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투과전자현미경에 의한 $Zn_{1-x}Co_xSe$ 박막 및 (ZnSe/FeSe) 초격자 박막의 미세구조 분석

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Microstructural Characterization of $Zn_{1-x}Co_xSe$ Epilayers and (ZnSe/FeSe) Superlattice by Transmission Electron Microscopy

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초 록 MBE에 의해 (001) GaAs기판 위에 성장된 $Zn_{1-x}Co_xSe$(x=1.0, 7.4, 9.5 %)반도체 박막과 (ZnSe/FeSe)반도체 초격자 박막의 미세구조를 투과전자현미경을 이용하여 연구하였다. $Zn_{1-x}Co_xSe$박막 시편의 경우, 박막과 기판 사이의 격자 불일치 때문에 $\frac{a}{2}$<110> 형태의 버거즈 벡터를 가지는 부정합 전위를 관찰하였다. 모든 $Zn_{1-x}Co_xSe$박막과 기판의 계면은 뚜렷이 구별되었고, 계면에서 산화물이나 이물질이 존재하지 않았다. 또한, (ZnSe/FeSe)초격자를 성장시키기 전에 GaAs기판 위에 ZnSe바닥층을 넣음으로써 고품질의 (ZnSe/FeSe)초격자를 얻었다. (ZnSe/FeSe)초격자에 있는 FeSe는 섬아연광 결정구조로 존재하였다.

Abstract The microstructure of $Zn_{1-x}Co_xSe$ epilayers(x=1.0, 7.4, and 9.5%) and (ZnSe/FeSe) superlattice grown on (001) GaAs substrates by molecular beam epitaxy was investigated by transmission electron microscopy. For all the $Zn_{1-x}Co_xSe$ epilayers, misfit dislocations with Burgers vectors of $\frac{a}{2}$<110> type were found inside the epilayers. The interfaces between the $Zn_{1-x}Co_xSe$ epilayers and GaAs substrates were sharp and also did not contain any oxides or foreign layers. In addition, high-quality (ZnSe/FeSe) superlattice was grown by introducing a ZnSe buffer layer on the substrates prior to the growth of the superlattice. The FeSe layer with a thickness of 1.1nm in the superlattice existed in a zinc-blende structure.

1. Introduction

Recently, there is considerable interest in the class of Diluted Magnetic Semiconductors (DMS), which are a class of materials formed by the substitutional incorporation of a transition magnetic ion, such as Mn, Fe, or Co, into a host compound semiconductor lattice[1]. The advances of molecular beam epitaxy (MBE) have led to the growth of Mn-based epilayers and superlattices with high structural quality[2~4]. Most of the work to date has focused on Mn-based DMS materials. Recently, there has been increased research activity on Fe- and Co-based DMS. The growth of $Zn_{1-x}Fe_xSe$ DMS alloys is of particular interest due to the wide alloy composition range ($0 \leq x \leq 1$)[5]. Especially, CuAu-I type ordering has been observed in $Zn_{1-x}Fe_xSe$ ($x \approx 0.5$) DMS alloys[6]. However, the incorporation of Co^{2+} into a host compound lattice is not easily accomplished, resulting in a limited alloy composition range. The non-equilibrium technique of MBE can not overcome this problem[7].

DMS alloys have not yet reached maturity, but offer a number of possibilities for device applications, such as blue and green light emitting devices, waveguides, and magnetic sensors. To understand DMS materials behavior and to facilitate the design of new or improved DMS materials and the potential applications of DMS materials, it is necessary to investigate both composition and microstructure at the highest levels of resolution possible. The high resolving power of a high-resolution transmission electron microscopy (HRTEM) allows for information on the structure of DMS materials at the atomic level. In this work, the microstructural properties of $Zn_{1-x}Co_xSe$ epilayers and (ZnSe/FeSe) superlattice grown on (001) GaAs substrates were investigated by transmission electron microscopy (TEM).

2. Experimental

The $Zn_{1-x}Co_xSe$ epilayers(x=1.0, 7.4, and 9.5%) and

Table 1. Sample specifications for Co-based DMS epilayers used.

Alloys	x (%)	Thickness (nm)	Substrate	Misfit (%)
$Zn_{1-x}Co_xSe$	1.0	800	GaAs	0.25
$Zn_{1-x}Co_xSe$	7.4	1000	GaAs	0.32
$Zn_{1-x}Co_xSe$	9.5	120	GaAs	0.34

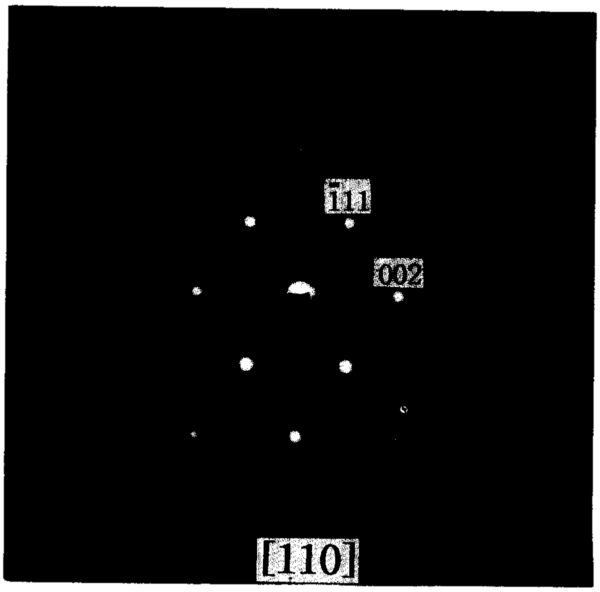

Fig. 1. (110) SAD pattern from the film of $Zn_{99.0}Co_{1.0}Se$ sample.

(ZnSe/FeSe) superlattice on (001) GaAs (lattice constant a=0.5654nm) substrates were grown by molecular beam epitaxy system equipped with Auger electron spectroscopy and reflection high energy electron diffraction. The sample specifications for Co-based DMS epilayers used are summarized in Table 1. All the $Zn_{1-x}Co_xSe$ epilayers were grown on (001) GaAs substrates. The (ZnSe/FeSe) superlattice structure was made by first depositing a buffer layer of ZnSe (50 nm) on the GaAs substrates followed by 12 alternating layers of ZnSe (3.4 nm) and FeSe (1.1 nm). The ZnSe buffer layer was introduced to compensate for the lattice mismatch between the substrates and superlattice, and hence improved the crystalline quality of the superlattice. The superlattice was capped with a ZnSe layer (3.1 nm) to protect it from potential degradation. The Co-based epilayers and (ZnSe/FeSe) superlattice were grown at a substrate temperature of 330 ℃ and at rates of 0.1-0.25㎛/h from elemental source ovens. Further details on the growth method may be found elsewhere[8, 9].

Cross-sectional TEM samples 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

A (110) selected area diffraction (SAD) pattern from the film of $Zn_{99.0}Co_{1.0}Se$ sample is shown in fig. 1. This Fig reveals that the $Zn_{1-x}Co_xSe$ film with x= 1.0 % and 800 nm thickness exists in a zinc-blende structure. The SAD pattern for other $Zn_{1-x}Co_xSe$ samples, i.e., $Zn_{92.6}Co_{7.4}Se$ and $Zn_{90.5}Co_{9.5}Se$, was found to be essentially equal to that shown in Fig. 1. The measured lattice constant of $Zn_{1-x}Co_xSe$(x=1.0%) film is 0.5669 nm. This value is consistent with that (0.5668 nm) of $Zn_{1-x}Co_xSe$ (x=1.0%) epilayers calculated from the expression reported by Jonker et al[10]. using X-ray diffraction. They reported that the average lattice constant $\bar{a}$ for $Zn_{1-x}Co_xSe$ increases linearly with Co concentration and is expressed as $\bar{a}$ =0.56676+0.00584x nm.

Fig. 2(a) and (b) show (220) dark field images of $Zn_{99.0}Co_{1.0}Se$ and $Zn_{90.5}Co_{9.5}Se$ epilayers grown on GaAs substrates, respectively. These figures clearly show the interface between the epilayers and substrates. In Fig. 2(a), a contrast caused by strain can be clearly seen near the interface. Strain contrast may result from the three-dimensional growth rather than layer-by-layer growth at the initial growth stages, resulting in high stress near islands. The misfit dislocations with a Burgers vector of $\frac{a}{2}[0\bar{1}1]$ or $\frac{a}{2}[101]$ are found inside the film of Fig. 2(a). The dislocations marked by arrows in Fig. 2(b) were found to be misfit dislocations with a Burgers vector of $\frac{a}{2}[10\bar{1}]$ or $\frac{a}{2}[101]$. Most dislocations in the film of $Zn_{90.5}Co_{9.5}Se$ sample extend from the interface to the surface of the film. For all the Co-based epilayers, the dislocation density (~$6\times10^8cm^{-2}$) near the interface is approximately the same as that near the surface and also no evidence for the phase decomposition or segregation was found.

In order to investigate the interface between the $Zn_{1-x}Co_xSe$ epilayers and the substrates at a microscopic

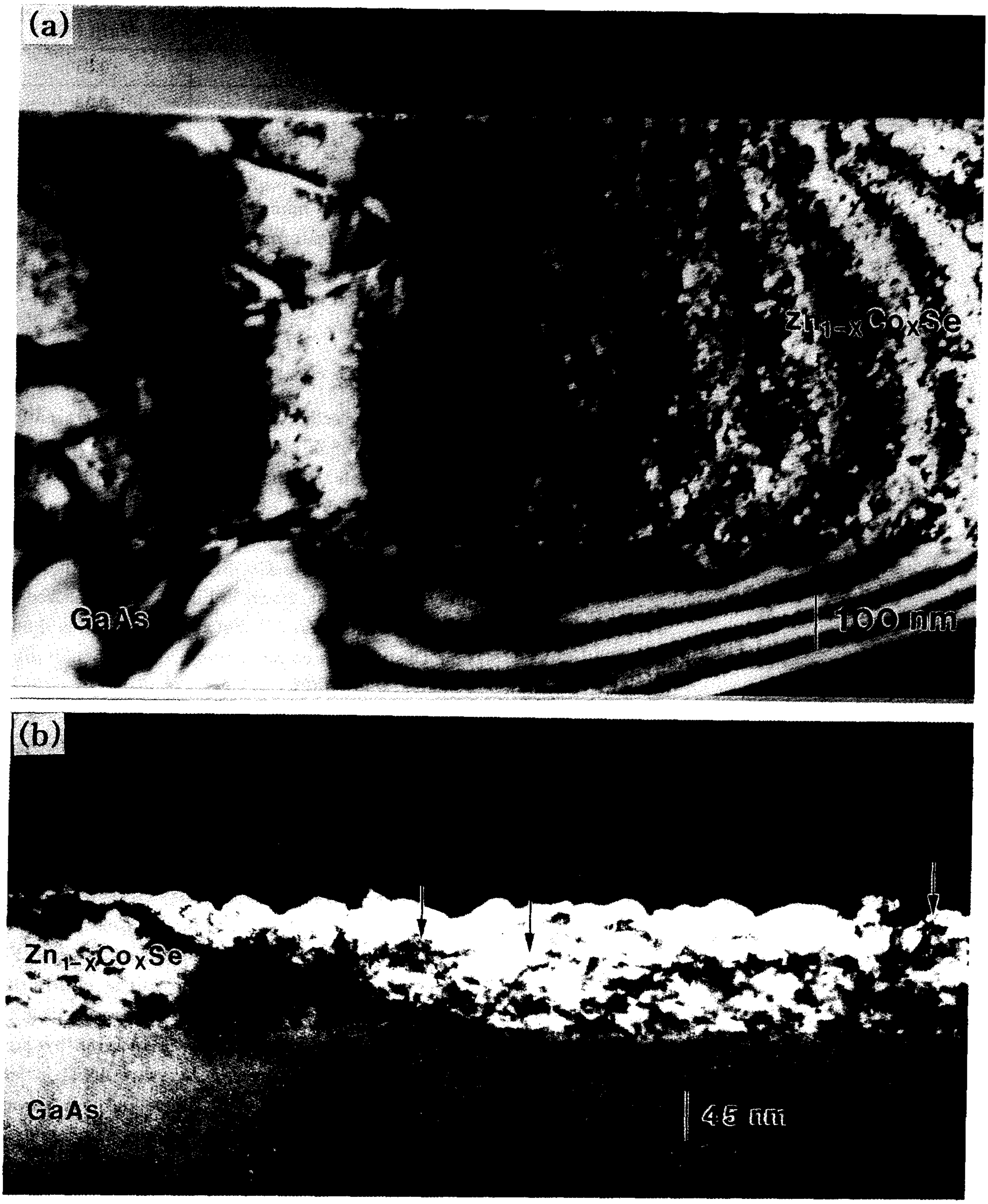

Fig. 2. (220) dark field images of (a) $Zn_{99.0}Co_{1.0}Se$ and (b) $Zn_{90.5}Co_{9.5}Se$ epilayers grown on GaAs substrates.

level, high-resolution lattice images were obtained. Fig. 3(a) and (b) show (110) high-resolution lattice images showing the interface (marked by arrows) between the epilayers and substrate for the $Zn_{92.6}Co_{7.4}Se$ and $Zn_{90.5}Co_{9.5}Se$ samples, respectively. The interface of both samples is clearly seen because of the difference in contrast between the epilayers and substrate. It was observed that the interfaces were abrupt within the resolution of the HRTEM. No evidence of an oxide or foreign layer in the interface and of stacking faults or microtwins in the film was found in all the $Zn_{1-x}Co_xSe$ samples studied. The high-resolution lattice image for $Zn_{99.0}Co_{1.0}Se$ sample was found to be essentially the same as that shown in Fig. 3.

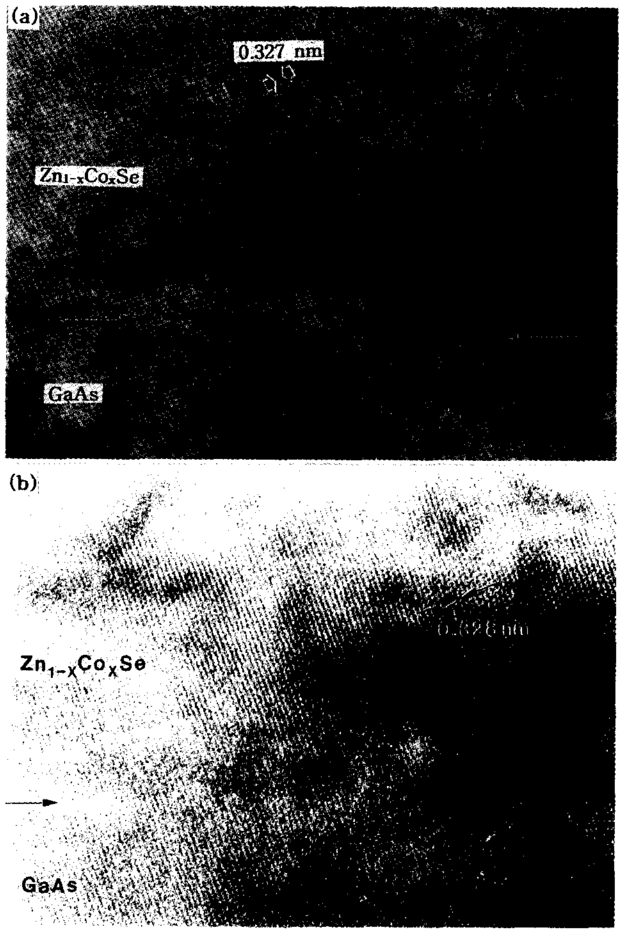

Fig. 3. (110) high-resolution lattice images showing the interface between the epilayers and GaAs substrate for (a) $Zn_{92.6}Co_{7.4}Se$ and (b) $Zn_{90.5}Co_{9.5}Se$ samples.

A periodic (ZnSe/FeSe) superlattice structure was grown on a ZnSe buffer layer as shown in fig. 4, which shows a (110) high-resolution lattice image from the (ZnSe/FeSe) superlattice. This figure represents that the interface between the constituent layers in the superlattice is coherent with no misfit dislocations, indicating that the lattice misfit between the constituent layers is totally accommodated by elastic strain. The lattice constant of zinc-blende FeSe calculated using the expression (a=0.5666+0.0051x) for the lattice constant of $Zn_{1-x}Fe_xSe$ is a=0.5717nm[5], indicating an elastic strain of 0.88 % in these layers. The equilibrium lattice constant $\bar{a}$ in the (ZnSe/FeSe) superlattice calculated using the expression proposed by People[11] is 0.5683 nm. For the calculation, since there is no reported value for the shear modulus of FeSe in the literature, it was assumed that the shear modulus of FeSe is equal to that of ZnSe. This sample did not contain any crystalline defects, such as misfit dislocations, stacking faults, and microtwins, in the superlattice.

Fig. 5 shows a (110) SAD pattern obtained from the ZnSe and FeSe constituent layers in the superlattice, confirming that the lattice mismatch between the constituent layers is accommodated by elastic strain. Also, this diffraction pattern suggests that the FeSe layers with a thickness of 1.1nm exist in a zinc-blende structure. It is important to note that bulk FeSe has a hexagonal NiAs structure[12].

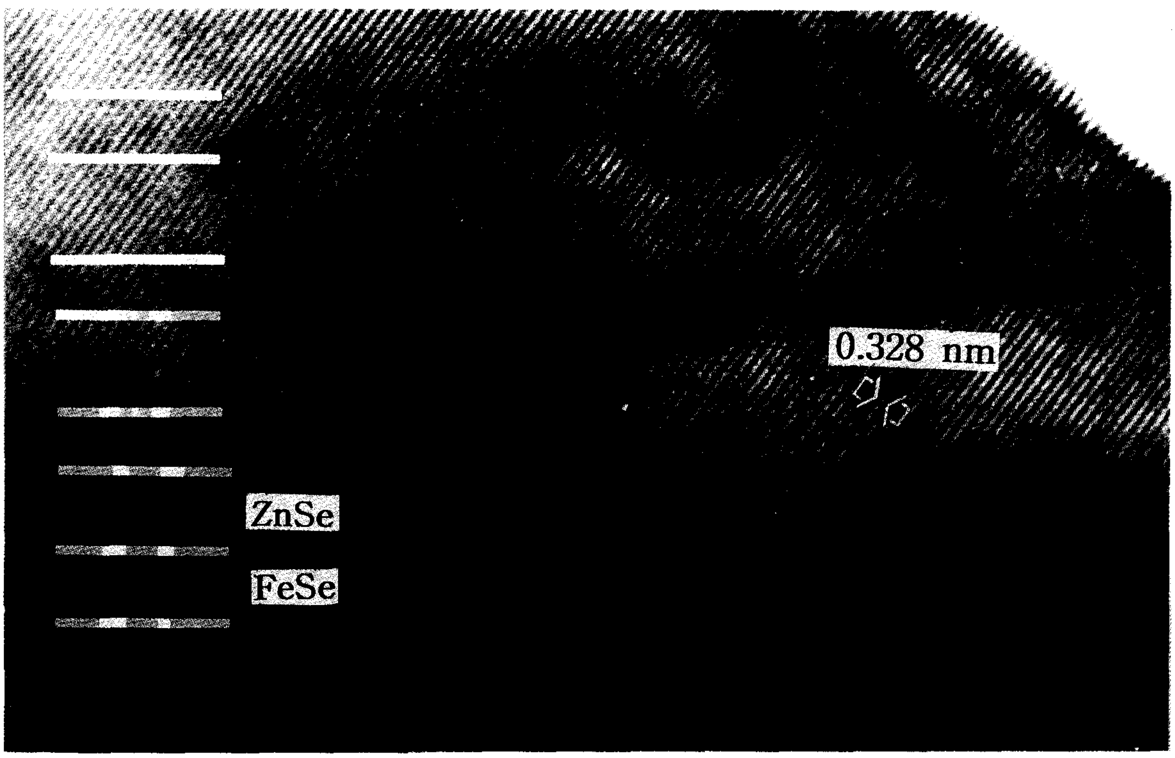

Fig. 4. (110) high-resolution lattice image taken from the (ZnSe/FeSe) superlattice.

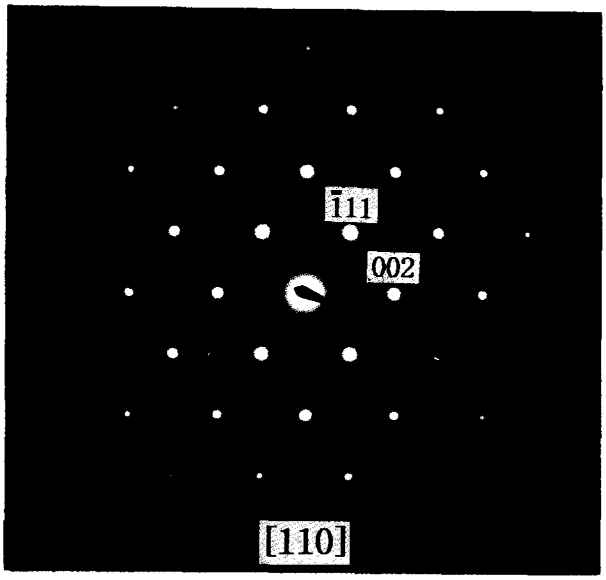

Fig. 5. (110) SAD pattern obtained from the ZnSe and FeSe constituent layers in the (ZnSe/FeSe) superlattice.

4. Conclusions

For the $Zn_{1-x}Co_xSe$(x=1.0, 7.4, and 9.5 %) samples, misfit dislocations with Burgers vectors of $\frac{a}{2}<110>$ type were found inside the epilayers. Also, the interfaces of all the $Zn_{1-x}Co_xSe$ samples were sharp within the resolution of the HRTEM. The oxide or foreign layer was not found at the interfaces. High-quality strained (ZnSe/FeSe) superlattice was grown with an incorporation of a ZnSe buffer layer on a (001) GaAs substrate prior to the growth of the superlattice, since the ZnSe buffer layer reduces the misfit strain in the superlattice. The lattice misfit (f=0.88%) between the constituent layers in the superlattice is totally accommodated by elastic strain. The FeSe layers (1.1 nm) in the superlattice had a zinc-blende structure.

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