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Microstructure of Intermixed $Zn_{1-x}Fe_xSe$ Alloys in (ZnSe/FeSe) Superlattices

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(ZnSe/FeSe) 초격자에 있어서 $Zn_{1-x}Fe_xSe$ 상호확산층의 미세구조

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요 약

(001) GaAs 기판 위에 성장된 (ZnSe/FeSe) 초격자의 구성층 사이에 상호확산으로 형성된 $Zn_{1-x}Fe_xSe$의 미세구조가 고분해능 투과전자현미경과 컴퓨터 이미지 시뮬레이션에 의해 연구되었다. 컴퓨터 이미지 시뮬레이션은 multislice 방법으로 여러 시편 두께와 초점 거리에서 실시되었다. 컴퓨터 시뮬레이션에 의해 얻은 이미지는 실험에 의해 얻은 이미지와 비교되었다. 또한, CuAu-I 형태 규칙화가 $Zn_{1-x}Fe_xSe$ 상호확산층에서 일어났다. 이 CuAu-I 형태 규칙격자는 <100>과 <110> 방향에 따라서 ZnSe와 FeSe 층이 교대로 구성되어 있다.

Key words : (ZnSe/FeSe) superlattices, Interdiffusion, CuAu-I type ordering, High-resolution transmission electron microscopy, Computer image simulations

INTRODUCTION

Diluted Magnetic Semiconductors (DMS) are ternary or quaternary semiconducting compounds whose lattices are made up of partial substitution of magnetic ions, such as Mn, Fe, and Co (Furdyna *et al.*, 1988). DMS alloys are important materials for a wide variety of applications, such as blue and green light emitting devices, waveguides, and magnetic sensors, since they possess very interesting and potentially useful magneto-optical properties. As an example, $Cd_{1-x}Mn_xTe$ has a large Faraday rotation at room temperature which has been exploited in the construction of optical isolators (Furdyna, 1982). To enhance utilization of DMS in practical integrated magneto-optical devices, it is necessary to grow epitaxial thin films with high quality. The growth of high quality epitaxial

thin films has been achieved using molecular beam epitaxy (MBE) (Kolodziejski *et al.*, 1984). The recent successful fabrication of DMS superlattices using MBE technique has stimulated interest in the DMS superlattices for novel devices.

It has been reported that $Zn_{1-x}Fe_xSe$ alloys formed by the interdiffusion between the constituent layers in (ZnSe/FeSe) superlattice (Park *et al.*, 1997). It is necessary to identify the detailed microstructure of intermixed $Zn_{1-x}Fe_xSe$ alloys to understand the effect of intermixing in (ZnSe /FeSe) superlattice on the magneto-optical properties. One of the useful techniques for analyzing the microstructure of superlattice structure is high-resolution transmission electron microscopy (HRTEM). HRTEM enables the structure of superlattice structure to be analyzed on an atomic scale. However, the interpretation of the lattice images is not always straightforward. It is therefore required to compare observed images with computer simulated images in order to establish the correspondence between structural features and the observed images. In this work, the microstructural properties of the intermixed $Zn1_{-x}Fe_xSe$ layers in the (ZnSe/FeSe) superlattices were investigated using high-resolution lattice images and selected area diffraction (SAD) patterns. The observed images were compared with computer simulated images.

EXPERIMENTAL

The (ZnSe/FeSe) superlattices were grown directly without a buffer layer on (001) GaAs substrates by MBE system equipped with Auger electron spectroscopy and reflection high energy electron diffraction. The (ZnSe/FeSe) superlattice structures were made by depositing six alternating layers of ZnSe (4.5 nm) and FeSe (2.0 nm) on the GaAs substrates. The superlattices were capped with a ZnSe layer (6.0 nm) to protect them from potential degradation. The (ZnSe/FeSe) superlattices were grown at a substrate temperature of 330°C and at rates of 0.1 ~0.25 μm/h from elemental source ovens.

Cross-sectional samples for 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.

Computer image simulations were carried out using the multislice programs (Cowley *et al.*, 1957, 1959(a), 1959(b)) for various sample thicknesses, t, and defocusing values of the objective lens, Δf. The principle of the multislice method is to divide the crystal into a number of thin slices perpendicular to the incident beam direction (Cowley, 1984). The sample thicknesses ranged from 0.8 to 40.2 nm and the defocusing values ranged from −46 to −96 nm with a step of 10 nm. The input microscope parameters used in the computation of the images are the operating voltage, $V=200$ kV, the radius of objective aperture, $r_s=3.37\ nm^{-1}$, spherical aberration coefficient, $C_s=2.3$ mm, semi-angle of illumination, $div=1.0$ mrad, half-width of Gaussian spread of vibration, $vib=0.0$ nm, and half-width of Gaussian spread of defocus, $del=5$ nm. The simulated lattice images were obtained with 566 beams. The total intensity of all beams used in the calculation for a thickness of 40.2 nm is ~90% of the incident intensity.

RESULTS AND DISCUSSION

The constituent layers in the (ZnSe/FeSe) superlattice were often intermixed during the epitaxial growth to form $Zn_{1-x}Fe_xSe$ alloys. Figure 1 shows a (110) high-resolution lattice image of the intermixed $Zn_{1-x}Fe_xSe$ layer in the (ZnSe/FeSe) superlattice. Contrast modulations with periodicities of ~0.573 nm and ~0.414 nm were found in the right-hand side of intermixed $Zn_{1-x}Fe_xSe$ alloys shown in Fig. 1 along the [001] and [1$\bar{1}$0] directions, respectively. The value of the periodicities was obtained from optical diffractograms taken from the negative of the lattice image. These contrast modulations indicate that CuAu-I type ordering occurred at the intermixed $Zn_{1-x}Fe_xSe$ alloys. The left- and right-hand side regions shown in Fig. 1 correspond to disordered and ordered $Zn_{1-x}Fe_xSe$, respectively. The boundary between the two regions is smooth and coherent. The interdiffusion and chemical ordering in the present superlattice most likely occur during epitaxial growth, since the diffusion coefficient in the solid at room temperature is too low to allow the interdiffusion and chemical ordering by solid state diffusion. In order to inhibit the interdiffusion betw-

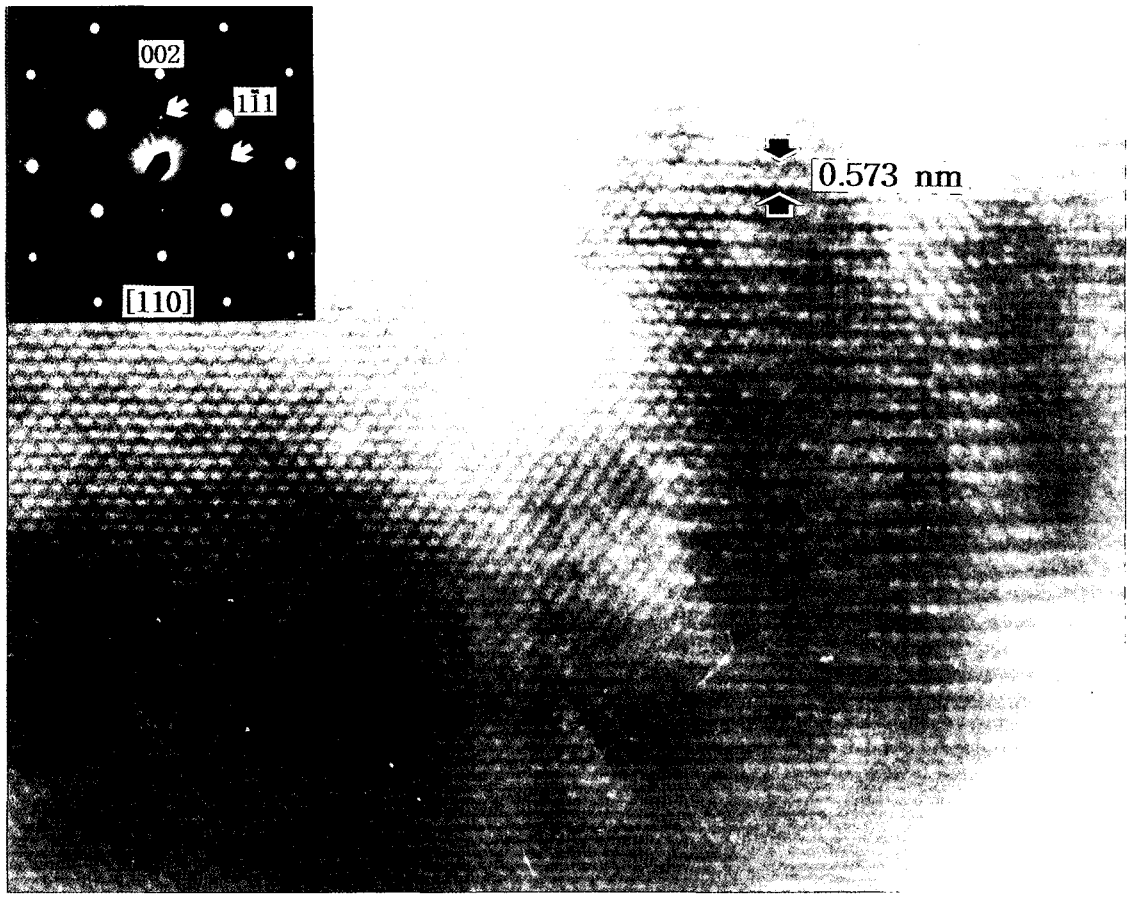

Fig. 1. (110) high-resolution lattice image of ordered and disordered regions in the intermixed $Zn_{1-x}Fe_xSe$ alloy of (ZnSe/FeSe) superlattice.

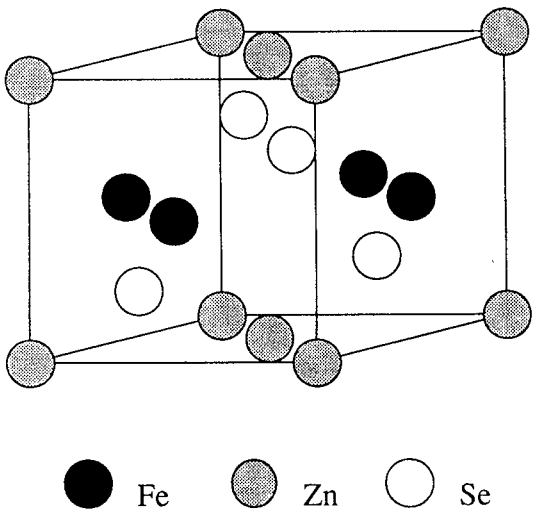

Fig. 2. Proposed model of the CuAu-I type ordered structure for $Zn_{0.5}Fe_{0.5}Se$ alloys.

een the constituent layers, it is desirable to grow at as low a substrate temperature as possible, since at low substrate temperatures the interdiffusion is strongly suppressed.

The inset to Fig. 1 shows a (110) SAD pattern obtained from the intermixed $Zn_{1-x}Fe_xSe$ layer. The existence of extra spots (marked by arrows) at the positions of the (001) and $(1\bar{1}0)$ reflections confirms the CuAu-I type chemical ordering in the $Zn_{1-x}Fe_xSe$ alloys. In the previous study (Park *et al.*, 1992), this type of ordering was observed in the $Zn_{1-x}Fe_xSe$ ($x\sim0.5$) epilayers grown on InP substrates. Detailed microstructures of ordered $Zn_{1-x}Fe_xSe$ alloys in the intermixed layer were investigated by computer simulations of lattice images.

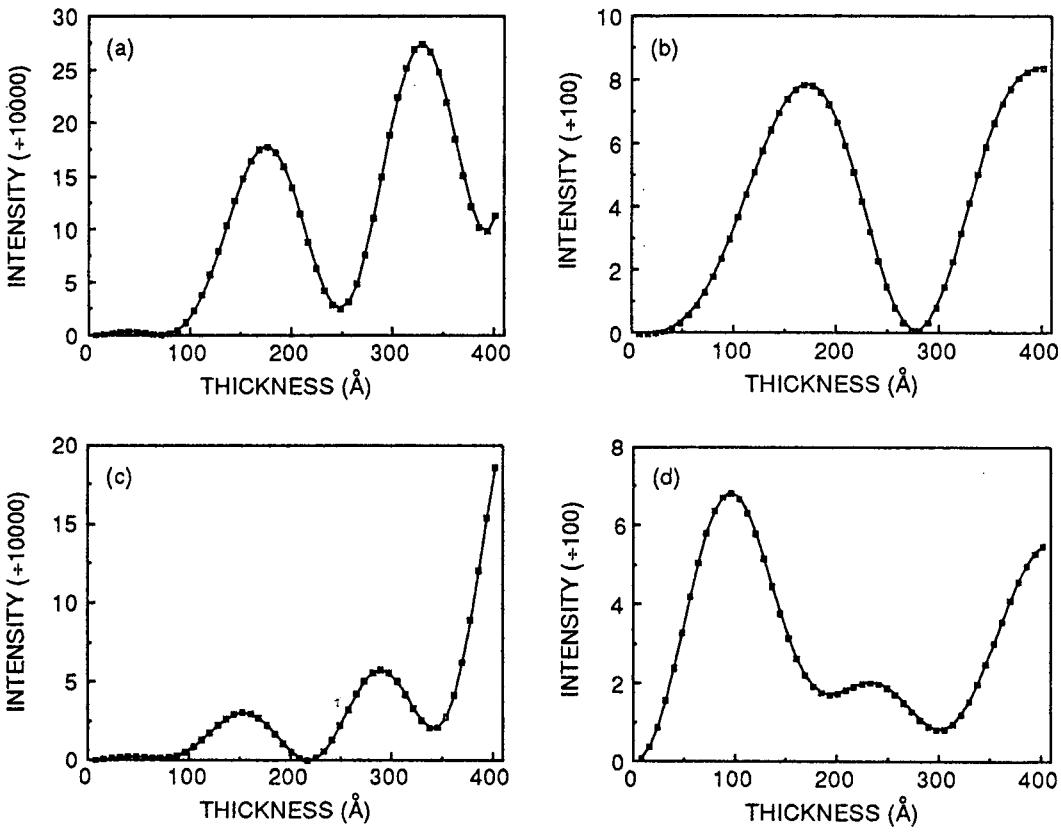

Fig. 3. Pendoll sung plots for (a) (001), (b) (002), (c) (110), and (d) (220) beams as a function of sample thickness for ordered $Zn_{0.5}Fe_{0.5}Se$ alloys.

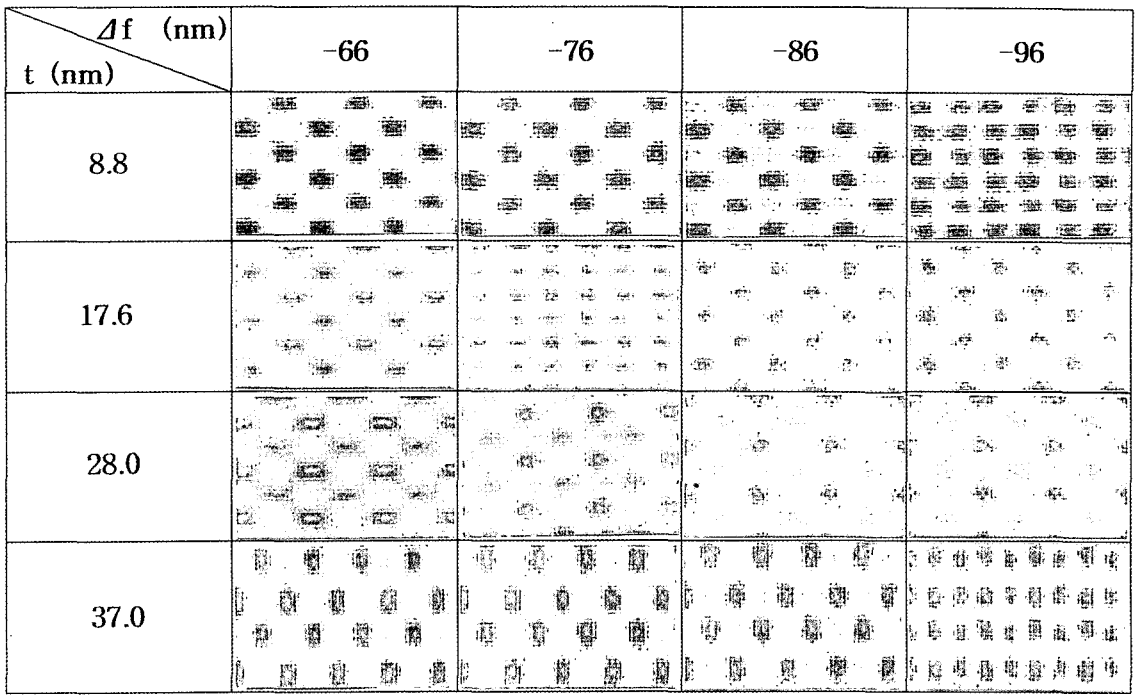

Fig. 4. Simulated lattice images obtained under various sample thicknesses and defocusing values for ordered $Zn_{0.5}Fe_{0.5}Se$ alloys.

Fig. 2 shows a proposed model for the atomic configuration of ordered $Zn_{0.5}Fe_{0.5}Se$ for computer image simulations. In Fig. 2, Zn atoms are located at (000) and $(\frac{1}{2}\frac{1}{2}0)$, Fe atoms are located at $(0\frac{1}{2}\frac{1}{2})$ and $(\frac{1}{2}0\frac{1}{2})$, and Se atoms are located at $(\frac{1}{4}\frac{1}{4}\frac{1}{4})$, $(\frac{1}{4}\frac{3}{4}\frac{3}{4})$, $(\frac{3}{4}\frac{1}{4}\frac{3}{4})$, and $(\frac{3}{4}\frac{3}{4}\frac{1}{4})$.

This ordered structure thus consists of alternating ZnSe and FeSe monolayers along the <100> and <110> directions.

Computer image simulations were performed using the multislice programs and the model shown in Fig. 2. The contrast in the simulated images is largely controlled by the sample thickness and microscope imaging condition. Figure 3 shows pendollösung plots for (001), (002), (110), and (220) beams as a function of sample thickness. The thickness of the strongest contrast for the ordered structure is ~28.0 nm.

The simulated lattice images obtained under sample thicknesses of 8.8, 17.6, 28.0, and 37.0 nm and defocusing values of −66, −76, −86, and −96 nm for ordered structure are shown in Fig. 4. In general, a good agreement was found between the experimental and simulated images, confirming the validity of CuAu-I type ordering in the $Zn_{1-x}Fe_xSe$ alloys. Clear contrast modulations caused by the ordering were found at ~28.0 nm. However, when the sample thickness is less than ~10.0 nm or greater than ~35.0 nm, weak contrast modulations were found. On the other hand, simulated images for disordered structure did not show any contrast modulations along the <100> and <110> directions. As an example, the simulated lattice images obtained under defocusing values of −46 to −96 nm at a

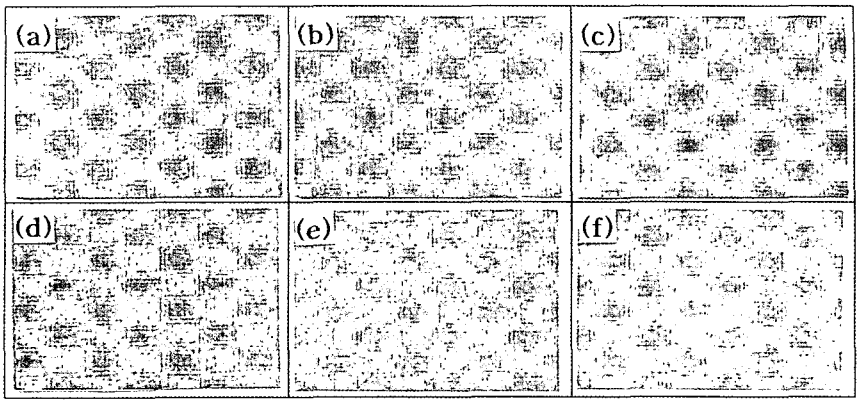

Fig. 5. Simulated lattice images obtained under defocusing values of (a) −46, (b) −56, (c) −66, (d) −76, (e) −86, and (f) −96 nm at a sample thickness of 28.0 nm for disordered $Zn_{0.5}Fe_{0.5}Se$ alloys.

sample thickness of 28.0 nm for disordered structure are shown in Fig. 5.

CONCLUSIONS

Intermixed $Zn_{1-x}Fe_xSe$ alloys were often observed in the (ZnSe/FeSe) superlattices because of interdiffusion between the constituent layers during the epitaxial growth. CuAu-I type ordering was observed in the intermixed $Zn_{1-x}Fe_xSe$ alloys. This CuAu-I type ordered structure of $Zn_{0.5}Fe_{0.5}Se$ has Zn atoms occupying the (000) and $(\frac{1}{2}\frac{1}{2}0)$ sites and Fe atoms occupying the $(0\frac{1}{2}\frac{1}{2})$ and $(\frac{1}{2}0\frac{1}{2})$ sites in the zinc-blende unit cell. The experimental images were well matched with the simulated images, confirming the validity of CuAu-I type ordering in the intermixed $Zn_{1-x}Fe_xSe$ alloys.

Abstract

The microstructure of intermixed $Zn_{1-x}Fe_xSe$ layers in the (ZnSe/FeSe) superlattices grown on (001) GaAs substrates has been investigated by high-resolution transmission electron microscopy and computer simulations of lattice images. Computer image simulations have been performed by the multislice method under various sample thicknesses and defocusing conditions.

The simulated lattice images were compared with the experimental lattice images. Also, CuAu-I type ordering was often observed in the intermixed $Zn_{1-x}Fe_xSe$ alloys. This CuAu-I type ordered structure consists of alternating ZnSe and FeSe monolayers along the <100> and <110> directions.

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