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Coexistence of the Cu_3Au type ordered structure and the fine modulation in $Cd_xZn_{1-x}Te$ epilayers grown on GaAs substrates

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Selected-area electron diffraction pattern (SADP) and transmission electron microscopy (TEM) measurements were carried out to investigate the spontaneously ordered structure in $Cd_xZn_{1-x}Te$ epitaxial layers grown on (001) GaAs substrates. The SADP showed superstructure reflections with symmetrical intensity, and the high-resolution TEM (HRTEM) image showed doublet periodicity in the contrast of the {100} and {110} lattice planes. The results of the SADP and HRTEM measurements showed that Cu_3Au type ordered structures were formed in the $Cd_xZn_{1-x}Te$ epitaxial layers. The dark-field TEM image showed that the size of the Cu_3Au type ordered domains with a rectangular-like shape was approximately 15~30 nm thick, with widths ranging from 30 to 200 nm. Fine modulations in the ordered domains were also observed. These results provide important information on the microstructural properties for enhancing the efficiencies of $Cd_xZn_{1-x}Te$-based optoelectronic devices operating at the blue-green region of the spectrum. © *2002 American Institute of Physics.* [DOI: 10.1063/1.1517177]

Ordering behavior in the ternary compound semiconductors has been very attractive for both scientific and technological reasons.[1] Even though some studies concerning several kinds of ordering structures, such as CuAu,[2–4] chalcopyrite,[5,6] and CuPt,[7–9] have been reported in various ternary compound semiconductor epilayers, very few works on the formation of the Cu_3Au type ordered structures in ternary semiconductor epilayers have been done. Doublet periodicity exists in the CuAu-I type ordered structure along the ⟨001⟩ and the ⟨110⟩ directions.[2] The chalcopyrite type ordered structure leads to $\{1\ \frac{1}{2}\ 0\}$ superlattice reflections on the electron diffraction pattern.[5] The CuPt-type ordered structure leads to $\{\frac{1}{2}\frac{1}{2}\frac{1}{2}\}$ superstructure reflections in the electron diffraction pattern,[7–13] and the corresponding high-resolution image shows the doublet contrast in periodicity on the {111} lattice planes. Since the existence of the ordering in the ternary compound semiconductors significantly affects its electrical and optical properties resulting from the change of the band gap energy,[13] investigations of the ordering in the layer have been particularly interesting. Even though the ordered structures in various II–VI compound semiconductors were reported,[7,14–17] to the best of our knowledge, studies concerning existence of the both the Cu_3Au type ordered structures and the fine modulations in $Cd_xZn_{1-x}Te$ epilayers have not yet been performed.

This letter reports data for the Cu_3Au type ordered structure and ordered domains in the $Cd_xZn_{1-x}Te$ epitaxial layers grown on (001) GaAs substrates by molecular beam epitaxy (MBE). The ordering phenomena of the $Cd_xZn_{1-x}Te$ epitaxial layers were characterized by using the selected area electron diffraction pattern (SADP) and the high-resolution transmission electron microscopy (HRTEM) measurements.

Elemental Cd, Zn, and Te with purities of 99.9999% were used as the source materials, and were precleaned by repeated sublimation. Cr-doped and semi-insulating (100) GaAs substrates were degreased in warm trichloroethylene (TCE), rinsed thoroughly in deionized water, etched in a HF solution, and rinsed in TCE again. As soon as the chemical cleaning process was finished, the GaAs substrates were mounted onto a molybdenum susceptor. Prior to $Cd_xZn_{1-x}Te$ thin-film growth, the GaAs substrates were thermally cleaned at 600 °C for 5 min *in situ* in the growth chamber at a pressure of 10^{-8} Torr. The depositions of the $Cd_xZn_{1-x}Te$ epilayers were done on GaAs substrates with the MBE technique at a substrate temperature of 320 °C and at a system pressure of 10^{-6} Torr. The source temperatures of the Cd, Zn, and Te sources for the $Cd_xZn_{1-x}Te$ epilayers were 160, 250, and 320 °C, respectively, and the typical growth rate was 0.2 μm/h. After the $Cd_xZn_{1-x}Te$ thin films were grown, the samples were annealed at the growth temperature for 5 min to stabilize the layer. The typical thickness of the $Cd_xZn_{1-x}Te$ film was 700 nm.

Transmission electron microscopy (TEM) measurements were performed using a JEOL JEM 3010 transmission electron microscope operating at 300 kV. The samples for the plan-view TEM measurements were prepared by cutting and polishing with a diamond paper to a thickness of approximately 30 μm, and then by argon-ion milling at liquid-nitrogen temperature to electron transparency.

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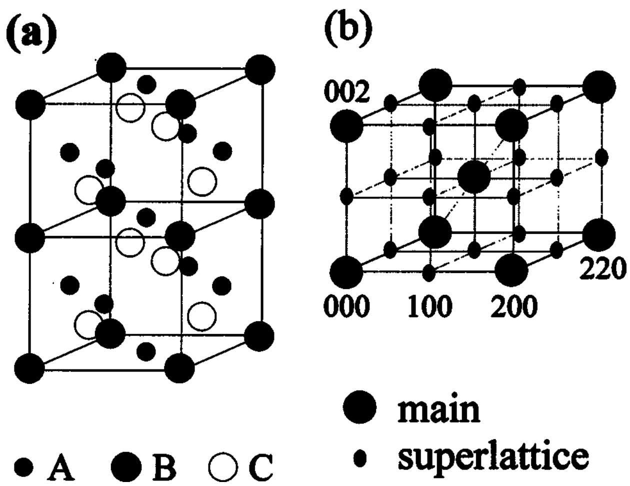

FIG. 1. Schematic diagrams of the real lattice (a) and the reciprocal lattice (b) of the Cu_3Au type $[A_3BC_4]$ structure in the zinc-blende structure.

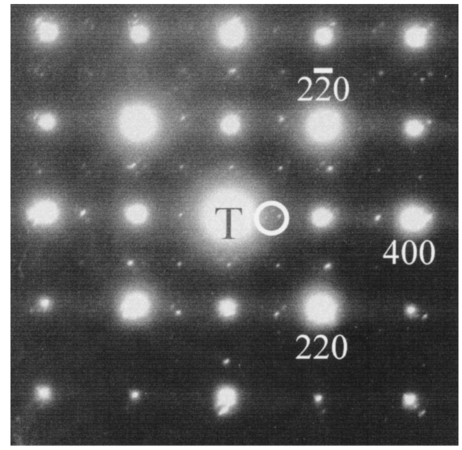

FIG. 2. The [001] selected area electron diffraction pattern of the $Cd_{0.15}Zn_{0.85}Te$ epilayer showing {200}, {220}, and {420} diffraction spots corresponding to the normal zinc blende and extra {100} and {110} spots regardless of the structure.

X-ray diffraction (XRD) measurements were performed to investigate the crystallinity and the composition of the $Cd_xZn_{1-x}Te$ layer. The XRD patterns for $Cd_xZn_{1-x}Te$ epilayers grown on GaAs (100) substrates clearly showed the (400) K_{a1} diffraction peaks corresponding to the $Cd_xZn_{1-x}Te(100)$ epilayers, together with those of GaAs (100) substrates. Using Vegard's law, the solid composition of the $Cd_xZn_{1-x}Te$ layer was obtained. Even though the $Cd_xZn_{1-x}Te$ epilayers with various Cd mole fractions had been grown, only the microstructural properties of the $Cd_{0.15}Zn_{0.85}Te$ film are described in this letter because both the Cu_3Au type ordered structures and the fine modulations are observed clearly in the $Cd_{0.15}Zn_{0.85}Te$ epilayer. The TEM measurements were carried out to characterize ordered structures in the $Cd_{0.15}Zn_{0.85}Te$ epitaxial layer. Schematic diagrams of the real lattice[1] and the reciprocal lattice[18] of the Cu_3Au type $[A_3BC_4]$ structure in the zinc-blende structure are shown in Figs. 1(a) and 1(b), respectively. The coordinates of the A atoms are located at 0 1/2 1/2, 1/2 0 1/2, 1/2 1/2 0, that of the B atom 0 0 0, and those of the C atoms 1/4 1/4 1/4, 1/4 3/4 3/4, 3/4 1/4 3/4, 3/4 3/4 1/4, as shown in the Fig. 1(a). The large filled circles in Fig. 1(b) indicate the fundamental reflections caused by the disordering of cation atoms, while the small and elongated filled circles in the Fig. 1(b) represent the superlattice reflections caused by the ordering of cation atoms. The electron diffraction pattern produced in the TEM measurement is simply a plane section of a three-dimensional reciprocal lattice.[19] When the c axis aligns with a beam direction, the superlattice spots, such as 100, 010, 110, $1\bar{1}0$,..., etc., are observed.

The [001] SADP for the $Cd_{0.15}Zn_{0.85}Te$ epilayers grown at 320 °C with a layer thickness of 700 nm is shown in Fig. 2. In addition to {200}, {220}, and {420} diffraction spots corresponding to the zinc-blende structure, extra {100} and {110} spots regardless of the structure appear, which is in reasonable agreement with a schematic electron diffraction pattern in Fig. 1(b). TEM images show that the lattice spacing of the observed ordered structure is smaller than those of ZnTe and CdTe. It is known that the lattice constant of ZnTe is 0.6101 nm and that of CdTe is 0.6480 nm. The lattice spacings of the ordered structure are measured by using the extra spots, and the corresponding lattice constant of the ordered structure was 0.5864 nm, which had contributed to {100} and {110} extra spots. The determined value of the lattice constant is close to that of the ideal Cu_3Au type ordered $CdZn_3Te_4$ ($a=0.6196$ nm) estimated by using the Vegard's law. The extra spots around the ordering reflections indicated by a white circle in Fig. 2 are also observed, which is due to the fine structure in the ordered domain, which will be explained subsequently below.

The detailed microstructural property of the strongly ordered $Cd_{0.15}Zn_{0.85}Te$ epilayer was examined by the plan-view TEM images. Figure 3 shows plan-view TEM images of the $Cd_{0.15}Zn_{0.85}Te$ epilayer through [001] projection. Figure 3(a) is a bright-field image, which shows ordered domains. Dark-field images obtained with the (100) ordering reflections represented by circles in Fig. 2 are shown in Fig. 3(b). The TEM images show clearly rectangular-like domains 15∼30 nm thick, with widths ranging from 30 to 200 nm. These rectangular-like domains are parallel to the ⟨220⟩ directions, which is consistent with the ordering reflections in Fig. 2. By dark-field imaging with the (100) superstructure reflection, a nanoscale fine structure is clearly resolved within the domains. The domain images consisted of the thin parallel lines parallel to the ⟨220⟩ directions. Their individual thicknesses are fairly regular, often 2.3 nm. These fringes contribute to the extra spots around the ordering reflections: by measuring the distance between the extra spots around the ordering reflections, an obtained thickness is approximately 2∼3 nm. Thus, the extra spots around the ordering reflections correlates with the size of this fine structure and not the overall thickness of the domains.

Figure 4 shows a HRTEM image from the $Cd_{0.15}Zn_{0.85}Te$ epitaxial layer grown on the (001) GaAs substrate along the [001] zone axis, and the image represents a doublet periodicity in the contrast of {100} and {110} lattice planes. The doublet periodicity shown in the {100} and the {110} planes is similar to the SADP shown in Fig. 2. The modulations around the ordered domains are also observed. The distance between them is approximately 2∼3 nm, which contribute to the extra spot around superlattice spots, as explained above.

Since the ordered structure must consist of Cd, Zn, Te

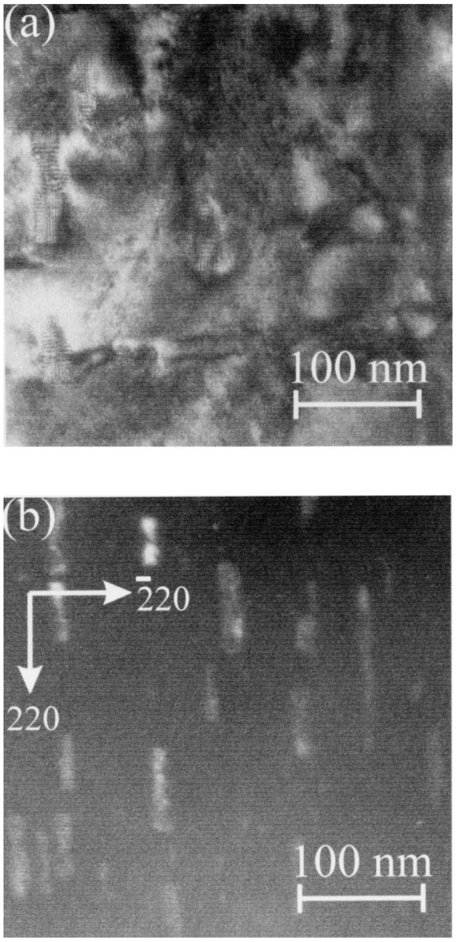

FIG. 3. Plan-view TEM images of the $Cd_{0.15}Zn_{0.85}Te$ epilayer: (a) Bright-field image through [001] projection and (b) dark-field image obtained with the (100) ordering reflections represented by circles in Fig. 2.

ternary elements for the formation of the ordering structure, the observed superstructure reflections and HRTEM image can be explained by the periodicity of atomic species Cd, Zn, and Te on their lattice sites. The resultant ordered structure might be obtained by arranging Cd atoms at 0 0 0 sites, Zn atoms at 0 1/2 1/2, 1/2 0 1/2, 1/2 1/2 0 sites, and Te atoms at 1/4 1/4 1/4, 1/4 3/4 3/4, 3/4 1/4 3/4, 3/4 3/4 1/4 sites. In disordered structure, Cd atoms and Zn atoms are randomly distributed at group II sublattice, and Te atoms at group VI sublattice. Thus, the stoichiometry composition of the Cu_3Au type ordered region might be expected to be $CdZn_3Te_4$.

In summary, the results of the SADP and the HRTEM measurements on $Cd_xZn_{1-x}Te$ strained epitaxial layers grown on (001) GaAs substrates showed the formation of a Cu_3Au type ordered structure. The SADP showed two sets of {100} and {110} superstructure reflections with almost same magnitudes of the symmetrical intensities along the [001] zone axis. Rectangular-like domains were 15~30 nm thick, with widths ranging from 30 to 200 nm. The fine modulations within the ordered domains were also observed. These present observations can help improve understanding for the microstructural properties of the $Cd_xZn_{1-x}Te$/GaAs heterostructures.

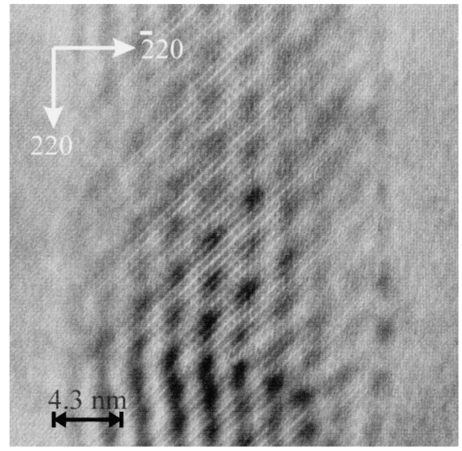

FIG. 4. A HRTEM image from the $Cd_{0.15}Zn_{0.85}Te$ epitaxial layer grown on the (001) GaAs substrate along the [001] zone axis. The image represents a doublet periodicity in the contrast of {100} and {110} lattice planes.

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