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Vapor Phase Epitaxy of (133) and (211) CdTe on (211) Si Substrates Using Metallic Cd Source

KENJI ISO,[1,2,3] YUYA GOKUDAN,[1] MASUMI SHIRAISHI,[1] MINAE NISHIKADO,[1] HISASHI MURAKAMI,[1,4] and AKINORI KOUKITU[1]

1.—Department of Applied Chemistry, Graduate School of Engineering, Tokyo University of Agriculture and Technology, Koganei, Tokyo 184-8588, Japan. 2.—R&TD Center, Tsukuba Plant, Mitsubishi Chemical Corporation, Ushiku, Ibaraki 300-1295, Japan. 3.—e-mail: iso.kenji.ma@m-chemical.co.jp. 4.—e-mail: murak@cc.tuat.ac.jp

Single-crystalline CdTe films were grown in both (133) and (211) surface orientations on (211) Si substrates by vapor-phase epitaxy using metallic Cd source as a group-II precursor. The orientation of epitaxial films depended on the ratio of group-II and -VI precursors, i.e., II/VI. The orientation of epitaxial films was changed from (133) to (211) by increasing the II/VI under the CdTe growth condition. The surface morphology for (133) CdTe was smooth, whereas the surface for (211) CdTe was composed of hillocks with (111), (110), (101), and (100) facets. The full width at half maximum (FWHM) of the epitaxial films with the same thickness showed that the crystalline quality of (133) CdTe was better than that of (211) CdTe. The dependence of the orientation between (133) and (211) CdTe films on (211) Si substrates on the II/VI was explained by the difference between the step-flow growth on the step and the spontaneous nucleation on the terrace.

Key words: CdTe, vapor phase epitaxy, twin, II/VI, metallic cadmium

INTRODUCTION

Cadmium telluride (CdTe) and their alloys such as CdZnTe and CdHgTe have zinc-blende (ZB) structures (space group:$F\bar{4}3m$). High-performance x-ray and gamma-ray detectors at room-temperature using CdTe are presented owing to its direct wide bandgap (1.44 eV) and higher average atomic mass number than Ge and Si.[1,2] In particular, CdTe growth on Si substrates with large areas using vapor phase epitaxy (VPE) is a promising candidate method due to its advantages such as high growth rate, homogeneous growth, high crystalline quality, and low cost.[3–5] We previously reported a successful epitaxial (211) CdTe growth on (211) Si substrates with VPE using cost-effective metallic Cd source as the group-II precursor, because metallic Cd is approximately 100 times cheaper than the metal–organic chemical Cd source, such as dimethylcadmium (DMCd) used by metal–organic chemical vapor deposition (MOCVD).[6,7]

CdTe films grown on Si or GaAs substrates suffer from the formation of twin crystals consisting of CdTe with (133) and (211) surface orientations with a mirror plane of (111), which is characteristic of ZB structures. Device performance can be decreased. For CdTe growth on GaAs substrates, some groups have tried to reduce twin crystals and investigated the generation mechanism. Yin et al. reported that the orientation of CdTe films on (211) GaAs by molecular beam epitaxy (MBE) could be controlled by the growth temperature.[8] Furthermore, Lange et al. suggested that the twin generation of CdTe on (211) GaAs was affected by the thermal cleaning process of the substrate prior to the growth.[9]

It is important to examine the twin generation and the mechanism of CdTe films grown on Si substrates, because they afford many advantages, including large size and less cost than GaAs. However, few research is reported for controlling CdTe twins on Si substrates. Kim et al. reported that a single-crystalline (133) CdTe film was grown

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on As-coated (211) Si substrates by MOCVD.[10] They adopted a two-stage growth method composing of a low-temperature buffer layer process and a high-temperature growth process. During these stages, the growth mode changed from a polycrystalline structure to a two-dimensional crystalline structure having a (133) surface orientation. Niraula et al. also performed the epitaxial growth on GaAs-coated (211) Si substrates without any buffer layer by MOCVD.[7] However, the single-crystalline CdTe film with a (211) surface orientation was obtained, instead of a (133) surface orientation. The cause of the difference in the surface orientation between these two groups is not clear.

The investigation of CdTe twin growth on (211) Si substrates is important to not only accomplish the orientation control of CdTe films having (133) and (211) planes, but to understand the growth mechanism as well. In this paper, we investigated the effects of growth conditions, such as the II/VI and the growth rate, on a twin formation using (211) Si substrates without any buffer layer. Single crystalline of CdTe with a surface orientation of (133) or (211) plane was successfully grown. The orientation relationship between the (211) Si substrate and the grown CdTe film was determined. The influence of the FWHM on the thickness of (133) and (211) CdTe films was also investigated. Lastly, the growth mechanism resulting in both (133) and (211) CdTe was discussed.

EXPERIMENTAL SECTION

CdTe films were grown in the originally designed horizontal flow reactor made of quartz at an atmospheric pressure with metallic Cd (6N) and diisopropyl-telluride (DiPTe) as group-II and -VI precursors, respectively. H_2 was the carrier gas. The supply rate of vapor Cd was controlled by changing the temperature of the heater around a metallic Cd reservoir. The detail of the experimental conditions has been reported in a previous paper.[6] The II/VI ratio was controlled by changing the input supply rates of gaseous Cd and DiPTe.

The surface orientation of Si substrates used in this study was (211) plane. Before the growth, a typical chemical cleaning process was employed.[11] After annealing the Si substrate at 1000°C for 30 min in H_2 ambient, CdTe films were grown for 60 min at a temperature of 600°C. The epitaxial growth was dependent on the annealing temperature. The single-crystalline CdTe was obtained at the annealing temperature of 900°C or higher. Otherwise, polycrystalline was achieved in grown films. Figure 1 shows the bird's-eye-view scanning electron microscope (SEM) image and x-ray diffraction (XRD) spectrum for polycrystalline CdTe film grown for 60 min after annealing the Si substrate at 600°C for 30 min in H_2 ambient. It was supposed that this result was attributed to a thin silicon oxide layer formed on Si substrates.[11] On the other hand, a thin ($\sim$ 4 nm) silicon oxide has been removed after annealing the Si substrate at 1000°C for 30 min in H_2 ambient, which was revealed by atomic force microscopy (AFM) (not shown).

Any buffer layer or a particular Si surface treatment was not adopted, such as As-passivation or GaAs treatment. XRD measurements were used to evaluate the CdTe film orientation and the crystalline quality. An x-ray beam size of 1 mm $\times$ 15 mm was adopted. The surface morphology and the thickness of CdTe films were observed by plan and cross-sectional views of SEM, respectively. AFM measurements were also performed to evaluate the macro-step of the surface.

RESULTS AND DISCUSSION

Figure 2 shows the schematics of the orientation relationship between (211) Si substrates and CdTe epitaxial films. The thin CdTe film with the thickness of a few of micrometers was used for the determination of the orientation relationship. The penetration length of x-ray into a CdTe film with an absorption coefficient of $\sim 10^3$ cm^{-1} was approximately 4.3 μm, which enabled the simultaneous azimuth measurement for both CdTe and Si by x-ray.[12] As described later, (133) and (211) CdTe films were grown selectively on (211) Si substrates by changing the II/VI and the growth rate. X-ray analysis using a (211) Si substrate as a reference crystal was performed for (133) and (422) reflections, as well as the (022) reflection to determine in-plane and out-of-plane orientation relationships between (211) Si substrates and grown CdTe films.

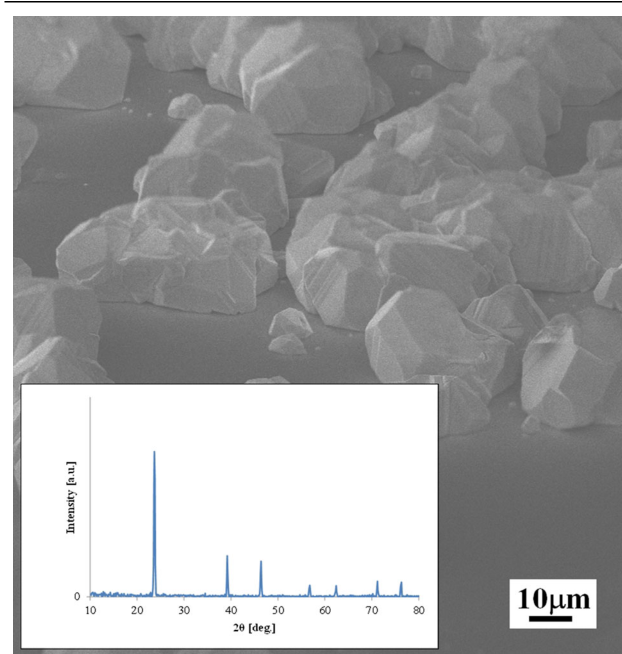

Fig. 1. Bird's-eye-view SEM image for CdTe film grown for 60 min after annealing the Si substrate at 600°C for 30 min in H_2 ambient. The inset shows x-ray diffraction spectrum of CdTe film.

It was revealed that the (133) axis of the CdTe film had no tilt with respect to the Si surface normal. The lattice match relationship between (133) CdTe and (211) Si was [01$\bar{1}$] CdTe ∥ [0$\bar{1}$1] Si and [$\bar{6}$11] CdTe ∥ [1$\bar{1}\bar{1}$] Si as shown in Fig. 2a, indicating that a rotation of the CdTe crystal occurred about the [111] axis by 180° with respect to the Si crystal.[13] The [111] axis of the CdTe film was tilted with respect to the [111] axis of Si substrates by 2.53°, which was explained by the lattice deformation to relieve the compressive stress to a CdTe epilayer near the interface.[14] This in-plane orientation relationship demonstrated the asymmetric lattice mismatch of 19.4% along [01$\bar{1}$] axis (between $d_{CdTe[011]}$ = 4.584 Å and $d_{Si[011]}$ = 3.840 Å, where d showed lattice spacing) and 0.6% along [$\bar{6}$11] axis (between $d_{CdTe[611]}$ = 1.052 Å and $d_{Si[333]}$ = 1.045 Å).[15]

Regarding (211) CdTe/(211) Si, as shown in Fig. 2b, the lattice of (211) CdTe was tilted approximately 2.53° with respect to the (211) Si substrate about [0$\bar{1}$1] CdTe ∥ [0$\bar{1}$1] Si coincident axis. The [111] axis of CdTe was tilted with respect to the [111] axis of Si by 2.53°, which was caused by accommodating the lattice mismatch at the interface, as well as (133) CdTe/(211) Si as shown in Fig. 2a.[9] The lattice match relationship between (211) CdTe and (211) Si was [0$\bar{1}$1] CdTe ∥ [0$\bar{1}$1] Si and tilted [1$\bar{1}\bar{1}$] CdTe ∥ [1$\bar{1}\bar{1}$] Si. The lattice mismatch was 19.4% along both [0$\bar{1}$1] and [1$\bar{1}\bar{1}$] axis (between $d_{CdTe[111]}$ = 3.743 Å and $d_{Si[111]}$ = 3.135 Å). It is worth noting that (255) is the exact twin of (211) with (111) as a mirror plane. Therefore, the (133) plane should be called a tilted (255) plane by 2.53°.

Figures 3 and 4 show plan-view SEM images and XRD spectra for (133) and (211) CdTe films grown for 60 min with the II/VI of 13 and 36, respectively. The input supply rates (partial pressures) of Cd and DiPTe were 114 μmol/min and 8.64 μmol/min (3.45×10^{-4} atm and 2.62×10^{-5} atm) for the II/VI of 13, as well as 316 μmol/min and 8.64 μmol/min (9.58×10^{-4} atm and 2.62×10^{-5} atm) for the II/VI of 36, respectively. The resulting thicknesses of CdTe films were 5 μm and 28 μm for the II/VI of 13 and 36, respectively, suggesting that the growth rate was increased by increasing the input supply rates of Cd. However, it was not a rate-limiting precursor. The (133) CdTe film exhibited a smooth surface with the striation along [0$\bar{1}$1]. However, the (211) CdTe had the morphology of triangle-shaped hillocks having width of ~ 10 μm and height of ~ 2 μm, composing of (111), (110), (101), and (100) facets.

XRD patterns of those films as shown in Fig. 4a and b were dominated by (133) and (422) CdTe reflections, respectively, which shows that the single crystalline was obtained on Si (211) substrates for both CdTe films. No peaks excepted for the main peak were observed in XRD patterns, indicating that no twinned crystalline CdTe was grown under each growth condition.[16]

Figure 5 indicates AFM images for (133) CdTe and for (111) plane of (211) CdTe, respectively. White and black regions showed high and low height, respectively. Thus, black regions in Fig. 5 indicated grooves, which were supposed to be due to the origin of the defect or dislocation. As shown in Fig. 5a, the tilt angle of facets about the surface and the average height forming the striation for (133) CdTe were ~ 4° and ~ 14 nm, respectively, indicating that a flatter surface was obtained than a previous paper.[10] For (211) CdTe, the morphology having the macro-step was observed for the step-bunching process during the growth. This shows that the step-flow growth proceeded in spite of the growth condition of the II/VI of as high as 36. The

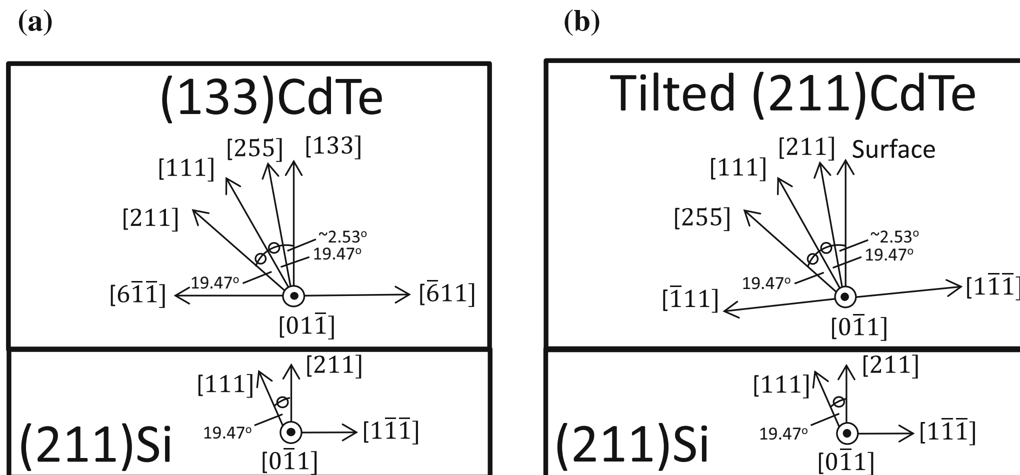

Fig. 2. Schematic for orientation relationship (a) between (211) Si substrate and (133) CdTe epitaxial film; (b) between (211) Si substrate and tilted (211) CdTe epitaxial film.

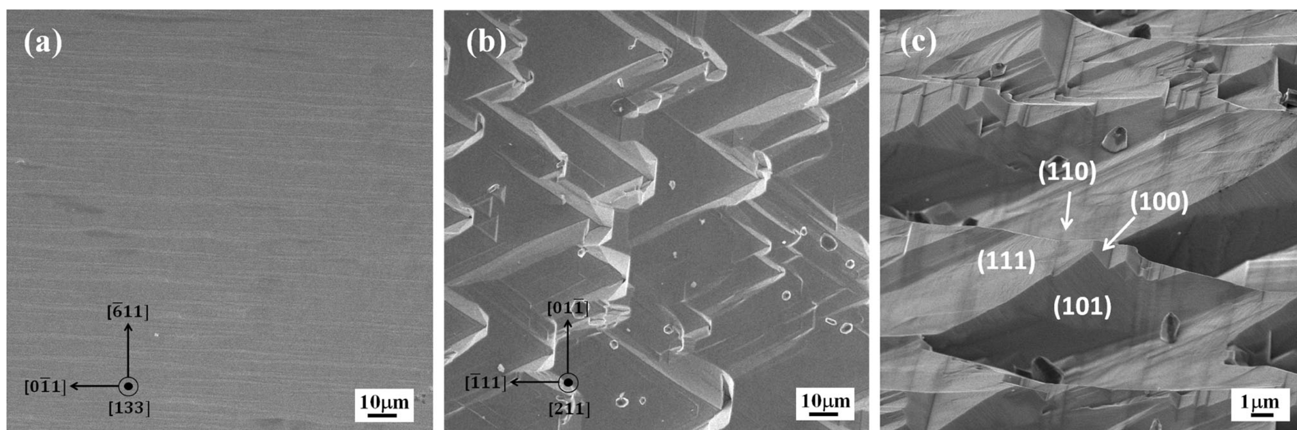

Fig. 3. Plan-view SEM images for CdTe films grown for 60 min with the II/VI of (a) 13 and (b) 36. (c) Bird's-eye-view SEM image for CdTe film grown for 60 min having the II/VI of 36.

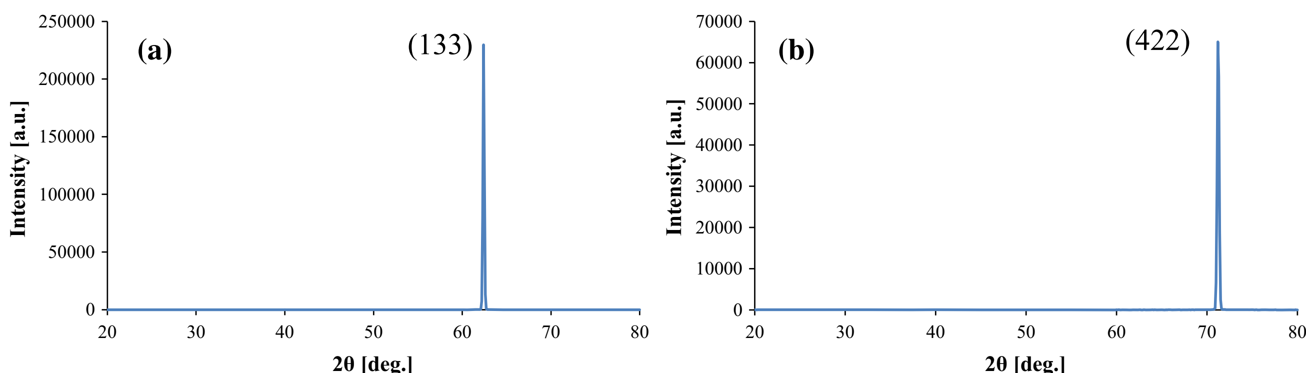

Fig. 4. X-ray diffraction spectra of CdTe films grown for 60 min with the II/VI of (a) 13 and (b) 36.

terrace width and the step height were ~ 30 nm and ~ 13 nm consisting of the multilayer step.

Dependence of the II/VI and the growth rate on the surface orientation of CdTe films is depicted in Fig. 6. The growth rate was controlled by changing the input supply rates of DiPTe for a rate-limiting precursor with keeping constant II/VI. When the II/VI was 26 or larger, a growth rate larger than 25 μm/h was achieved. On the other hand, when the II/VI was 18 or smaller, the growth rate larger than 12 μm/h could not be obtained, resulting in polycrystalline growth.

The obtained CdTe film indicated three different surface orientations: (133) CdTe, (211) CdTe, and the mixed phase consisting of (133) and (211) CdTe, i.e., twins. It is obviously seen that the (133) CdTe was obtained when the II/VI of 18 or smaller was adopted except for the formation of a mixed phase. When the II/VI of 26 was employed, the CdTe surface orientation was unstable. Moreover, when the II/VI of 36 was employed, (211) CdTe was consistently obtained irrespective of the growth rate.

Figure 7 summarizes the dependence of the FWHM on the thickness of (133) and (211) CdTe films. The growth was performed using the II/VI of 9–36 for 1 h. The FWHM was improved by increasing the CdTe film thickness. Furthermore, when the (133) CdTe and (211) CdTe having the same thickness were compared, the FWHM of (133) CdTe was consistently smaller than that of (211) CdTe. This trend was consistent with the results for (133) and (211) CdTe films on (211) GaAs substrates by MBE.[8]

A possible reason for controlling the orientation of (133) CdTe and (211) CdTe on (211) Si is explained as follows. Firstly, we consider the growth at the interface and evaluate the lattice mismatch between (211) Si and CdTe. As mentioned previously, for the case of (133) CdTe grown on (211) Si, the lattice mismatch for the $[\bar{6}11]$ axis was as small as 0.6% and as large as 19.4% for the $[01\bar{1}]$ axis. Stress from the large lattice mismatch caused by the latter was probably relieved by glide motions along $[01\bar{1}]$ axis.[17] However, in the case of (211) CdTe grown on (211) Si, the lattice mismatch for both $[0\bar{1}1]$ and $[1\bar{1}\bar{1}]$ axis was as large as 19.4%. We suppose that the (133) CdTe was grown preferably on (211) Si substrates despite of the II/VI due to the difference of lattice mismatch between (133) CdTe and (211) CdTe on (211) Si, which was in agreement with the result of the epitaxial (133) CdTe layer

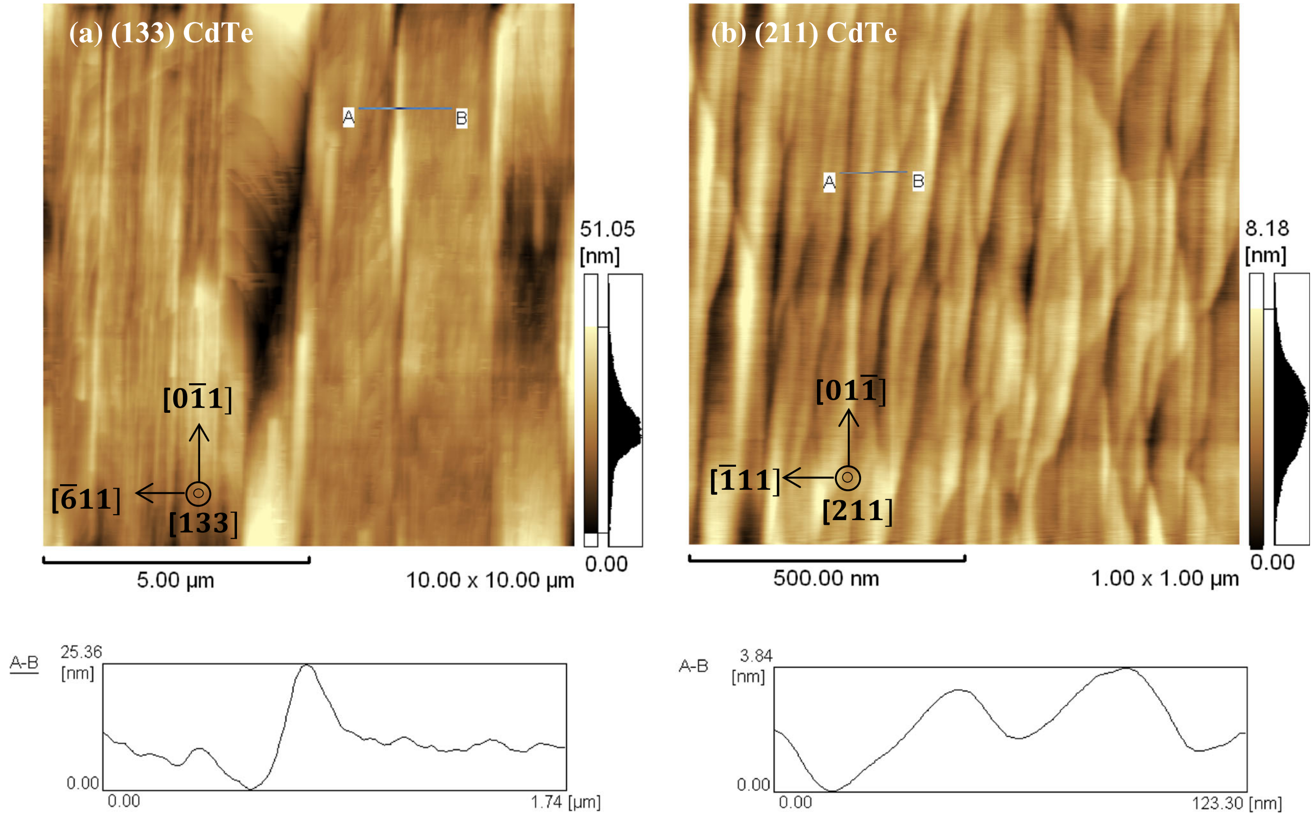

Fig. 5. Plan (upper) and cross-sectional (lower) AFM images along line A-B for CdTe films grown for 60 min with the II/VI of (a) 13 and (b) 36.

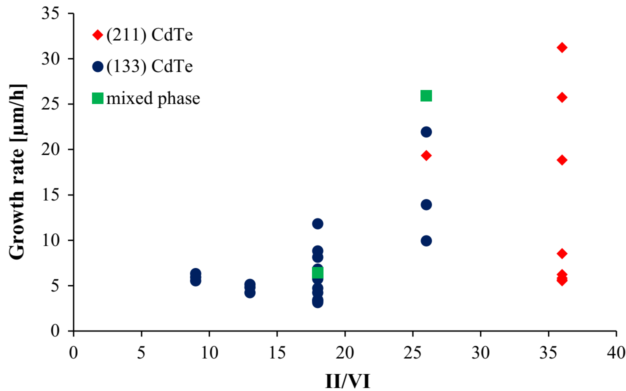

Fig. 6. Dependence of the II/VI and the growth rate on the surface orientation of CdTe film. Mixed phase shows CdTe film including XRD peaks assigned to both (133) and (211) planes.

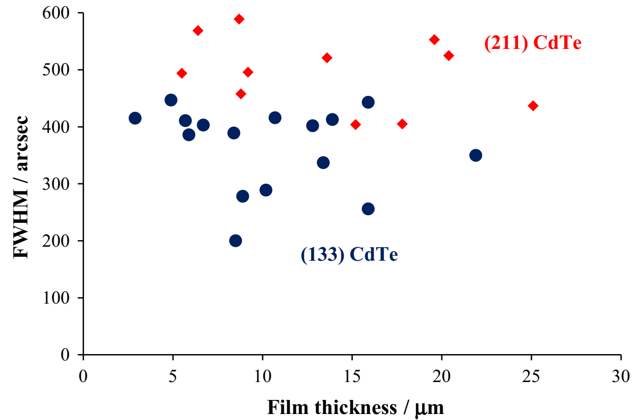

Fig. 7. Dependence of the FWHM on the film thickness of (133) and (211) CdTe.

grown on As-coated (211) Si by MOCVD.[10] We performed the initial growth of CdTe with a thickness of a few tens of nanometers on (211) Si substrates. XRD measurements showed that the (133) CdTe was grown preferably at the interface for any II/VI. The detail will be published in a separate paper.

Subsequently, the growth mechanism on (133) CdTe resulting in both (133) and (211) CdTe is discussed. The twin formation is affected by the growth temperature and the supersaturation of a precursor at the vapor phase.[14,18] As the adatom surface diffusion length is increased, increasing the growth temperature or decreasing the supersaturation promotes the step-flow growth and suppresses the spontaneous nucleation on the terrace. It is assumed that (133) CdTe and (211) CdTe are composed of a periodic array of (111) terrace planes and (100) step planes with an interplanar angle of 54.8°.[18] As shown Fig. 8, the change in the II/VI would afford the similar effects on the growth mode as the growth temperature and the supersaturation.

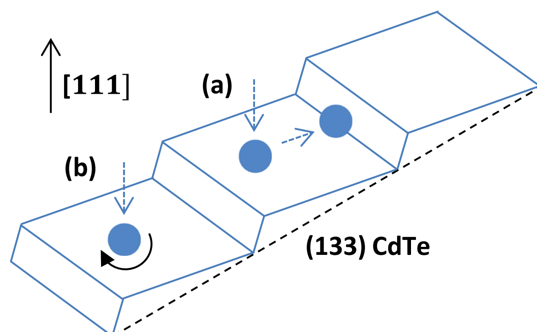

Fig. 8. Schematic illustration for the incorporation of the Te adatoms on (133) CdTe: (a) low II/VI; (b) high II/VI. Dashed line indicates (133) CdTe plane.

Thus, when relatively low II/VI is adopted, Te atom adsorbed on the (133) CdTe surface from the vapor phase migrates to the (100) step site on the surface or the kink site and is incorporated into the crystalline, leading a homo-orientation with (133) plane. On the contrary, the increase in the II/VI would increase the concentration of Cd atom near the surface, decreasing the Te adatom surface diffusion length.[19] Hence, when relatively high II/VI is employed, Te adatom on the surface tends to stay on the (111) terrace and easily rotates around the [111] axis by 180° followed by a spontaneous nucleation on the terrace, resulting in the twin formation with a (211) surface orientation.[20]

CONCLUSIONS

We investigated the effect of the growth condition such as the II/VI and the growth rate on the twin formation using (211) Si substrates with vapor-phase epitaxy using metallic cadmium source as a group-II precursor. The orientation of the epitaxial films was dependent on the II/VI. The orientation of the epitaxial films was changed from (133) to (211) plane by increasing the II/VI for the CdTe growth condition. Single-crystalline CdTe films were successfully grown in both (133) and (211) surface orientations on (211) Si substrates. The FWHM determined by XRD measurement revealed that the crystalline quality of (133) CdTe was better than that of (211) CdTe when the (133) CdTe and (211) CdTe had the same film thickness. We explained the formation mechanism of (133) and (211) CdTe having the difference between the step-flow growth on the step and spontaneous nucleation on the terrace depending on the II/VI.

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