Epitaxial growth of ZnMgTe with a wide composition range on ZnTe substrate by molecular beam epitaxy

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Abstract. Zn1-xMgxTe layers with a wide composition range of 0 ≤ x ≤ 0.66 were grown on ZnTe (001) substrates by molecular beam epitaxy. Zn1-xMgxTe epitaxial layers with Mg composition below 0.66 have a zincblende structure, suitable for fabrication of LED. Strained pseudomorphic epitaxial layer is obtained at the Mg composition x up to 0.05. Mg composition in epitaxial layer was controlled by the flux ratio of Mg/(Zn+Mg), but it was also affected by the flux ratio of Te/(Zn+Mg).

1. Introduction

ZnTe is expected as a promising material for a variety of optoelectronic devices such as pure green light emitting devices because of its direct transition band gap of 2.26 eV at room temperature. This material can be doped in p-type easily, but the n-type doping was difficult due to so-called self-compensation effects. Recently, several techniques including metalorganic vapor phase epitaxy (MOVPE) [1,2], molecular beam epitaxy (MBE) [3,4], and Al thermal diffusion [5,6], have overcome the difficulty, and pure green light emitting diodes (LEDs) based on ZnTe have been realized [5,6]. In order to increase an external quantum efficiency of the LED, it is essential to fabricate single hetero or double hetero structure using an adequate cladding layer material with larger band gap than ZnTe, leading to an increase in the radiative recombination efficiency by confined carriers and the light extraction efficiency by higher transmittance against the emitted light.

Among several materials, Zn1-xMgxTe ternary alloy is one of the best candidates for the cladding layer of ZnTe LED since it has a wider band gap than ZnTe and expects to form type-I heterostructure with ZnTe [7,8]. Since ZnTe has a zincblende structure while MgTe a wurtzite structure, the crystal structure of Zn1-xMgxTe is changed depending on the Mg composition x in the growth under the thermal equilibrium condition. The epitaxial growth under a non-equilibrium condition such as MBE and MOVPE often results in phase modification. For fabricating LED on ZnTe substrate, Zn1-xMgxTe is desired to have a zincblende structure as same as the substrate. The epitaxial growth of Zn1-xMgxTe has been investigated using GaAs, InAs, and CdZnTe as the substrate, but there are no reports on ZnTe substrate except for ours in which the Zn1-xMgxTe (0 ≤ x ≤ 0.3) was grown by MOVPE [9]. In this study, we have grown Zn1-xMgxTe epitaxial layers with a wide Mg composition range of 0 ≤ x ≤ 0.66 on ZnTe (001) substrate by MBE.
2. Experiments
The epitaxial growth was carried out using solid-source MBE system. The background pressure of the growth chamber is less than $3 \times 10^{-8}$ Pa. ZnTe (001) substrates were cleaned ultrasonically by organic solvents, and etched in a 1% Br-methanol solution and HF-distilled ionized water solution. In order to remove the native oxide and the contamination from the surface of ZnTe substrate, \textit{in-situ} H radical cleaning was performed at room temperature before the growth. In the growth, a low-temperature ZnTe buffer layer was grown at 250 °C for 5 min, followed by the growth of Zn$_{1-x}$Mg$_x$Te layer at 350 °C for 60 min. In this study, the Mg/(Zn+Mg) flux ratio was changed between 0 and 0.26 under the Te/(Zn+Mg) flux ratio of 1. Also, Te/(Zn+Mg) flux ratio was changed between 0.60 and 1.44 under the Mg/(Zn+Mg) flux ratio of 0.02.

During the growth, a reflection high-energy electron diffraction (RHEED) pattern was observed. High-resolution X-ray diffraction (HR-XRD) analysis was performed using a Philips X'pert XRD system equipped with a beam monochromator consisting of a four-bounce Ge (220) crystal and X-ray mirror in the primary optics, and a secondary optics with a three-bounce Ge analyzer crystal between the sample and the detector. The in-plane lattice parameter, $a_{||}$, and that in growth direction, $a_{\perp}$, were calculated by the $\omega$-2$\theta$ scans of symmetrical 004 and asymmetrical 224 reflections.

3. Results and discussion
Figure 1 shows in-plane lattice parameter, $a_{||}$, and that in growth direction, $a_{\perp}$, of Zn$_{1-x}$Mg$_x$Te epitaxial layer against the flux ratio of Mg/(Zn+Mg) under the Te/(Zn+Mg) flux ratio of 1. The Zn$_{1-x}$Mg$_x$Te epitaxial layers grown at high Mg/(Zn+Mg) flux ratio above 0.10 decomposed quickly by hydration just after exposing in air, probably due to the high Mg composition, and could not be characterized. The unstrained lattice parameter, $a_{\text{relax}}$, was calculated according to the formula

$$a_{\text{relax}} = \frac{a_{\perp} + 2(c_{12}/c_{11})a_{||}}{1 + 2(c_{12}/c_{11})}, \quad (1)$$

where $c_{11}$ and $c_{12}$ are the elastic coefficients of the material. For ZnTe, the elastic coefficients ratio is given by ($c_{12}/c_{11}$)$_{\text{ZnTe}} = 0.57$ [10], while ($c_{12}/c_{11}$)$_{\text{MgTe}} = 0.53$ for MgTe [11]. Since Mg composition of the layer is expected to be not so high, we used the elastic coefficients ratio for ZnTe in the calculation. The unstrained lattice parameter, $a_{\text{relax}}$, is also indicated in figure 1. With increasing the flux ratio of Mg/(Zn+Mg), the unstrained lattice parameter is increased proportionally. The variation of the lattice parameter $a$ with Mg composition $x$ is described by the following equation

$$a = 6.1026 + 0.36x, \quad (2)$$

that was obtained by using the Zn$_{1-x}$Mg$_x$Te bulk crystals [7]. The relationship between the flux ratio of Mg/(Zn+Mg) and Mg composition $x$ of Zn$_{1-x}$Mg$_x$Te layer is shown in figure 2. The Mg composition $x$ is increased linearly with increasing the flux ratio of Mg/(Zn+Mg), indicating the ability to control the Mg composition by the flux ratio of Mg/(Zn+Mg) under the constant flux ratio of Mg/(Zn+Mg).
Te/(Zn+Mg). It should be noted that the Mg composition $x$ was also affected by the flux ratio of Te/(Zn+Mg) under the constant flux ratio of Mg/(Zn+Mg), as shown in Figure 3. Mg composition $x$ is decreased with increasing the flux ratio of Te/(Zn+Mg). In the case of MOVPE growth of Zn$_{1-x}$Mg$_x$Te, similar decrease of Mg composition was observed when the transport rate of diethyltelluride (DETe) was increased, that was speculated to be associated with the premature reaction between DETe and bis-methylcyclopentadienyl-magnesium ((MeCp)$_2$Mg) in gas phase [9]. In the MBE growth, since the mean free path of gas molecules is much larger than that in the case of MOVPE, the occurrence of similar reaction is unlikely. Instead, the surface reaction, such as the desorption or the re-evaporation of Mg, may be enhanced by increasing the flux ratio of Te/(Zn+Mg) although the detailed study is necessary to clarify the mechanism.

Figure 4 (a), (b), and (c) show the RHEED patterns for Zn$_{1-x}$Mg$_x$Te epitaxial layer with $x=0.12$, 0.24, and 0.66, respectively. In the Zn$_{1-x}$Mg$_x$Te layer with $x \leq 0.24$, the streak patterns are observed while the Zn$_{0.34}$Mg$_{0.66}$Te layer shows the spot pattern, indicating the surface of the epitaxial layer becomes rough by increasing of Mg composition. No other spots except for those from Zn$_{1-x}$Mg$_x$Te with zincblende structure were observed, and therefore, Zn$_{1-x}$Mg$_x$Te epitaxial layer on ZnTe (001) substrate is found to crystallize in zincblende structure when the Mg composition $x$ is below 0.66.

In figure 1, the in-plane lattice parameter of the Zn$_{1-x}$Mg$_x$Te layer grown at low Mg/(Zn+Mg) flux ratio is in good agreement with that of the ZnTe substrate, implying that the epitaxial layer is fully strained. In order to examine the strain state of the epitaxial layer more clearly, the reciprocal lattice maps around the asymmetrical (224) reflection were recorded for Zn$_{1-x}$Mg$_x$Te layers with $x=0.05$ and 0.24. The results are shown in figure 5. In figure 5(a), since the 224 reciprocal lattice point (RLP) of Zn$_{0.95}$Mg$_{0.05}$Te layer is located just below that of ZnTe, the Zn$_{0.95}$Mg$_{0.05}$Te layer is found to be grown pseudomorphically with respect to ZnTe, probably due to the small lattice mismatch of 0.3 %. On the
other hands, the 224 RLP of Zn$_{0.76}$Mg$_{0.24}$Te layer is not aligned with that of ZnTe in both in-plane and perpendicular direction, and therefore the Zn$_{0.76}$Mg$_{0.24}$Te epitaxial layer is partially relaxed. This would result from a large lattice mismatch of 1.4 % between ZnTe and Zn$_{0.76}$Mg$_{0.24}$Te.

4. Summary
Zn$_{1-x}$Mg$_{x}$Te epitaxial layers with a Mg composition range of 0$\leq$$x$$\leq$0.66 were grown on ZnTe (001) substrates by MBE. Mg composition in the epitaxial layer can be controlled by the flux ratio of Mg/(Zn+Mg), but it was also affected by the flux ratio of Te/(Zn+Mg). Zn$_{1-x}$Mg$_{x}$Te epitaxial layers with $x$$\leq$0.66 have a zincblende structure on ZnTe (001) substrates, suitable for fabrication of LED. Strained pseudomorphic epitaxial layer is obtained at the Mg composition below 0.05.

Acknowledgement
This study was partly supported by Industrial Technology Research Grant Program in 2005 from New Energy and Industrial Technology Development Organization (NEDO) of Japan.

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