Growth and Characterization of ZnMgS and ZnMgS/ZnSe Quantum Wells grown on GaAs (100) by Using MBE

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Structures containing Zn$_{1-x}$Mg$_x$S have been grown lattice matched to GaAs by using molecular beam epitaxy (MBE) with ZnS as the source of S. The composition of the alloy produced has been determined using double-crystal X-ray spectroscopy and X-ray interference measurements. Both techniques indicate that $0.88 \leq x \leq 0.93$. This result is confirmed by both secondary ion mass spectroscopy and an Auger analysis carried out on the material. These results show that the crystalline quality of the material produced is excellent and that it has been grown coherently to the GaAs substrate. Photoluminescence spectroscopy shows a high intensity emission with a narrow full width half maximum, confirming the suitability of this alloy as a high-bandgap barrier material.

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I. INTRODUCTION

Mg-containing II-VI alloys have generated much interest in recent years. This group of materials has great potential in development of wide-band-gap barrier materials for semiconductors that not only emit in the UV but also work at room temperature [1, 2]. The wide band-gap Zn$_{1-x}$Mg$_x$S alloy system, in particular, has potential applications as UV detectors and electroluminescent displays with both the lattice constant and the band-gap energy increasing with $x$ [3, 4]. Unfortunately, to date, single-phase materials with high mole fractions of Mg have been difficult to realize due mainly to strain effects, with dislocation generation and inclusion of second-phase (rocksalt) precipitates degrading the structural quality of the materials produced [5]. Understanding the stability limits of these compounds is, therefore, a crucial prerequisite for successful fabrication of high quality devices to be realised.

Growth of this ternary alloy has been reported on GaP [3-5] and GaAs [6] substrates, but growth of single-phase material is difficult to achieve for $x > 0.3$. We have shown previously that metastable MgS with a band-gap of $\sim 5$ eV can be grown on GaAs by using molecular beam epitaxy (MBE) with ZnS as the only source of sulphur. Material produced using this method is shown to have excellent crystalline quality and can be grown in the zincblende crystal structure with thicknesses up to 140 nm [7, 8].

In this paper, we demonstrate, using the same growth method, how modification of the flux ratios can influence the Mg incorporation, allowing growth of Zn$_{1-x}$Mg$_x$S ($x \sim 0.9$) on GaAs. A thick Zn$_{1-x}$Mg$_x$S layer can be grown without any degradation of the crystal quality, despite having a large mismatch ($\sim 1\%$). Samples with the structure GaAs/ZnSe/Zn$_{1-x}$Mg$_x$S /ZnSe have also been grown for analysis by X-ray interference (XRI). The use of these layers as barriers with ZnSe quantum wells has also been determined by using photoluminescence spectroscopy (PL).

II. EXPERIMENTS

Characterization of the samples described here was by in-situ reflection high energy electron diffraction (RHEED) measurements and ex-situ X-ray double-crystal spectrometry and PL measurements. X-ray spectra were recorded using copper Ka radiation on a Bede 200 system. PL spectra were taken at 77 K by using the 351-nm line from an Ar-ion laser and were collected by using a 0.88 m Spex monochromator. An additional analysis of the ZnMgS layers by using secondary ion mass spectrometry (SIMS) and Auger electron spectroscopy (AES) was carried out at Loughborough Surface Analysis Ltd.

All samples were grown in a Vacuum Generators V80H MBE system on GaAs (100) substrates by using 6N elemental sources of Mg, Zn and Se together with a 6N ZnS compound source. A liquid-nitrogen-cooled
shutter was used in front of the high-temperature ZnS source in order to eliminate contamination of the GaAs substrate with sulphur during the thermal cleaning. The substrates were etched in a H$_2$O$_2$ : H$_2$O : H$_2$SO$_4$ solution and then degassed at 350 °C before being transferred to the growth chamber where the oxide layer was removed by heating to ~580 °C. The characteristic 4 × RHEED reconstruction was routinely maintained to a growth temperature of ~240 °C.

Typical cell temperatures for these growths were 890 °C for ZnS and 375 °C for the Mg cell. The Mg flux was not routinely measured due to the known interaction with the ion gauge, which causes a residual high background ion current. Prior to the growth of the Zn$_{1-x}$Mg$_x$S layers, a thin ZnSe layer was deposited in order to protect the GaAs interface from S contamination. Zn$_{1-x}$Mg$_x$S was grown by using the same method utilized previously to grow zinc-blende MgS [7, 8], but for these layers, an additional Zn flux was supplied during growth in order to reduce the VI : II ratio during the growth. A thin ZnSe capping layer was used to prevent oxidation of the Zn$_{1-x}$Mg$_x$S surface in air.

In order to determine both the composition and the crystalline quality of the material produced, we grew a layer with the structure GaAs / ZnSe(20 nm) / Zn$_{1-x}$Mg$_x$S(5 nm) / ZnSe(10 nm) / Zn$_{1-x}$Mg$_x$S(60 nm) / ZnSe(10 nm). The extra ZnMgS and ZnSe layers were introduced to improve the crystalline quality of the thick layers [8]. RHEED observations during the growth of the final Zn$_{1-x}$Mg$_x$S layer show a sharp c(2 × 2) reconstruction up to a thickness of 50 nm, after which spotty RHEED was observed along the [110] azimuth. In MgS, this same change in the RHEED pattern is associated with the formation of ridges on the surface along the [011] direction after only ~20 nm [9], with subsequent degradation associated with the formation of off-axis spots in the RHEED pattern, which coincide with a change of phase to the rocksalt crystal structure [8]. Therefore, growth of the ZnMgS structure was ended before the onset of the phase transformation was observed.

Figure 1 shows the experimental (400) rocking curve of the sample. The presence of fringes and well resolved diffraction peaks indicates that the material quality is good and has grown coherently on the GaAs substrate. The ZnMgS peak at 2200 arcsec has a FWHM of ~250 arcsec, which is also an indication that the crystalline quality is good. Simulations of the structure have been made using BEDE RADS software, with Zn$_{1-x}$Mg$_x$S compositions between $x = 0.88$ and 0.93 producing good fits to the experimental curve while compositions outside this range gave much poorer fits. In the simulations, the relaxation, $r$, of each layer can be varied, and we find that the upper Zn$_{1-x}$Mg$_x$S layer is partially relaxed, with $r$ being a function of $x$ and varying from $r = 0.6$ ($x = 0.93$) to $r = 0.4$ ($x = 0.88$).

A second series of structures of the form ZnSe(50 nm) / Zn$_{1-x}$Mg$_x$S / ZnSe(50 nm) was grown for XRI analysis, as was done previously on MgS [7, 8]. In XRI, a completely pseudomorphic structure behaves effectively as a Bragg interferometer, modifying the characteristic Pendellösung fringes in a way that is very sensitive to the chemical composition, the planar spacing, and the thickness of the central thin spacer layer [10]. 400 DCXRD rocking curves were obtained for these samples, and again the excellent resolution of the fringes fit almost exactly to the simulated spectrum for a range of compositions. Figure 2 shows the experimental data, with the simulation shown being the best match. This has a goodness of fit value of 0.07 and $x = 0.93$ (Figure 2(a)). However, simulations almost as good are possible with $x = 0.90$ and 0.88, and these are shown in Figures 3(a) and 3(b), respectively. The 400 XRI spectrum alone is unable to provide a unique solution within this composition range. Therefore, if a unique value is to
be determined for the ternary layer composition, further XRI analysis of reflections with a different planar spacing such as the 511 or 620 reflections, will be required [11].

The composition of the ZnMgS alloy was also determined from an analysis of a 60 nm-thick ZnMgS layer by using both SIMS and AES. The results show that in this ZnMgS layer, there is ~5% more Zn than in the corresponding MgS layers grown without an additional Zn flux. As the maximum Zn mole fraction present in the MgS is 2%, this is again consistent with an alloy of composition Zn_{0.07}Mg_{0.93}S.

Finally, the suitability of the compound for use as a barrier with ZnSe quantum wells was determined by using the 77 K PL measurements carried out on a series of single ZnSe quantum wells in structures of the form GaAs / ZnSe (buffer) 36 nm / Zn_{1-x}Mg_{x}S (barrier) 10 nm / ZnSe (QW, L_w) / Zn_{1-x}Mg_{x}S (barrier) 10 nm / ZnMgSSe (cap) 10 nm. The same growth temperature (240 °C) and flux ratios were maintained throughout the growth. Figure 4 shows PL spectra taken from two samples with values of L_w of (a) 10 nm and (b) 3 nm.

Excitation by the Ar-ion laser was at an energy below the bandgap of the barrier, and no barrier-related features were observed. Emission from the quantum wells in both these samples is intense and comparable with that of samples grown with MgS barriers. In the sample with the 3 nm wide well, the peak is broad, but is much narrower in the 10-nm-wide well. In both cases, the spectral width of the emission peaks is consistent with fluctuations of less than a monolayer at the interface and again is comparable to that of samples grown with MgS barriers [1].

III. CONCLUSION

Structures containing Zn_{1-x}Mg_xS have been grown lattice matched to GaAs by using MBE with ZnS as a source of S. DCXRD carried out on an ~60-nm-thick layer indicates that 0.88 ≤ x ≤ 0.93. This result is also obtained from XRI scans and is confirmed by both SIMS and Auger analyses carried out on the material. These results show that the crystalline quality of the material produced is excellent and that it has been grown coherently to the GaAs substrate and is single phased. PL spectroscopy shows high-intensity emission with a narrow FWHM, confirming the suitability of this alloy as a high-bandgap barrier material.

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REFERENCES