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Assessment of MOCVD-Grown ZnSe Epilayers on GaAs by Means of Synchrotron Radiation Topography

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Synchrotron X-ray reflection topography was used to observe the onset of formation of the strain-relieving misfit dislocations in ZnSe epilayers grown by metalorganic chemical vapor deposition (MOCVD) on low dislocation density (100)GaAs substrates. ZnSe epilayers were 84, 249 and 341 nm thick. Grazing incident topographs were recorded from four of equivalent 224 reflections in the substrate and epilayer rocking curves at a wavelength of 0.148 nm. Very short misfit dislocations were detected in the 341 nm thick epilayer specimen, whereas we cannot observe misfit dislocations in both the 84 nm and 249 nm thick epilayer specimens. The critical thickness of present MOCVD-grown ZnSe epilayers was thus estimated to be close to 340 nm. This value is greater than that found in MBE-grown ZnSe epilayers (97.5 nm) and that of Matthews and Blakeslee's theory (105 nm).

Key words: synchrotron radiation, topography, ZnSe epilayer, misfit dislocation, critical layer thickness

I. INTRODUCTION

The development of blue light emitting laser diodes is important for the next generation of opto-electronic systems. Studies on the degradation of laser diodes have shown that the degradation mechanism proceeds by the development of dark line defects, originating from both dislocations and stacking faults, which propagate through the active layer of the device [1]. Therefore, it is very important to ensure that the active region of the laser remains defect-free.

Many investigations concerning the determination of the critical layer thickness of ZnSe on (100)GaAs have been reported. The onset of relaxation in the ZnSe/GaAs heterostructure has been mostly determined by X-ray diffraction rocking curves and photoluminescence (PL) measurements, resulting in critical thickness values ranging from 50 nm to 350 nm. Both X-ray rocking curve and PL methods measure the residual average strain in the epilayers; as these methods are insensitive to dislocation densities below $\sim10^4$ cm^{-2}, they cannot measure the critical layer thickness for the onset of relaxation, the latter being defined by the formation of the first misfit dislocation in the epilayer. Furthermore, previous investigations lack systematic discussion of the results, as most studies do not report carefully on the impurities induced in the layers by the growth technique.

Recently, synchrotron based double-crystal X-ray reflection topography has been employed, revealing the onset of dislocation formation in ZnSe/GaAs samples grown by molecular beam epitaxy (MBE). The critical layer thickness was estimate to be 97.5 nm [2], which is markedly lower than the widely accepted value of 150 nm [3].

The present investigation aims at clarifying the details of strain relaxation by misfit dislocations in the ZnSe/(100)GaAs heterostructure. We used synchrotron X-ray reflection topography to determine the onset of formation of the first strain-relieving misfit dislocation in metal organic chemical vapor deposition (MOCVD)-grown ZnSe epilayers on low dislocation density GaAs substrates.

II. EXPERIMENTAL PROCEDURES

Specimens used in this investigation were grown on a 2 inch diameter semi-insulating (100)-oriented GaAs wafer grown by the vertical gradient freeze Bridgman technique and supplied by Wafer Technology, UK. The etch pit density in the wafers ranged between 630 and 1100 cm^{-2}. The ZnSe epilayers were grown on (100) GaAs substrate after wet chemical etching and *in-situ* thermal annealing by low pressure MOCVD in an Aixtron AIX200RD horizontal chamber reactor [4]. Halide-free $^{t}Bu_2Se$ was used as Se precursor in conjunction with dimethyl-zinc : triethyl-ammine

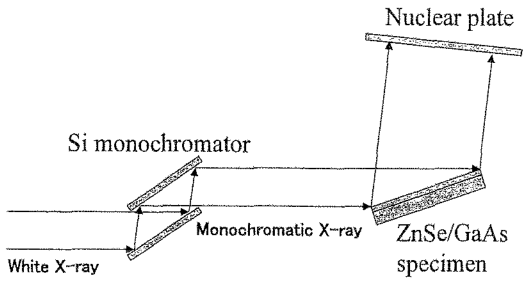

Fig.1 Schematic experimental arrangement of grazing incident X-ray reflection topography.

($Me_2Zn:Et_3N$) adduct as Zn precursor. The growth temperature and the growth rate of ZnSe epilayers were 342 °C and 0.497 μm/h, respectively. The epilayer thickness were 84, 249 and 341 nm.

The topographic observations were carried out at the Photon Factory (PF), the High Energy Accelerator Research Organization (KEK) in Japan. White beam transmission topographs were taken on the experimental station BL-15B using four of symmetrical equivalent 111 and 220 reflections for the determination of the number density and the Burgers vector of grown-in dislocations in the GaAs substrate. The wavelength of the diffracted X-ray beam was 0.04 nm and the exposure time of the topographs was 2.0 sec.

Monochromatic reflection topographs were taken on BL-15C of KEK-PF. A silicon double crystal monochromator employing the symmetric 111 reflection was used. Four of the equivalent 224 reflections were recorded under grazing incidence geometry from the substrate and epilayer rocking curves at a wavelength of 0.148 nm. Figure 1 shows the schematic experimental arrangement of the grazing incident X-ray reflection topography. With the synchrotron operation at 2.5 GeV and 400 mA, typical exposure times were 3 sec. and 8 min. for the substrate peak and epilayer peak, respectively. All topographs were recorded on Ilford L-4 Nuclear plate with 25 μm thickness emulsion.

III. RESULT AND DISCUSSION

3.1. Determination of Burgers vector and nature of the residual dislocations

Figure 2 shows a transmission topograph of the GaAs substrate recorded with the white X-ray beam. A few residual dislocation lines are observed. The number density of these dislocations was 6×10^2 cm^{-2}, slightly lower than that obtained by etching.

The Burgers vector of the dislocations was determined by finding the reflections for which the dislocation lines became invisible (corresponding to the condition $\boldsymbol{g}\cdot\boldsymbol{b}=0$). Figure 3 shows high magnification topographs taken for different diffraction planes. The diffraction planes, $\boldsymbol{g}$, in Figs.3 (a), 3(b), 3(c) 3(d) and 3(e) were (111), (1-11), (-1-11), (220) and (2-20), respectively. The dislocation line, indicated by the arrow, is visible in Figs. 3(b) and 3(d) in contrast with 3(a), 3(c) and 3(e). The visibility condition of the dislocation is summarized in Table I. In the present case, the possible Burgers vectors, $\boldsymbol{b}$, of the dislocation are of the type $\boldsymbol{a}$/2<110>. Table II shows the dislocation visibility conditions for the images obtained for four 220 reflections. A comparison between

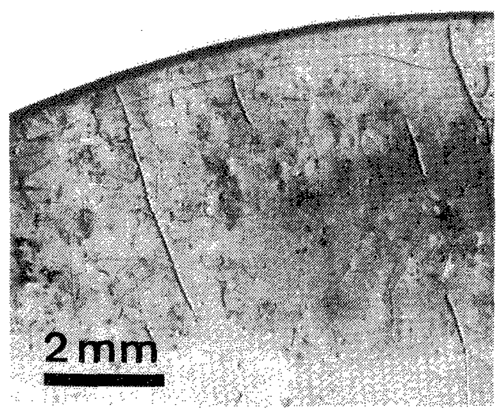

Fig.2 Transmission topograph with white beam X-ray of GaAs substrate.

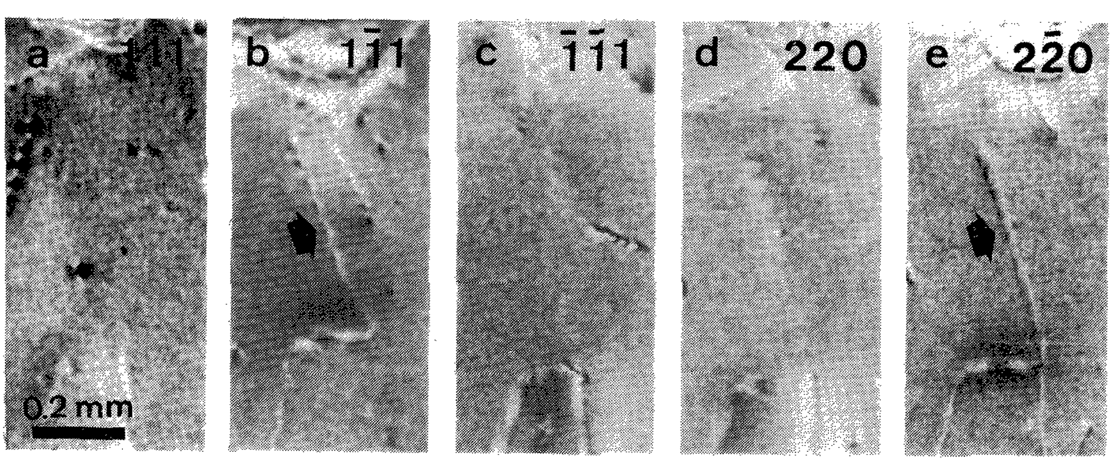

Fig.3 Transmission topographs of GaAs substrate with different diffraction plane.

Table I. Summarized visible or invisible image of the residual dislocations in Fig. 3.

g	(111)	($\bar{1}$11)	(1$\bar{1}$1)	($\bar{1}\bar{1}$1)	(220)	(2$\bar{2}$0)
Contrast	×	○	○	×	×	○

Table II. Visible possibility of the image obtained from the inner product of **g** and **b**.

b \ g	(111)	($\bar{1}$11)	(1$\bar{1}$1)	($\bar{1}\bar{1}$1)	(220)	(2$\bar{2}$0)
a/2[110]	1	0	0	-1	2	0
a/2[101]	1	0	1	0	1	1
a/2[011]	1	1	0	0	1	-1
a/2[1$\bar{1}$0]	0	-1	1	0	0	2
a/2[10$\bar{1}$]	0	-1	0	-1	1	1
a/2[01$\bar{1}$]	0	0	1	1	-1	1

Table I and II, indicates that the Burgers vector of the loop can be identified as being *a*/2[1-10]. The direction of the dislocation [101] was determined from the stereographic plot of the orientations of the longitudinal axis and the normal of the specimen surface. Therefore, the residual dislocation is confirmed to be a 60° dislocation.

3.2 Critical layer thickness of ZnSe epilayer

Typical (442) reflection topographs for the three ZnSe samples having thickness 84, 249 and 341 nm are shown in Fig.4(a), Fig.4(b) and Fig.4(c), respectively. For all ZnSe layer thickness up to 250 nm, no strain-relieving misfit dislocation could be detected across the entire 4 cm^2 area of the samples. In contrast, for the 341 nm thick layer the onset of formation of [011] strain-relieving misfit dislocation was visible. Figure 5 shows a higher magnification topograph of Fig.4(c).

The critical layer thickness for the formation of the first misfit dislocation must thus occur between 249 and 341 nm for present growth conditions and we estimate a value close to 340 nm, as the number density of generated misfit dislocations is still very low for the 341 nm thick sample. A similar value of 340 nm was previously reported [6].

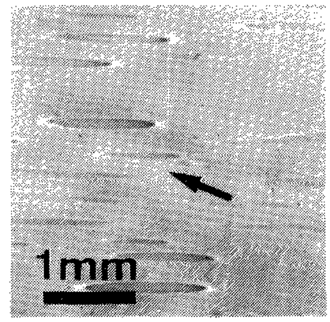

Fig.5 Higher magnification topograph of Fig. 4(c). This panel corresponds to the boxed area in Fig. 4(c). A few misfit dislocations were observed.

This critical thickness for MOCVD-grown epilayers is much greater from that of MBE-grown ZnSe [2]. In many semiconductor heteostructures, initial dislocation generation takes place by the Matthews and Blakeslee mechanism which involves the bending of pre-existing threading dislocations to form misfit segments at the heterointerface [5]. The value of critical layer thickness calculated by this model for the ZnSe/(100)GaAs structure is around 105 nm, thus close to that found for MBE-grown materials. The dramatic increase of the ZnSe critical thickness for MOCVD-grown epilayers from these values may be a result of the characteristic growth mechanisms and/or interface preparation conditions of the MOCVD technique. Indeed, it has been reported that surface preparation conditions of GaAs immediately before the ZnSe growth have a strong influence on the amount of epilayer strain relaxation. As these conditions greatly differ between MOCVD and MBE this could well explain the observed differences between the two growth methods. Also, as hydrogen is used as carrier gas in MOCVD, as-grown epilayers should contain small amounts of hydrogen in contrast with MBE grown specimens, which may influence the

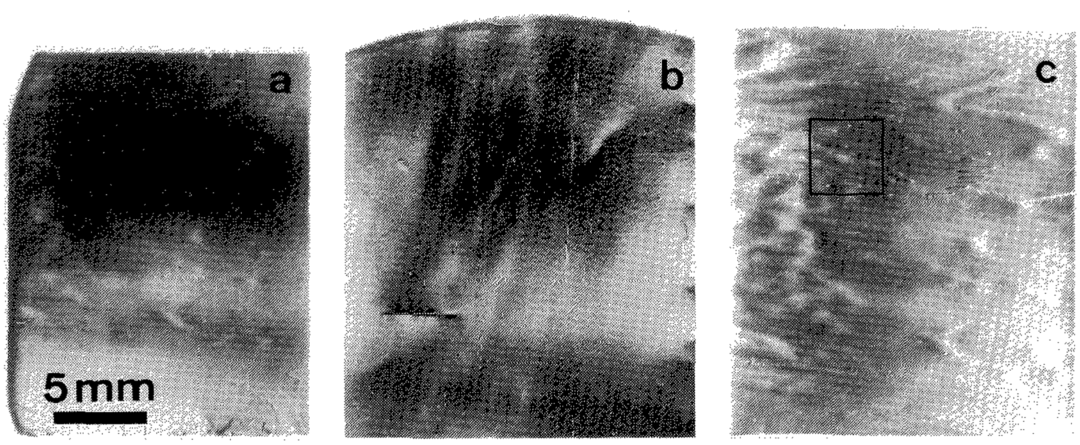

Fig.4 Reflection topographs of ZnSe/GaAs samples with different epilayer thickness.

strain relieving of the hetero-epitaxal structures. More detailed studies of the misfit dislocation generation in MOCVD-grown ZnSe are thus needed. To this purpose, a systematic determination of the Burgers vector and of the dislocation nucleation at early stages of this process are now in progress.

In summary, using monochromatic synchrotron X-ray topography, we have found that the critical layer thickness of MOCVD-grown ZnSe on low dislocation density GaAs substrates is about 340 nm, i.e. much higher than the about 100 nm value previously reported for MBE-grown ZnSe epilayers.

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References

[1] S. Guha, H. Cheng, M. A. Haase, J. M. DePuydt, J. Qiu, B. J. Wu and G. E. Houfler, Appl. Phys. Lett. **65**, 801(1994).

[2] G. Horsburgh, K. A. Prior, W. Meredith, I. Galbraith, B. C. Cavenett, C. R. Whitehouse, G. Lacey, A. G. Cullis, P. J. Parbrook, P. Moeck and K. Mizuno, Appl. Phys. Lett., **72**, 3148(1998).

[3] C. R. Whitehouse, A. G. Cullis, S. J. Barnett, B. F. Usher, G. F. Clark, A. M. Keir, B. K. Tanner, B. Lunn, J. C. H. Hogg, A. D. Johnson, G. Lacey, W. Spirkl, W. E. Hagston and J. H. Jefferson, J. Crystal Growth, **150**, 85(1995).

[4] N. Lovergine, P. Prete, G. Leo, L. Calcagnile, R. Cingolani, A. M. Mancini, F. Romanato and A. V. Drigo, Cryt. Res. Technol., **33**, 183(1998).

[5] J. W. Matthews and A. E. Blakeslee, J. Crystal Growth, 27, 118(1974).

[6] S. Ichikawa, N. Matsumura, K. Yamawaki, K. Senga and J. Saraie, J. Crystal Growth, **138**, 14(1994).

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