Proceedings of the XXV International School of Semiconducting Compounds, Jaszowiec 1996

MBE GROWTH AND PROPERTIES OF ZnYbTe LAYERS

J. SADOWSKI, K. SZAMOTA-SADOWSKA, K. ŚWIĄTEK, L. KOWALCZYK

Institute of Physics, Polish Academy of Sciences Al. Lotników 32/46, 02-668 Warszawa, Poland

A. Abounadi and A. Rajira

Université Montpellier 2, Place E. Bataillon, Montpellier, France

The MBE grown ZnYbTe layers were characterized by X-ray diffraction, photoluminescence and reflectivity measurements. The MBE growth conditions allowing to obtain monocrystalline ZnYbTe layers were found to be metal-rich (MBE growth with excess of Zn flux). In optical measurements (photoluminescence, reflectivity), both transitions connected with ternary ZnYbTe compound and with Yb³⁺ ions were detected. The quality of ZnYbTe layers with Yb content of 3% and 1% is inferior to the quality of pure ZnTe MBE layers, which is clearly seen in the results of photoluminescence and reflectivity measurements. In the ZnYbTe layers with 3% Yb, exhibiting monocrystalline character in reflection high-energy electron diffraction and X-ray diffraction measurements, optical transitions characteristic of pure YbTe were detected. In ZnYbTe layers with 1% Yb, no transitions connected with YbTe were observed.

PACS numbers: 81.15.Gh, 61.14.Hg

1. Introduction

Because of different crystallographic structure of II-VI (zinc blende) and rare earth (RE) tellurides (rock salt) it is difficult to obtain ternary II-RE-Te alloys. Bulk crystal growth methods allow one to obtain II-VI compounds doped with rare earth elements with Re concentrations of $10^{17}-10^{20}$ cm⁻³ [1]. Using MBE crystallization technique it is possible to obtain monocrystalline layers of RE alloyed II-VI compounds with RE concentrations of a few percent [2]. We present here the properties of MBE grown ZnTe layers alloyed with Yb, with Yb content of 1% to 3%. The solubility limit of Yb in ZnTe was evaluated previously [2] to be about 3%.

2. MBE growth of ZnYbTe layers

MBE growth processes were performed in a two chamber MBE growth system manufactured in the Institute of Physics of the Polish Academy of Sciences in Warsaw. As substrates the Freiberger epi-ready, semi-insulating GaAs(100) wafers, 2° off-oriented towards [011] direction were used. After the thermal oxide desorption by heating to 585°C the substrates were cooled to the ZnTe buffer growth temperature (320°C) in Zn flux. The MBE growth of ZnTe buffers and ZnYbTe layers was performed in Te-rich (sample 1), or Zn-rich conditions (samples 2, 3 and 4). The parameters of samples are listed in Table. The excess of Zn or Te flux

TABLE

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| Sample No. | ZnTe buffer | ZnYbTe | ZnTe cap layer | Yb content | Growth |
|------------|-----------------|-------------|----------------|------------|-----------------------------|
| | thickness | thickness | thickness | | $\operatorname{conditions}$ |
| 1 | $1.5~\mu{ m m}$ | $1 \ \mu m$ | 0 | 3% | Te-rich |
| 2 | $3.5 \ \mu m$ | 100 Å | 1800 Å | 1% | Zn-rich |
| 3 | $1.5 \ \mu m$ | 100 Å | 1200 Å | 1% | Zn-rich |
| 4 | $1.5 \ \mu m$ | 1200 Å | 0 | 3% | Zn-rich |

Parameters of ZnYbTe layers crystallized on the GaAs(100) substrates.

was controlled by choosing the value of Te/Zn flux ratio for which the (2×1) Te or $c(2 \times 2)$ Zn reconstruction of the ZnTe buffer layer surface was observed. As the MBE growth temperature of ZnTe and ZnYbTe, the optimal temperature for growth of ZnTe MBE layers was chosen (about 320°C). For all the samples the streaky reflection high-energy electron diffraction (RHEED) patterns were observed after growing the first 600 Å of ZnTe buffer. During the ZnYbTe growth in Te-rich conditions, the streaky RHEED patterns turned to the spotty ones after growing of about 100 Å thick ZnYbTe and when the film thickness increased, the diffraction picture typical of textured layers was observed during the whole growth process.

3. X-ray diffraction measurements

All samples were measured by X-ray diffraction system with Cu $K_{\alpha_1}K_{\alpha_2}$ incident beam. Sample 1 was measured in the polycrystalline scan mode, samples 2, 3, 4 in rocking curve configuration. Sample 3 was also measured by the 4-crystalline diffractometer. For sample 1 the broad diffraction peak connected with ZnYbTe was observed, with additional peak resulting from pure YbTe rock-salt phase. In the case of samples 2, 3 and 4 only diffraction peaks from ZnTe buffer layers were seen (due to the small thickness and little difference between ZnTe and ZnYbTe lattice constants). The full width at half maximum of 400 Bragg reflection from 1.5 μ m thick ZnTe buffer of sample 3 was about 200 arc s, which indicates a good quality of ZnTe/GaAs(100) buffer.

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4. Optical measurements

The photoluminescence (PL) experiments were performed using a doublegrating GDM-1000 monochromator and EMI 9558 S20 photomultiplier. Investigated samples were mounted in a Leybold closed-cycle cryostat and illuminated by 458, 488 or 514 nm lines of an Ar laser. Figure 1 shows a comparison of PL spectra



Fig. 1. Low temperature PL spectrum of ZnYbTe layers: (a) 1200 Å thick $Zn_{0.97}$ Yb_{0.03}Te — sample 4, (b) 100 Å thick $Zn_{0.99}$ Yb_{0.01}Te — sample 3.

of two ZnYbTe layers: (a) sample 3, (b) sample 4, with different thicknesses and Yb concentration, measured at 10 K under 488 nm laser light excitation. A set of narrow emission peaks in the energy range 2.35–2.4 eV was detected. The near band-gap luminescence of ZnYbTe/ZnTe (sample 3) structures exhibits a weak free exciton PL split into a heavy- and light-hole exciton at 2.385 and 2.378 eV, respectively. This splitting is probably caused by strain. We assign a set of three sharp PL peaks in the energy range 2.35-2.375 eV to recombination of excitons bound to neutral acceptors. A strong luminescence at approximately 2.372 eV is most probably related to recombination of nitrogen bound exciton. The strong and wide emission with maximum at ≈ 2.3 eV, seen in both samples (Fig. 1a, 1b), comes from the ZnYbTe layer. Its energy is situated between band-gap energy of pure ZnTe (2.396 eV) and YbTe (1.97 eV) crystals. Large inhomogeneous broadening of this emission indicates a significant fluctuations of Yb concentration present in the investigated ZnYbTe layers. Moreover, in infrared region of PL spectra of some samples we have found a weak emission at ≈ 1.27 eV related most probably to the Yb³⁺ $4f^{13}({}^{2}F_{5/2} - {}^{2}F_{7/2})$ intra-ion transition.

At high excitation power density (using 3rd harmonic of Nd:YAG laser) a remarkable shift of the PL signal connected with ZnYbTe (wide maximum about 2.3 eV), towards higher energies was observed.



Fig. 2. Room temperature reflectivity of MBE grown ZnTe and 1200 Å thick $Zn_{0.97}$ Yb_{0.03} Te layer — sample 4.

Figure 2 presents the room temperature (RT) reflectivity spectra obtained for energies in the range 1.5-12 eV for pure ZnTe and ZnYbTe (sample 4) layer. The details of the detection system are given elsewhere [2]. The results are presented in the sequence which allows one to compare spectra obtained for ZnTe and ZnYbTe. The reflectivity peaks were labeled as: E_1 at 3.53 eV, $E_1 + \Delta_1$ at 4.101 eV, E_2 at 5.5 eV, E'_1 at 6.8 eV, $E' + \Delta$ at 7.52 \pm 0.2 eV, A at 9.5 eV and a at 11.26 eV. Maxima E_1 and $E_1 + \Delta_1$ were assigned to transition in Λ direction in Brillouin zone [3]. The E_2 maximum was attributed [3] to the transition at the X point in Brillouin zone and E' as well as $E'_1 + \Delta$ were attributed [3] to the transitions at the L point. In the case of ZnYbTe layer (sample 4), the transition at the X point is marked by A_1 [4]. The experimental values of these maxima are in accordance with the published ones. A significant change in behavior of the ZnYbTe spectrum in comparison to the pure ZnTe can be seen. For ZnYbTe, the shoulder appears between 3 and 4 eV. It can be caused by two effects: the transition observed for pure YbTe in this energy region [5], or the transition visible for ZnTe at 3.53 eV. The peak marked as A can be assigned to the transition characteristic of pure YbTe [4]. It seems that the peak named B is connected with the same transition as the one named E_2 for ZnTe. The *a* peak detected for ZnYbTe is also similar to the same peak observed in the case of ZnTe.

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The important effect observed for measured ZnYbTe samples was the decrease in the reflectivity signal. As we know, in the UV energy region decay of the oscillator strength of the valence to conduction band transition [4] takes place, on the other hand, RE atoms usually occupy more than one type of the site in zinc blende crystal lattice [5]. Therefore the decrease in reflectivity is probably caused by these two effects.

5. Discussion

In the case of ZnYbTe films with 3% Yb, optical transitions characteristic of pure YbTe rock-salt phase were detected for both films grown in Zn-rich and in Te-rich conditions. However, during MBE growth process the streaky RHEED patterns, indicating smooth monocrystalline ZnYbTe surface, were observed only for layers grown in the Zn-rich conditions. In the case of sample 3, the heavy hole (hh)-light hole (lh) exciton recombination energy splitting of the ZnYbTe cap layer was observed, which indicates that this layer is partially strained. As the thickness of ZnYbTe layer is only 100 Å in this case and the lattice constant difference between ZnTe and ZnYbTe with 1% Yb is very little (about 0.002 Å), the strain is already present in 1.5 μ m thick ZnTe buffer (it is known from literature: e.g. [6] that even about 3.5 μ m thick ZnTe layers crystallised on GaAs substrates are still not strain-free). The well-resolved lh-hh exciton lines of the 1800 Å thick ZnTe cap layer prove the high quality of the whole structure (ZnTe buffer/100 Å thick ZnYbTe layer/1800 Å thick ZnTe cap).

6. Conclusions

The monocrystalline ZnYbTe films with Yb concentrations up to 3% can be grown by MBE in Zn-rich conditions. In the films with 3% Yb content the optical transitions characteristic of pure YbTe were observed. In the 100 Å thick ZnYbTe layers with 1% Yb no traces of YbTe inclusions were found, however the quality of the layers estimated by optical methods is inferior to the quality of pure ZnTe layers. XRD measurements and RHEED diffraction pictures showed a much better crystalline quality of ZnYbTe layers grown in Zn-rich conditions in comparison to the layers grown in Te-rich conditions, however in RT reflectivity and low temperature PL measurements no big differences between these layers were observed. In all the layers weak PL signal connected with Yb³⁺ ion transitions was detected.

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