2s$), all peaks lying between 0 and 100 eV. Therefore the photoelectrons all have about the same attenuation length which is necessary to be comparable. Because of the diminishing intensity of the Mg $2s$ peak, we also investigated the Mg $1s$ peak at 1305 eV. The peak intensities were obtained by subtracting the linear background, integrating over the peak area and multiplying each peak by its cross-section. Each intensity was normalized to the total sum of all peaks, the latter serving as a measure of the X-ray photon flux. A scale factor of the Mg $1s$ peak was obtained by multiplying the ratio of the counting rates of Mg $2s$ to Mg $1s$ by the cross-section of Mg $2s$ for a reasonably high surface coverage. Subsequently the growth start of ZnSe on the Mg/Se/GaAs surface was observed by RHEED. We studied the growth on three different Mg coverages, namely 0.5, 1 and 2 minutes. As deduced from a MgSe growth rate under Se rich conditions this corresponds to coverages of approximately 0.75, 1.5 and 3 monolayers (ML).

For each Mg coverage a doped and an undoped ZnSe layer of 140 nm was grown (Zn BEP 5×10^{-7} mbar). For low Mg coverage the RHEED pattern exhibited a two-dimensional growth after 30 seconds, whereas for two monolayers an island growth mode persists for almost a period of two minutes.

4. Results and discussion

XPS measurements reveal a linearly increasing surface concentration of Mg for the first minute (Fig. 1). The coverage can reach even more than one monolayer. Therefore Mg binds to Se/GaAs but does not reach saturation. For exposure times longer than 120 seconds a second Mg $2s$ peak appears which is shifted by 0.9 eV. This chemical shift can be interpreted as the formation of metallic Mg in addition to the Mg bond to Se/GaAs. The component of the Mg-Se/GaAs binding remains approximately constant, whereas the further increase in the total Mg signal is completely due to the metallic component. Therefore, in contrast to Te which

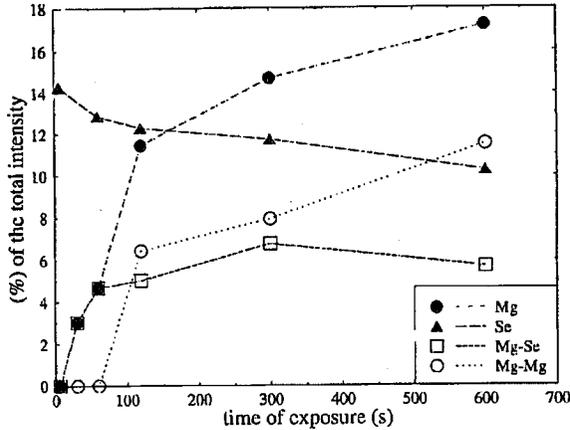


Fig. 1. Surface concentration of magnesium and selenium as a function of time of exposure. The unfilled markers show the contribution of the Mg-Se and Mg-Mg components.

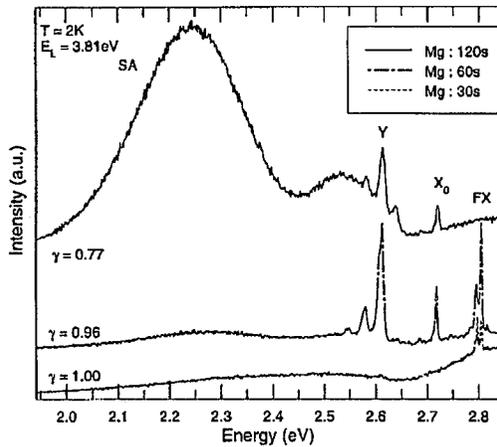


Fig. 2. Photoluminescence spectrum of 140 nm undoped ZnSe on different Mg coverages. γ is the strain parameter depicting the degree of relaxation.

saturates after 0.5 monolayers, the amount of Mg deposited may influence the growth start.

This is confirmed by photoluminescence measurements on undoped ZnSe layers grown on different Mg coverages (Fig. 2). For higher Mg coverages the defect emission increases drastically, whereas for the low Mg coverage almost no photoluminescence is observed. A good optical quality is only obtained for a Mg coverage around one monolayer.

Figure 3 compares a PL spectrum of a doped sample grown directly on Se/GaAs with the one of a sample grown on Mg/Se/GaAs with optimized Mg

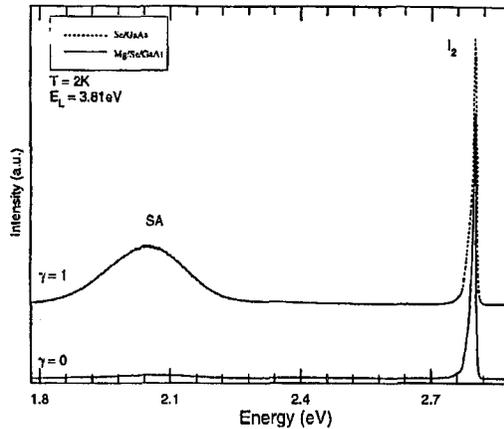


Fig. 3. Comparison of 180 nm doped Se/GaAs and 240 nm doped Mg/Se/GaAs with optimised Mg coverage.

coverage. The spectrum of the layer grown on Mg/Se/GaAs shows a significantly lower ratio of the excitonic to defect emission compared to ZnSe/Se/GaAs layers. As we have shown previously [4] this indicates an improved interface quality.

By using HRXRD the strain parameter and the structural quality of the samples was determined. If the epilayer is pseudomorphic the 004-rocking curves show oscillations from which the layer thickness can be determined. The position of the epilayer peak relative to the substrate peak depends on the lattice constant and thus is a measure of the relaxation. The relaxation of the Mg initiated ZnSe layers was compared to conventionally grown and Te initiated ZnSe layers of the same thicknesses.

For low Mg coverage (0.75 ML) the 140 nm ZnSe layers are fully strained, whereas for higher coverages the layers of the same thickness are partially relaxed. The Mg seems to be incorporated into the compound as a Mg(Zn)Se layer and thus introduces additional strain. MgSe has a larger lattice constant than ZnSe and GaAs and thus increases the compressive strain.

One measure for the structural quality of epilayers is the critical thickness of pseudomorphic grown layers which is determined by the defect density and the built-in strain. Since the additional strain introduced by the MgSe layer leads to an earlier relaxation we calculated the stored strain. According to the Hooke law the strain energy stored in a fully or partially coherent epitaxial layer is proportional to the layer thickness and the square of the lattice displacement parallel to the interface. For multilayers, the total energy is simply the sum of the strain energy for each layer [7].

We therefore calculated the energy stored in 140 nm ZnSe grown on the above described MgSe interfaces. The Mg initiated epitaxial layers can sustain about the same amount of strain energy as normally grown layers, but significantly less than those initiated with Te coverage.

5. Conclusions

The growth of ZnSe starts, due to the small sticking coefficient of Zn, on a Se terminated GaAs surface. Since Zn can only bind to defects, an island growth mode results, leading to a high stacking fault density.

We investigated the nucleation of Mg on Se terminated GaAs to improve the initial growth mode. In contrast to Zn, Mg sticks to Se/GaAs, according to XPS measurements. We were able to show that the structural quality of epitaxial ZnSe layers on different MgSe coverages is as good as conventionally grown layers, whereas the optical quality increases. Nevertheless the Te initiated layers possess a significantly higher structural quality.

References

- [1] M.D. Pashley, D. Li, *J. Vac. Sci. Technol. A* **12**, 1884 (1994).
- [2] A. Ishibashi, *IEEE J. Sel. Topics Quantum Electron.* **1**, 741 (1995).
- [3] M.D. Pashley, D. Li, *Proc. SPIE* **2346**, 142 (1994).
- [4] S. Guha, H. Munekata, L.L. Chang, *J. Appl. Phys.* **73**, 2294 (1993).
- [5] S. Saito, P.J. Parkbrook, S. Nakamura, Y. Nishikawa, G. Hatakoshi, in: *Proc. Intern. Symposium on Blue Laser and Light Emitting Diodes, Chiba 1996*, Eds. A. Yoshikawa, K. Kishino, M. Kobayashi, T. Zsuda, Ohmsha Ltd, Tokyo 1996, p. 66.
- [6] W. Spahn, H.R. Reß, K. Schüll, M. Ehinger, D. Hommel, G. Landwehr, *J. Cryst. Growth* **159**, 761 (1996).
- [7] J.Y. Tsao, in: *Materials Fundamentals of Molecular Beam Epitaxy*, Ed. H.B. Jovanovich, Academic Press, Boston 1993.