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Growth and characterization of $Zn_{1-x}Mn_xTe$ epilayers grown by hot wall epitaxy on (001)GaAs substrates

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In this letter we report the first growth of $Zn_{1-x}Mn_xTe$ epitaxial films. The films were grown by hot wall epitaxy on 2° misoriented (001) GaAs substrates up to a Mn concentration of 70%. The Mn content was determined by optical reflection and x-ray diffraction. All the epilayers ($0.0 \leqslant x \leqslant 0.7$) grew in the [001] direction in the zinc-blende structure. The full width at half maximum of the (004) reflex of the x-ray rocking curves proved the good crystalline quality of the grown layers and increased monotonically as the Mn content increased. The relative tilt between epilayer and substrate was also determined from high resolution x-ray diffraction.

$Zn_{1-x}Mn_xTe$ belongs to a class of materials called diluted magnetic semiconductors (DMS). In these crystals, the Mn magnetic ion substitutes the Zn cation in the semiconductor compound, creating a ternary alloy which offers possibilities of lattice matching and band-gap tunability. In addition, the exchange interaction between the magnetic moments of the Mn ions and the band electrons of the host semiconductor leads to a number of magneto-optic and magnetotransport effects such as large Zeeman splitting and giant Faraday rotation.[1]

Recently, the growth of DMS epitaxial films allowed the investigation of such magnetic effects also in quantum well (QW) systems and superlattices (SL) consisting of these DMS materials.[2] Among the wide-gap DMS materials, epitaxial films of $Cd_{1-x}Mn_xTe$ (Ref. 3) and $Zn_{1-x}Mn_xSe$ (Ref. 4) as well as QWs and SLs composed of both systems[5,6] have been grown successfully. However, to our knowledge, the growth of $Zn_{1-x}Mn_xTe$ epitaxial films has not been reported so far. High quality crystalline $Zn_{1-x}Mn_xTe$ epilayers are required in order to produce the desired QW and SL from this alloy system. $Zn_{1-x}Mn_xTe$ bulk crystals have been grown in the zinc-blende structure up to a composition of $x \cong 0.80$ but good quality crystals were only obtained for low x values ($x \leqslant 0.10$). For higher x values the crystal quality deteriorates and the ingot consists of relatively small crystals presenting frequently twinning problems.[7]

$Zn_{1-x}Mn_xTe$ epilayers were grown using the hot wall epitaxy (HWE) technique.[8] The HWE reactor was modified by placing the Mn source between the ZnTe source and the substrate. A special oven was constructed to achieve the desired Mn source temperatures. The HWE reactor was mounted in a vacuum chamber with a background pressure of 5×10^{-7} Torr during growth.

The substrates used were [001] oriented semi-insulating undoped GaAs with a misorientation of 2° towards the next [011] direction. Following results of previous experiments on ZnTe growth,[9] the substrates were preheated at 600 °C during 17 min prior to the growth in order to desorb the oxide layer.

The substrate temperature was kept constant at 400 °C during the growth. The ZnTe source temperature was varied between 530 and 550 °C leading to growth rates between 1 and 3 μm/h. The thickness of the layers was measured from interference fringes in the transmission spectra obtained in a Fourier spectrometer and ranged from 4 to 11 μm. The Mn source temperature was varied from 800 to 900 °C in order to provide the various Mn mole fractions.

The Mn concentration of all the grown $Zn_{1-x}Mn_xTe$ epilayers was determined by two different methods: from optical reflection measurement near to the fundamental absorption edge and from the lattice constant determined by x-ray diffraction.

Reflection measurements were made using a Bruker IF66 Fourier spectrometer with a resolution of 2 cm^{-1} equipped with a reflection kit. Figure 1 shows the reflectivity spectra at 300 K for samples with selected Mn compositions. To determine the Mn mole fraction, the linear relation $E(x)=E(0)+0.518x$ (eV) obtained for the energy gap of $Zn_{1-x}Mn_xTe$ ($0.0 \leqslant x \leqslant 0.6$) bulk crystals was used.[10] The energy values $E(x)$ corresponding to the energy gap of the $Zn_{1-x}Mn_xTe$ epilayers were determined by the point where the interference fringes cease, indicated by arrows in Fig. 1. For the energy gap of ZnTe, we use the mean value $E(0)=2.250 \pm 0.004$ eV obtained from measurements on various ZnTe epilayers.

X-ray diffraction spectra were recording using Cu $K\alpha$ radiation with a standard goniometer. Figure 2 shows the $\theta/2\theta$ scans of the (004) reflex of the $Zn_{1-x}Mn_xTe$ epilayers with different Mn compositions together with the respective (004) reflex of the GaAs substrate. The lattice constants were determined from the angular distance between the epilayer and the substrate (004) reflex using the (004) GaAs $K\alpha_1$ peak as a reference to avoid offset problems. The Mn atomic composition of the layers was determined using the relation for the lattice constant of $Zn_{1-x}Mn_xTe$ bulk crystals: $a(x)=6.102+0.2376x$ (Å).[7]

The x values obtained from reflectivity measurements and from x-ray diffraction for representative $Zn_{1-x}Mn_xTe$ samples are listed in Table I. The difference between both x values remains within 0.02 for samples with a Mn concentration $x \leqslant 0.2$ increasing up to 0.07 for samples with higher Mn concentration ($x=0.6$). This agreement indi-

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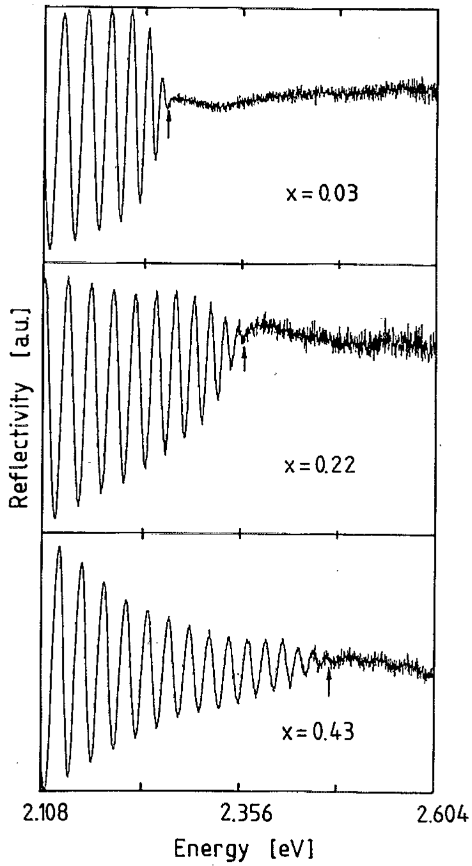

FIG. 1. Reflectivity spectra of three $Zn_{1-x}Mn_xTe$ epilayers at 300 K. The arrows indicate the point where the interference fringes cease. This photon energy is used to determine the x values.

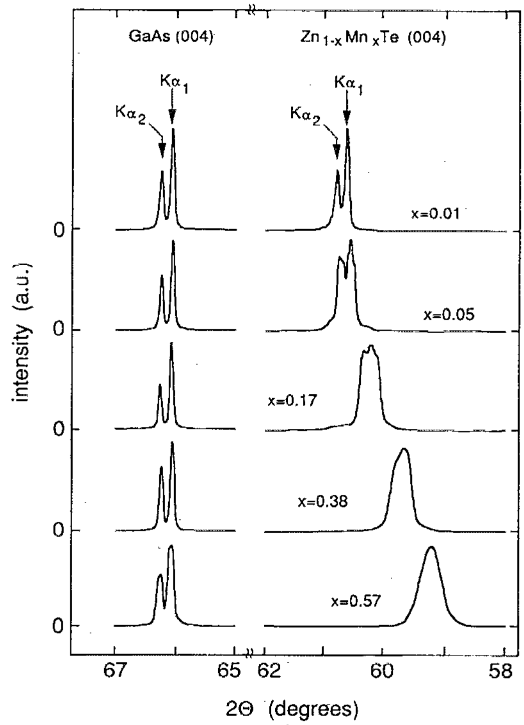

FIG. 2. $\theta/2\theta$ scans of the (004) reflex of the $Zn_{1-x}Mn_xTe$ epilayers and respective GaAs substrate.

cates that the x dependence of the energy gap and the lattice constant obtained for bulk crystal can also be applied for the $Zn_{1-x}Mn_xTe$ epilayers.

X-ray diffraction analysis also showed that the epilayers were monocrystalline and grew in the [001] direction in the zinc-blende structure with no indication of any other crystallographic orientation or any other phase for the whole range of Mn composition studied ($0.0 \leqslant x \leqslant 0.7$). As shown in Fig. 2, with increasing Mn composition of the $Zn_{1-x}Mn_xTe$ epilayers the lattice mismatch to the GaAs substrates increases and the $K\alpha_{1\text{-}2}$ doublet becomes less pronounced. For $x \geqslant 0.4$ it cannot be resolved any more.

In order to investigate the crystalline quality of the samples, high resolution x-ray diffraction was also performed using a high resolution goniometer with independent ω and 2θ drivers equipped with a four-crystal Ge monochromator. X-ray rocking cures were measured for all the $Zn_{1-x}Mn_xTe$ epilayers and the full width at half maximum (FWHM) of the (004) Bragg reflex was used as a criterion for the crystalline quality of the epilayers. The line shapes of the rocking curves were single Gaussian-like peaks.

Figure 3 shows the FWHM of the (004) reflex as a function of the Mn atomic composition for epilayers with thicknesses varying from 4 to 6 μm. The lattice misfit between the epilayer and the substrate $f(x) = [a^L(x) - a^S]/a^S$, where $a^L(x)$ and a^S are the bulk lattice constants of $Zn_{1-x}Mn_xTe$ and GaAs, respectively, is also represented in Fig. 3. The FWHM of $Zn_{1-x}Mn_xTe$ epilayers increases monotonically with increasing Mn atomic concentration. The increasing lattice misfit and the Mn incorporation in the crystal lattice are the two factors which contribute to this behavior. The lattice misfit between substrate and epilayer produces dislocations in the epilayer and the FWHM of the rocking curve is very sensitive to these extended crystal defects. Since the number of dislocations increases with increasing lattice misfit, an increase in the FWHM is expected as the Mn content increases. It is also known from $Zn_{1-x}Mn_xTe$ bulk crystal growth that the incorporation of Mn atoms in the crystal lattice deteriorates the crystalline quality. Good quality bulk crystals have only been obtained for low values of x ($x \leqslant 0.10$). For higher x values, the ingots consisted of small crystals presenting also twinning problems.[7] As a term of comparison, we refer here to the FWHM of the (004) reflex of $Zn_{1-x}Mn_xSe$ epilayers grown on (001) GaAs substrates by molecular beam epitaxy[11] which increases from 160 arcsec for $x = 0.0$ to 1050 arcsec for $x = 0.31$. Considering that the lattice misfit in the $Zn_{1-x}Mn_xSe$/GaAs heterostructure (it increases from 0.3% for $x = 0.0\%$ to 1.6% for $x = 0.31$) is much smaller than in the case of $Zn_{1-x}Mn_xTe$/GaAs, our results show that relatively good $Zn_{1-x}Mn_xTe$ epilayers can be grown on GaAs substrates despite the large lattice misfit.

A relative tilt between epilayer and substrate lattice planes, $\Delta\alpha$, has been observed in lattice mismatched heterostructures grown on misoriented substrates with a miscut angle α.[12] By means of high resolution x-ray diffraction

TABLE I. Thickness, the x values obtained from reflection measurements (x_{RM}), x-ray diffraction (x_{XD}), and high resolution x-ray diffraction (x_{HRXD}) and the relative tilt between epilayer and substrate lattice planes obtained from HRXD with the x-ray beam parallel ($\Delta\alpha_{PL}$) and perpendicular ($\Delta\alpha_{PD}$) to the substrate miscut direction of representative $Zn_{1-x}Mn_xTe$ layers.

Sample	Thickness (μm)	x_{RM} ± 0.006	x_{XD} ± 0.005	x_{HRXD}	$\Delta\alpha_{PL}$ (deg.)	$\Delta\alpha_{PD}$ (deg.)
hwe 81	9.5	0.020	0.025	0.027	0.03	0.11
hwe 77	7.1	0.051	0.049	0.046	0.14	0.04
hwe 71	4.9	0.086	0.071	0.086	0.07	0.06
hwe 92	10.6	0.157	0.175	0.208	0.03	0.11
hwe 74	5.0	0.201	0.247	0.214	0.09	0.06
hwe 79	4.0	0.38	0.431	0.463	0.19	0.23
hwe 84	4.2	0.50	0.57	0.60	0.32	0.33

(HRXD) with independent ω and 2θ drives, the relative tilt as well as the epilayer Bragg angle and hence the lattice constant can be determined measuring the angular separation between epilayer and substrate Bragg reflections in at least two opposite directions.[12] The lattice constant of representative $Zn_{1-x}Mn_xTe$ samples was measured using the angular separation between epilayer and substrate (004) Bragg reflections and taking the GaAs (004) Bragg angle as a reference. The Mn content of the samples were calculated using the above cited relation for bulk $Zn_{1-x}Mn_xTe$ crystals and the values are listed in Table I. As can be seen in this table, the difference between these x values and the ones obtained from θ-2θ scans using the standard goniometer remains within 0.03. The relative tilt $\Delta\alpha$ of these samples was also determined with the x-ray beam parallel ($\Delta\alpha_{PL}$) and perpendicular ($\Delta\alpha_{PD}$) to the substrate miscut direction. The results are given in Table I. The relative tilt $\Delta\alpha_{PD}$ is expected to be approximately zero, i.e., the direction of maximum relative tilt is expected to be parallel to the direction of substrate miscut. However, a rotation in the direction of the maximum relative tilt in relation to the substrate miscut direction has been observed for heterostructures with large lattice misfit such as the case of $Zn_{1-x}Mn_xTe$/GaAs.[12] This rotation explains why $\Delta\alpha_{PD}$ was higher than zero in some samples and that it was even higher than $\Delta\alpha_{PL}$ in other samples. It is to be noted from the table that the relative tilt increases as the Mn content increases, according to the published data in which the maximum relative tilt between epilayer and substrate increases as the lattice misfit increases.[12]

In order to test the lateral homogeneity of the Mn atomic composition, the lattice constant was measured using HRXD in different spots along the diagonal of a sample with $x=0.08$ and the Mn content was calculated. The measurement showed a maximum deviation in the Mn content x of 0.0016 indicating the excellent homogeneity of the grown epilayers.

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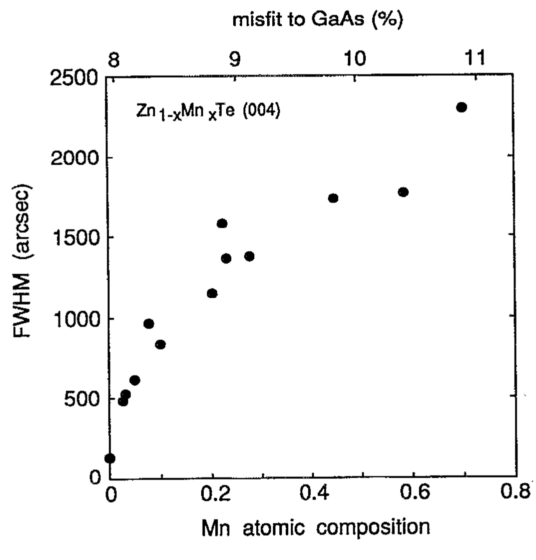

FIG. 3. FWHM of the (004) reflex of x-ray rocking curves as a function of the Mn content. The lattice misfit is also represented in this figure.

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