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Short-Period ZnTe-Zn(S, Te) Superlattices

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ZnTe-Zn(S,Te) short-period superlattices were grown on (001) GaAs substrates with very good structural quality. The growth conditions were found to be quite reproducible, leading to a series of samples with periods between 12 Å and 29 Å. Characterization of the samples with high resolution x-ray diffraction confirmed high structural quality showing that all samples were peudomorphically grown. The relaxation behavior was strongly influenced by the ZnTe well-width with two critical observed ZnTe-thicknesses.

Key words: MBE, high resolution x-ray diffraction, GaAs, relaxation, substrate, barrier

The II-VI semiconductor ZnSe has the same crystal structure and nearly the same lattice constant as GaAs and $Al_xGa_{1-x}As$, two of the semiconductors which form the bases of optoelectronic devices in the near-infrared and red spectral range. With ZnSe emitting blue to green, high quality light emitters and detectors are developed as well. Materials that are lattice matched to GaAs with energy gaps corresponding to the wavelengths between red and blue will allow one to cover the entire visible range with GaAs as substrate. One such material is ZnS_xTe_{1-x}. The combination of ZnS and ZnTe to a superlattice that is lattice matched to GaAs is thus of considerable interest for optoelectronic devices and efficient pin detectors with quantum efficiencies of up to 60% have already been fabricated (Faschinger et al. 1999).

In most ZnSe-based laser structures, mixed crystals containing selenium are used as p-cladding and contact materials (Morkoç et al. 1994). Because of their high p-dopability, tellurium-containing alloys and superlattices are possible candidates for p-claddings and contacts. Besides (Be, Zn)Te (Verie 1995, Walter et al. 1997), the only ternary alloy containing tellurium which can be grown-lattice matched on GaAs substrates is Zn(S, Te) (Fan et al. 1992). Earlier experiments on Zn(S, Te) mixed crystals show that this system has growth properties which are difficult to control especially when elemental sulfur is used as a source material. All of these earlier samples are of inhomogeneous composition and have much higher tellurium content at the surface than in the bulk (Korn et al. 1996). This could be attributed to tellurium diffusion to the surface while the much smaller sulfur atoms tend to remain in the bulk. Since transport measurements show that electrical transport takes place by hopping, the new Zn(S, Te) samples are grown as a superlattice using ZnS as a binary source material. Besides this technical aspect, this extremely strained superlattice system is also of basic interest because it is a strong type II quantum well structure with very high hole confinement (Petruzzello et al. 1996, Spahn et al. 1997). It can also serve as a model system to study growth mechanisms of extremely strained mixed crystals and superlattices.

This paper presents the growth techniques and characterization of the physical properties of ZnTe-Zn(S,Te) superlattices.

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Materials and Methods

A substrate temperature of 280°C was chosen in order to avoid tellurium clustering. This temperature was rather far from the ideal ZnS growth temperature of 150°C (Lang 1994). To determine if ZnS could be used as a barrier material at this substrate temperature, binary ZnS was deposited from a compound source, allowing the growth rate of ZnS at four different substrate-temperatures to be measured. Our group found from laser interferometric oscillations that the growth rate decreased from one angstrom per second (Å/S) at 150°C to 0.8 Å/S at 180°C to 0.18 Å/S at 220°C. No ZnS growth could be observed at 240°C. Since it was known that the optimum growth temperature was much higher for Zn(S, Te), our group decided to grow Zn(S, Te) barriers with low Te content instead of ZnS barriers.

A 200 nm-thick GaAs buffer was grown on (001) GaAs substrate in a III-V epitaxy-chamber after oxygen desorption. The sample was then transferred under ultra-high vacuum to a II-VI chamber. Here, a 20 nm-thick ZnSe buffer was deposited followed by a ZnTe-Zn(S, Te) superlattice structure. A series of lattice matched samples with intended periods of 12, 18, 24, and 30 angstroms were grown. The number of periods were chosen to be between 120 and 200 leading to total layer thickness of 200 nm to 400 nm. All considered samples are listed in Table 1.

The superlattices were grown under the same Zn-rich conditions since group II-rich conditions lead to the best results for Zn(S, Te) mixed crystals (Korn et al. 1996). Zn, Se, and Te were evaporated from elemental sources while ZnS was used in its compound form. A growth temperature of 280°C was chosen for all samples. The shutter opening times were varied to achieve lattice-matched samples with different periods. The beam fluxes were kept constant during the growth of the whole series.

ZnTe grown on GaAs substrates tend to relax immediately because of very high lattice mismatch. To circumvent this, one had to make the first ZnTe well only half as thick as the other ones. This first ZnTe well was then counter-strained by the succeeding Zn(S, Te)-barrier. All samples with a period larger than 20 Å were grown using this method.

All samples were characterized with high resolution x-ray diffractometry (HRXRD), using a Phillips X'Pert diffractometer. To determine the superlattice period, lattice constant, and the strain, omega - 2 theta scans were performed around the 004- and the asymmetrical 115-reflections of the GaAs substrate. To distinguish between mosaicity and inhomogeneity, omega scans around the (004)-reflex of the zero-order-satellite of the superlattice were carried out using a 220 four-crystal monochromator with an x-ray mirror on the incident side and a three-reflection 220 Ge analyser-crystal on the exit side of the diffractometer.

Results and Discussion

All samples turned out to be psedomorphic with respect to the GaAs substrate. The average mismatch of the layers with the substrate was between 0.34% to 0.47%. The full width at half maximum (FWHM) of the omega - 2 theta scan of the zero-order satellite varied between 52 arcsec and 280 arcsec, which corresponded approximately to the intrinsic finite thickness broadening for the first four samples. With the exception of sample 7, the FWHM in omega was 12 arcsec, corresponding to the substrate peak FWHM. The results of the x-ray measurements are summarized in Table 1.

The omega - 2 theta scan of sample 3 is shown together with a simulation in Figure 1a. Finite thickness oscillations coming from the ZnSe buffer can be observed. The simulation fits the measured peaks very well. These results show that the superlattice is of nearly ideal structural quality with well-defined interfaces. The simulation is found to have the best fit for a ZnTe-well thickness of 5.9 Å and a Zn(S, Te) barrier width of 19.2 Å with a sulfur content of 84.5% in the barrier. In Figure 1b, the omega - 2 theta scan of sample 3 is shown. On the left side of the zero-order satellite, two satellite peaks are observable, while

Table 1. Results of x-ray measurements.

Sample #	Number of Periods	Period (A)	Superlattice Thickness (A)	$\mathrm{FWHM}_{\mathrm{theo}}$ $\mathrm{Sat}_{0,\alpha\text{-}2\theta}$ (arcsec)	FWHM $\mathrm{Sat}_{0,\alpha\text{-}2\theta}$ (arcsec)	FWHM $\mathrm{Sat}_{0,\alpha}$ (arcsec)	Total Mismatch Sat_0(%)	ZnTe Thickness (A)	Period Variation (A)
1	200	12.6	2520	66	74	12	0.47	3.2	
2	200	16.1	3220	52	56	12	-0.38	5.2	0.32 ± 0.15
3	150	24.9	3735	46	52	12	-0.32	5.9	0.33 ± 0.15
4	150	24.5	3675	46	52	12	-0.34	5.9	
5	120	24.2	2904	58	110	12	-0.29	6.9	0.48 ± 0.15
6	120	24.2	2904	58	169	12	0.30	7.5	0.37 ± 0.15
7	120	28.7	3444	49	280	12	0.25	8.6	0.37 ± 0.15

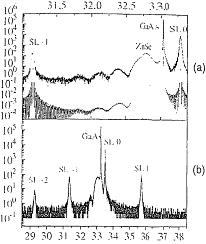

Figure 1. Upper plot: Omega-2 theta scan of sample 3 and its simulation (fine line). Lower plot: The whole omega - 2 theta scan of the same sample.
Legend: SL - satellite peaks

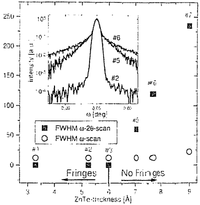

Figure 2. FWHM of the zero-order satellite in q_z direction and in q_x direction as a function of the ZnTe-well width. The inset shows the omega scans of samples 2, 3 and 6.

on the right side only one satellite is visible. In most samples, four satellite peaks are obtained. However, sample 1 with the shortest period and sample 4 which was nitrogen-doped exhibited only three satellite peaks. The broadening of the satellite peaks with increasing order can be used to estimate the period variation (Fewster, 1988). The period variation of the superlattices is found to be between 0.32 to 0.48 Å.

The omega – 2 theta FWHM of the zero-order peak increases significantly with increasing periods. To make this evident, the omega – 2 theta FWHM (Fig. 2) of the zero-order satellite minus the intrinsic broadening coming from the finite thickness of the layer is plotted versus the ZnTe-thickness as determined by multiplying the growth time of the ZnTe well by the calibrated Te flux as indicated in the Bayart-Alpert gauge (Korn et al. 1999). The omega FWHM of the zero-order satellite is also plotted in Figure 2. It turns out that for a ZnTe-well thickness of more than 6 Å, the omega – 2 theta FWHM of the zero-order satellite increases strongly while the broadening in omega remains constant at 12 arcsec. These samples also show no finite thickness fringes. A broadening in the q_x-direction is only observed for a ZnTe thickness of more than 8 Å. The inset of Figure 2 shows the omega-scans of samples 2, 5 and 6. One can see that with increasing well width, the mosaic background increases, too. While the diffused background of sample 2 is 3.5 orders of magnitude below the peak intensity, it is only one order of magnitude below the maximum in samples 5 and 6 which had a ZnTe width of 6.9 and 7.5 Å, respectively. These results confirm that the crystalline perfection of the entire epitaxial layer strongly depends on the thickness of the ZnTe-well width. In fact, the system seems to be characterized by two critical thicknesses. The samples with a ZnTe-well width below 6 Å are of perfect crystalline quality: they show finite thickness oscillations and the FWHM both in the q_x and q_z direction are intrinsic. Samples with a ZnTe-well width higher than the first critical thickness of 6 Å but below the second critical thickness of 8 Å are broadened in q_z but intrinsic in q_x with an increased diffused scattering in this direction. This means that while the mosaicity in these samples is still very small, they are inhomogeneous in composition. The most probable interpretation for this behavior is the formation of ZnTe islands, so that a certain amount of strain can be relaxed elastically without formation of misfit dislocations. Finally, the sample with a ZnTe-well width higher than 8 Å shows a mosaic broadening, indicating the onset of plastic relaxation by the formation of dislocations. This conventional critical thickness is somewhat smaller than the value of four monolayers reported for ZnTe on GaAs (Etgens et al. 1992), especially if one considers that as ZnTe is counterbalanced by Zn(S, Te), the critical thickness increases.

Two additional factors influence this relaxation behavior. Firstly, there is a difference between compressive and tensile average strain: samples 5 and 6 have the same period length, the same total thickness and the same mismatch but the strain is tensile in sample 5 and compressive in sample 6. As a consequence, the omega – 2 theta FWHM of sample 6 is about 50% larger and the background in q_x direction is significantly higher. Secondly, nitrogen doping also influences the onset of relaxation. Even as samples 3 and 4 were grown under the same conditions, sample 4 was doped with nitrogen coming from a nitrogen plasma source. The table shows that both samples have the same structure. The difference between the samples can only be revealed by comparing their respective omega scans. The FWHM of both samples is 12 arcsec but the mosaic background of sample 4 is much higher.

Summary

The results show that short period ZnTe-Zn(S, Te) - superlattices can be grown on GaAs substrates with high structural quality and reproducibility. The ZnTe well thickness is the crucial factor for growing samples of perfect crystalline quality. In fact, one can observe two critical ZnTe-well widths, 6 and 8 Å. Six (6) Å-width determines the starting point for crystal inhomogeneity and eight (8) Å-width determines the formation of dislocations. The relaxation behavior is additionally influenced by the amount of the average strain in the sample and the incorporation of nitrogen.

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