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Microstructure of $Zn_{1-x}Fe_xSe$ Epilayers Grown by Molecular Beam Epitaxy

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MBE에 의해 성장된 $Zn_{1-x}Fe_xSe$ 반도체 박막의 미세구조

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초 록 MBE에 의해 성장된 $Zn_{1-x}Fe_xSe$ 박막의 미세구조가 고분해능 투과전자현미경에 의해 연구되었다. $Zn_{1-x}Fe_xSe$ 박막에서 CuAu-I과 CuPt의 규칙격자가 발견되었다. 이 규칙격자는 전자 회절과 단면 고분해능 격자 이미지에 의해 조사되었다. CuAu-I 규칙격자는 (001) InP 기판 위에 성장된 $Zn_{1-x}Fe_xSe(\chi=0.43)$에서 관찰되었고, 반면에 CuPt 규칙격자는 (001) GaAs 기판 위에 성장된 $Zn_{1-x}Fe_xSe(\chi=0.4)$에서 관찰되었다.

Abstract The microstructure of $Zn_{1-x}Fe_xSe$ epilayers grown by molecular beam epitaxy was studied by high-resolution transmission electron microscopy. Two types of ordered structures, CuAu-I and CuPt, in $Zn_{1-x}Fe_xSe$ epilayers were observed. The ordered structures were investigated by electron diffraction patterns and cross-sectional high-resolution lattice images. The CuAu-I ordered structure was observed in $Zn_{1-x}Fe_xSe(\chi=0.43)$ epilayers grown on (001) InP substrates, while the CuPt ordered structure was observed in $Zn_{1-x}Fe_xSe(\chi=0.4)$ epilayers grown on (001) GaAs substrates.

1. Introduction

Diluted Magnetic Semiconductors (DMS) are a class of materials formed by the substitutional incorporation of a magnetic ion into a host compound semiconductor lattice[1]. DMS alloys are of considerable interest in the area of heterostructures and superlattices because the lattice parameter, energy gap, and effective mass can be tuned in a controlled fashion by varying the composition[2]. This tunability has recently been exploited in the fabrication of DMS superlattices. The first reported DMS epilayers are $Hg_{1-x-y}Cd_xMn_yTe$ prepared by the close-spaced isothermal vapor transport growth technique[3]. The advances of molecular beam epitaxy (MBE) have led to the growth of $Cd_{1-x}Mn_xTe$ epilayers and ($Cd_{1-x}Mn_xTe/Cd_{1-y}Mn_yTe$) superlattices with high structural quality[4~6]. Since 1984, the field has made truly remarkable progress, including successful preparation of epilayers and superlattices of $Zn_{1-x}Mn_xTe$ and $Hg_{1-x}Mn_xTe$ by MBE[6,7]. Most of the DMS compounds grown and studied to date have used Mn as the substitutional magnetic ion.

The growth of $Zn_{1-x}Fe_xSe$ alloys is of particular interest due to the wide alloy composition range ($0 \leqq \chi \leqq 1$)[8]. Especially, ordering in $Zn_{1-x}Fe_xSe$ alloys is important because it could be associated with magnetic ordering and ordered alloys have a lower energy gap than the disordered alloys. This system is different from the Ⅲ-Ⅴ alloys because the end members do not have the same crystal structure. Namely, ZnSe has a zinc-blende structure, while FeSe has a hexagonal NiAs structure.

Since the first ordered structure in a semiconductor alloy was observed in (AlGa)As by Kuan *et al.*[9], a number of ordered structures have been observed in epilayers of Ⅲ-Ⅴ[9~14], Ⅳ-Ⅳ[15], and Ⅳ-Ⅵ[16] semiconductors. The CuPt ordered structure is the dominant structure in Ⅲ-Ⅴ alloys[17]. The CuAu-I ordered structure has been observed in some Ⅲ-Ⅴ semiconductors, such as (AlGa)As[9] and (InGa)As[10], and, recently, in Ⅱ-Ⅵ semiconductors, such as (ZnFe)Se[18]. Both CuAu-I type and CuPt type ordered structures have been reported in (InGa)As[10,12] and in Ga(AsSb)[11,13,14]. Important factors that influence the ordering are growth temperature and kinetics, difference in ionic sizes and lattice constants of the alloy members, substrate orientation, and strain energy of the surface phase[19].

It has been reported that, both theoretically[20] and experimentally, for (GaIn)P[21,22] and In(AsSb)[23], that the energy gap of the ordered structures is smaller than that of the disordered structures[20]. More recently, the stabilization of the CuPt ordered phase has been proposed to be due to the surface reconstruction during growth[17]. Ordered structures in semiconductor films have been predicted to be thermodynamically more stable than the disordered structures partially due to strain effects[24,25]. In this work, two types of ordered structures, CuAu-I and CuPt, in $Zn_{1-x}Fe_xSe$ epilayers grown on the two different substrates, InP and GaAs, by MBE are investigated.

2. Experimental

The $Zn_{1-x}Fe_xSe$ epilayers studied here were grown by molecular beam epitaxy system equipped with Auger electron spectroscopy and reflection high energy electron diffraction. The $Zn_{1-x}Fe_xSe(\chi=0.43)$ epilayers with 52nm thickness were grown on (001) InP substrates, and the $Zn_{1-x}Fe_xSe(\chi=0.4)$ epilayers with 48nm thickness were grown on (001) GaAs substrates. The epilayers were grown at a substrate temperature of 330℃ and at rates of 0.1-0.25μm/h from elemental source ovens. Further details on the growth method may be found elsewhere[26].

Cross-sectional samples for high-resolution transmission electron microscopy (HRTEM) were prepared by mechanical grinding, dimpling, and ion-milling. The samples were ion-milled with 3 keV Ar^+ ions, 1 mA current, and 12° incident angle using liquid nitrogen cold stage, in order to minimize ion-induced damage. The microstructural features of these samples were investigated using Jeol 2000FX-Ⅱ and Philips EM 430 transmission electron microscopes operated at 200 and 300 keV, respectively.

3. Results and Discussion

Figure 1 shows a (110) high-resolution lattice image of the $Zn_{0.57}Fe_{0.43}Se$ film grown on InP substrate. Generally, the $Zn_{0.57}Fe_{0.43}Se$ film showed high structural quality. Stacking faults(marked by arrows) were often observed on the {111} planes in some areas of the lattice image. The interface between the film and substrate is

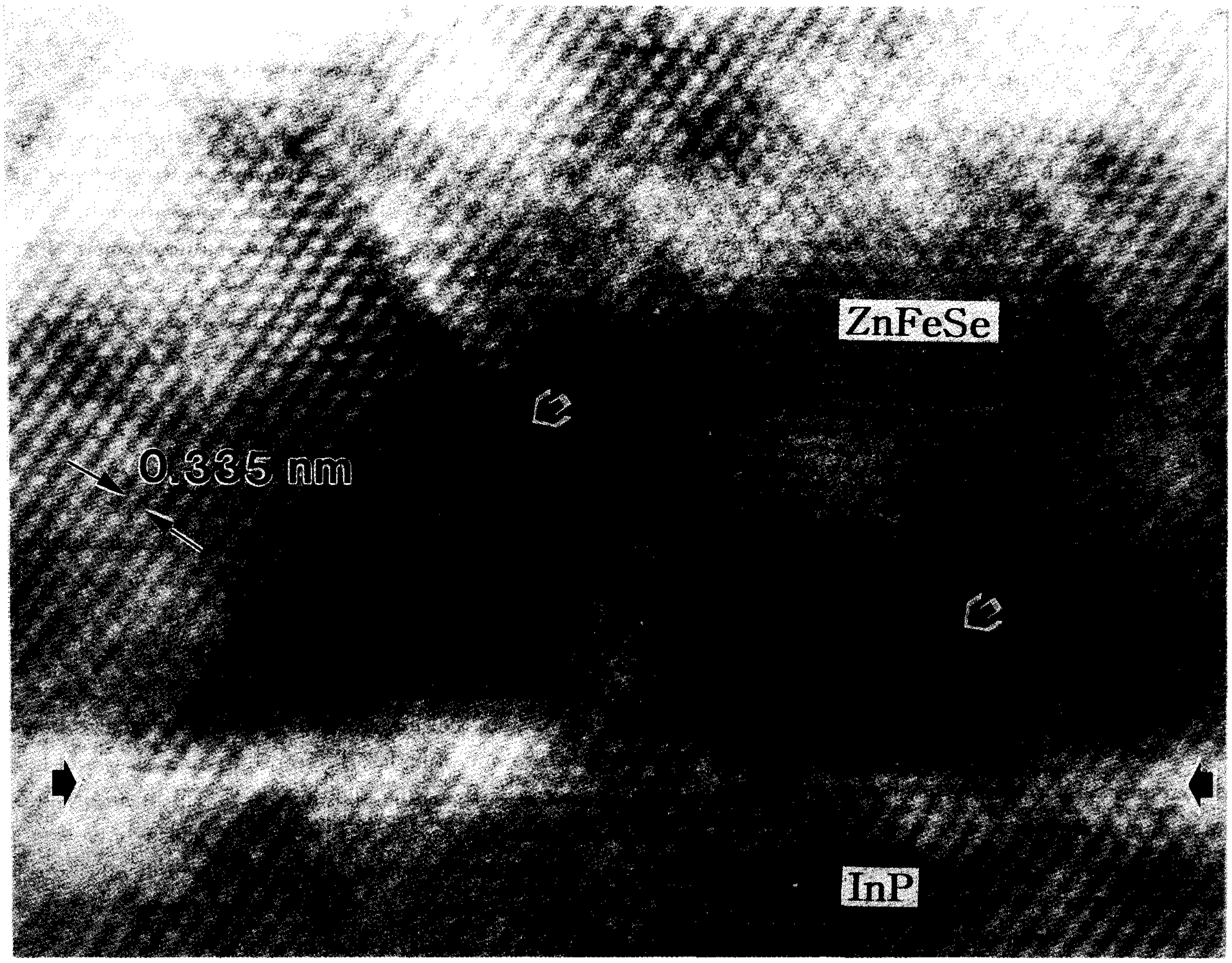

Fig. 1. (110) high-resolution lattice image of the $Zn_{0.57}Fe_{0.43}Se$ film grown on InP substrate.

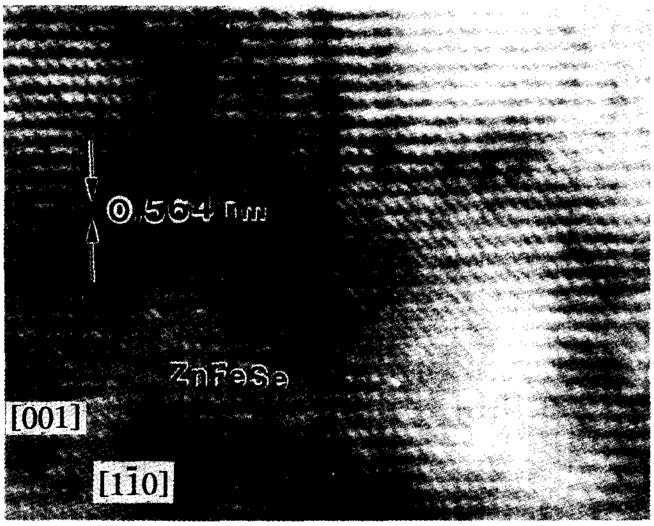

Fig. 2. (110) high-resolution lattice image from an ordered region of the $Zn_{0.57}Fe_{0.43}Se$ film.

also marked by arrows in this figure. No evidence of an oxide or foreign layer in the interface was found. Since the thickness(52nm) of $Zn_{0.57}Fe_{0.43}Se$ epilayers grown on InP substrates is above the critical thickness for the generation of misfit dislocations[27], the lattice mismatch of $\sim 3.0 \times 10^{-2}$ was accommodated by misfit dislocations and by residual elastic strain[28]. The residual elastic strain was estimated to be $\sim 0.24 \times 10^{-2}$ or ~8% of the lattice mismatch.

The ordered region in the $Zn_{0.57}Fe_{0.43}Se$ film was often observed, as shown in Fig. 2, which shows a (110) high-resolution lattice image from the $Zn_{0.57}Fe_{0.43}Se$ film. Contrast modulation with periodicities of ~0.564 nm and ~0.402 nm along the [001] and [1$\bar{1}$0] directions, respectively, is observed, indicating the CuAu-I type ordering in the $Zn_{1-x}Fe_xSe$ alloy along these directions. These periodicities correspond to the (001) and (1$\bar{1}$0) interplanar spacings of $Zn_{0.5}Fe_{0.5}Se$ alloy.

The (110) and (100) selected area diffraction (SAD) patterns from the interface between the $Zn_{0.57}Fe_{0.43}Se$ film and InP substrate are shown in Figs. 3(a) and (b), respectively. These diffraction patterns show the appearance of extra (weak) spots at the (001) and (1$\bar{1}$0) reflections originating from the CuAu-I type ordering of Zn and Fe atoms[18]. Ordering in this system takes place along the [001] growth direction and the [1$\bar{1}$0] direction and thus gives rise to the alternating layers of ZnSe and FeSe along these directions. It is interesting to note that the variants along (100) and (010) were not observed in the $Zn_{0.57}Fe_{0.43}Se$. This variant of the CuAu-I ordered structure is different from those observed in $GaAs_{0.5}Sb_{0.5}$ where ordering was observed along the [100] and [010] directions[11].

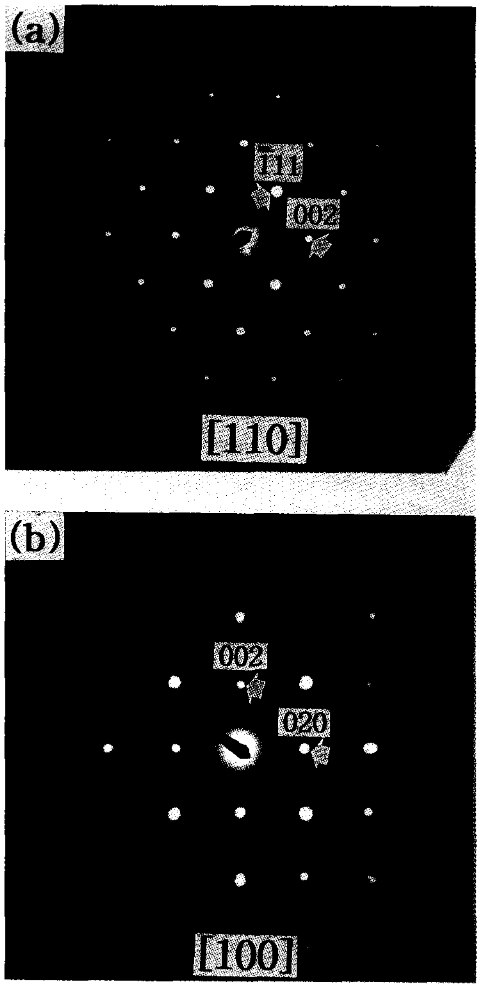

Fig. 3. (a) (110) and (b) (100) SAD patterns from the interface between the $Zn_{0.57}Fe_{0.43}Se$ film and InP substrate.

Figure 4 shows a $\frac{1}{2}$ ($\bar{1}$11) dark field image of the $Zn_{0.6}Fe_{0.4}Se$ epilayer grown on a (001) GaAs substrate. The regions indicated by arrows in Fig. 4 correspond to the ordered $Zn_{1-x}Fe_xSe$ alloys. No misfit dislocations were observed in the epilayer, indicating that the thickness (48nm) of the $Zn_{0.6}Fe_{0.4}Se$ film is below the critical thickness. The lattice mismatch of $\sim 0.65 \times 10^{-2}$ is totally accommodated by elastic strain in the film. Detailed microstructures of the ordered and disordered regions in the $Zn_{0.6}Fe_{0.4}Se$ epilayer were investigated by high-resolution lattice image as shown in Fig. 5. Figure 5 shows a (110) high-resolution lattice image showing coexistence of an ordered region(right-hand side) and a disordered region(left-hand side) in the $Zn_{0.6}Fe_{0.4}Se$ epilayer. It is also important to note that the boundary between the ordered and disordered regions is coherent and smooth. A doubling in the lattice fringe periodicity along the [$\bar{1}$11] direction is clearly observed in the ordered region, indicating the existence of atomic order-

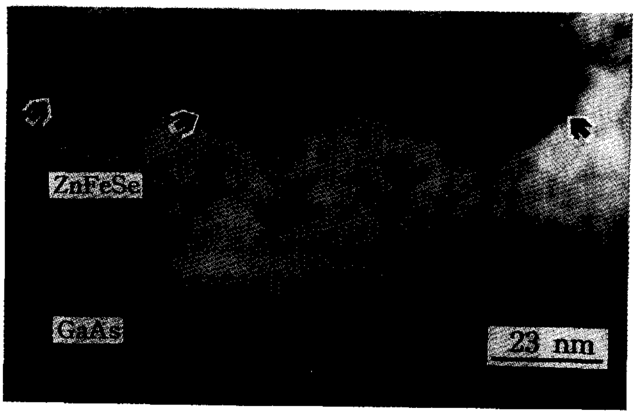

Fig. 4. $\frac{1}{2}(\bar{1}11)$ dark field image of the $Zn_{0.6}Fe_{0.4}Se$ epilayer grown on GaAs substrate. The regions with ordered structure were indicated by arrows.

ing of Zn and Fe atoms in $Zn_{1-x}Fe_xSe$ along this direction. This figure demonstrates that a different type of ordering, not the CuAu-I type ordering, occurred in the $Zn_{0.6}Fe_{0.4}Se$ film grown on (001) GaAs substrate.

Figures 6(a) and (b) show (110) SAD patterns from the interfacial areas between the $Zn_{0.6}Fe_{0.4}Se$ film and GaAs substrate. In Fig. 6(a), in addition to allowed (strong) spots originating from the zinc-blende structure, $\frac{1}{2}(\bar{1}11)$ and $\frac{1}{2}(1\bar{1}1)$ reflections with slightly unequal intensities are appeared. The existence of these superspots corresponds to two variants of the CuPt ordered structure with alternating ZnSe and FeSe layers along the $[\bar{1}11]$ and $[1\bar{1}1]$ directions. The shape of the superspots is nearly circular without any distortion or streaking, indicating the absence of antiphase boundaries[29]. Occasionally, only one set of superspots (one variant), $\frac{1}{2}(\bar{1}11)$ or $\frac{1}{2}(1\bar{1}1)$, was observed in the SAD patterns from some areas, as shown in Fig. 6(b). This figure shows a total suppression of ordering along the $[1\bar{1}1]$ direction. The selectivity of the ordering directions in CuPt ordering may result from asymmetry of the surface of the growing epilayers. Since there is no major difference in the growth conditions for the two kinds of $Zn_{1-x}Fe_xSe$ epilayers, $Zn_{0.6}Fe_{0.4}Se$ and $Zn_{0.57}Fe_{0.43}$

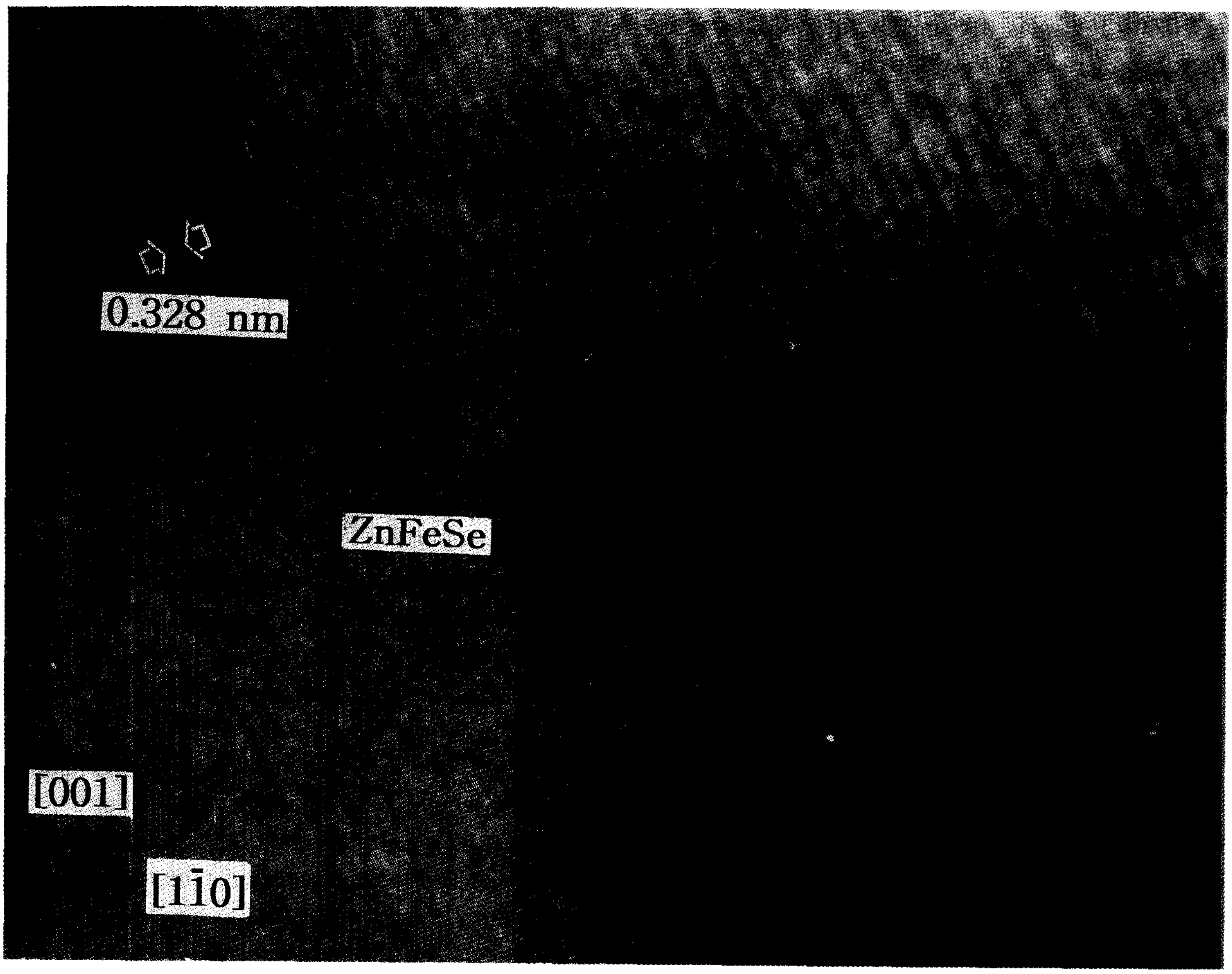

Fig. 5. (110) high-resolution lattice image showing coexistence of an ordered region (right-hand side) and a disordered region (left-hand side) in the $Zn_{0.6}Fe_{0.4}Se$ epilayer.

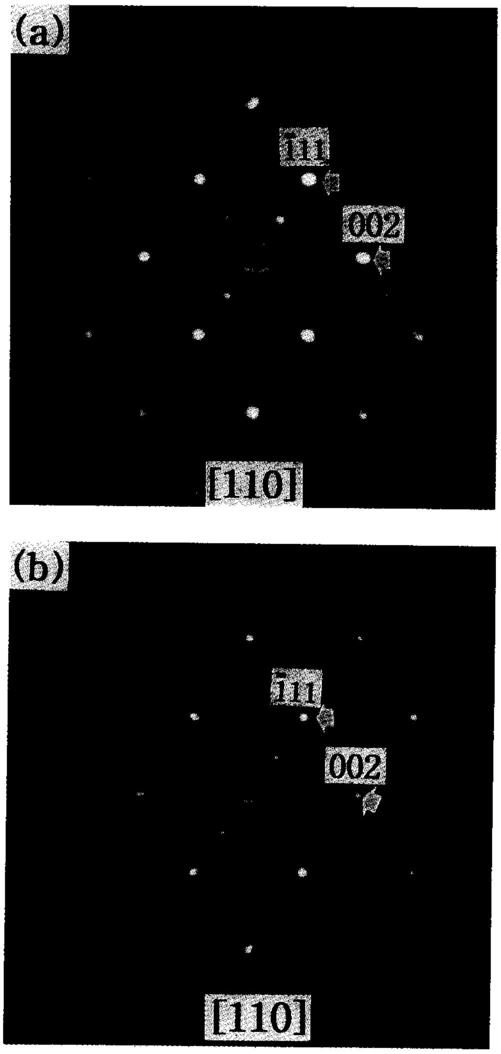

Fig. 6. (a) and (b) (110) SAD patterns from the interfacial area between the $Zn_{0.6}Fe_{0.4}Se$ film and GaAs substrate.

Se, except for the choice of substrate, the type of ordering in the $Zn_{1-x}Fe_xSe$ system may be dependent on the substrate used. The different strain levels caused by the lattice mismatch between the film and substrate for the two $Zn_{1-x}Fe_xSe$ epilayers could lead to different nucleation and growth modes during early stages of deposition and thus give rise to the two different ordering types.

4. Conclusions

For the $Zn_{0.57}Fe_{0.43}Se$ epilayers grown on (001) InP substrates, the lattice mismatch of $\sim 3.0 \times 10^{-2}$ was accommodated by misfit dislocations and by residual elastic strain. The CuAu-I ordered structure was often observed in the $Zn_{0.57}Fe_{0.43}Se$ epilayers. The CuAu-I ordered structure of $Zn_{0.57}Fe_{0.43}Se$ epilayers consists of alternating ZnSe and FeSe monolayers along the [001] growth direction and the [$1\bar{1}0$] direction. On the other hand, for the $Zn_{0.6}Fe_{0.4}Se$ epilayers grown on (001) GaAs substrates, the lattice mismatch of $\sim 0.65 \times 10^{-2}$ was totally accommodated by elastic strain in the film. The CuPt ordered structure was often found in the $Zn_{0.6}Fe_{0.4}Se$ epilayers. This ordered structure consists of alternating ZnSe and FeSe layers along the <111> directions. These ordered structures could give rise to very interesting magnetic properties, since they correspond to the ordering of the magnetic atom, Fe, in the $Zn_{1-x}Fe_xSe$ alloys.

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