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Characterization of (211) and (100) CdTe Layers Grown on Si Substrates by Metalorganic Vapor-Phase Epitaxy

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Single-crystal (211) and (100) CdTe layers have been grown by metalorganic vapor-phase epitaxy using the same condition on (211) and (100) Si substrates, respectively. Prior to the growth, substrates of both orientations were pretreated using the same pretreatment procedure. The crystal qualities of the grown layers were evaluated by full-width at half-maximum values of double-crystal x-ray rocking curves, and photoluminescence spectra at 4.2 K. (211) CdTe layers showed better crystallinity than (100) layers. The crystal quality of the (100) CdTe layers was also compared with that of layers grown on an epitaxial (100) GaAs layer on Si substrate. The results suggest that (100) CdTe layers with improved crystal quality could be obtained by optimizing the procedure of the Si substrates.

Key words: CdTe MOVPE, CdTe on Si, (211) CdTe, (100) CdTe

INTRODUCTION

We have been developing x-ray and gamma-ray detectors using single-crystal (211) CdTe layers grown on (211) Si substrate by metalorganic vapor-phase epitaxy (MOVPE).[1–3] The growth procedure and characterization of the (211) CdTe layers on Si substrates have been reported elsewhere.[4,5] Although CdTe layers with other orientations can be grown on Si substrates using the same procedure as applied for (211) CdTe layers, characterization of layers grown with other orientations had not been carried out. We report herein our early investigation on (100) CdTe layers grown on (100) Si by MOVPE, and compare their crystal properties with those of (211) layers, as well as (100) CdTe grown on (100) GaAs/Si substrate.

EXPERIMENTAL PROCEDURES

Undoped (211) and (100) CdTe layers were grown on (211) and (100) n^+-Si substrates at growth temperature of 450°C using diethyltelluride (DETe) and dimethylcadmium (DMCd) as precursors at constant DETe:DMCd supply rate ratio of 3.0. The growth rate of the CdTe layers was about 10 μm/h. Prior to CdTe growth, the Si substrate was pretreated to obtain single-crystal layers and avoid peel-off from the substrate. The pretreatment procedure was as follows: both (211) and (100) Si substrates were heated with GaAs pieces at temperature of 900°C for about 10 min to remove residual surface oxide, then cooled down gradually to around 550°C to passivate the surface with As and Ga. This pretreatment was carried out in a low-pressure hydrogen flow environment.[4,5] Grown CdTe layers were evaluated by x-ray diffraction measurements to confirm that single-crystal CdTe layers were grown. The thickness of the CdTe layers ranged from 5 μm to 40 μm. After growth of the CdTe layer, postgrowth annealing, typically at 700°C for 90 s, was carried out to reduce the residual strain in the grown layers.[6]

The grown layers were characterized by double-crystal x-ray rocking curve (DCRC) and photoluminescence (PL) measurements. The DCRC measurements were carried out on (422) reflection plane for (211) CdTe layers, and on (400) plane for (100) CdTe layers. The PL measurements were carried out at excitation wavelength of 488 nm and temperature
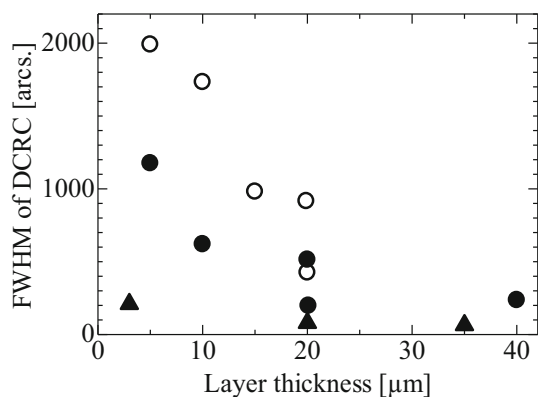
Fig. 1. FWHM from DCRC measurements for (211) (solid circle) and (100) (open circle) CdTe layers as function of CdTe layer thickness, plus data for (100) layers grown on (100) GaAs/Si substrate (solid triangle).[7]

of 4.2 K. The crystal quality of the (100) CdTe layers was also compared with that of layers grown on (100) GaAs/Si substrates, which had a 2-μm-thick GaAs epitaxial layer on a (100) Si substrate, with typical FWHM value of about 240 arcsec.[7]

RESULTS AND DISCUSSION

Figure 1 shows the variation of the DCRC FWHM values of the (211) and (100) CdTe layers with their thickness, as well as the FWHM values of (100) CdTe layers grown on (100) GaAs/Si (discussed later). The x-ray diffraction peak broadens due to crystal imperfections such as defects, threading dislocations, and twins in the grown layers as well as due to the intrinsic broadening of the CdTe materials and wafer curvature.[8] However, the latter effects on the DCRC FWHM values are very minor and can be neglected. Hence, we used the DCRC FWHM values to compare the crystal quality of grown epilayers with different orientations. The FWHM values of (211) layers decreased with increase of the CdTe thickness from 5 μm to 20 μm, and remained at around 200 arcsec for thickness from 20 μm to 40 μm. For the (100) layers, the FWHM values also decreased with the thickness of the CdTe layer. However, the FWHM values were larger than for the (211) layers, with a lowest value of 300 arcsec at thickness of 20 μm.

(100) CdTe layers exhibited polycrystalline characteristics when the thickness exceeded 30 μm, containing both (100) and (111) domains. However, the (211) CdTe layers were single domain, independent of their thickness. Growth of double-domain (111)-oriented CdTe layers on (100) Si has been reported using molecular beam epitaxy (MBE) at around 300°C.[9] Growth of single-crystal (100) CdTe layers on Ge/(100) Si substrates has been reported at growth temperature above 420°C by MOVPE; however, CdTe layers grown at lower temperature exhibited a mixture of (100) and (111) domains.[10] We believe that single-crystal (100) CdTe growth

occurred in this experiment due to the high growth temperature of 450°C. The polycrystalline nature of the (100) CdTe layers with increase of thickness may be caused by reduced surface migration of Cd and Te species on (100) CdTe compared with the (211) surface. Such reduced surface migration would promote formation of islands, leading to three-dimensional growth. This difference could be due to the inherent property of the substrate orientation. Periodical growth interruptions or use of a lower growth rate should inhibit island formation, because reactant species would have more time to migrate over the substrate and unstable islands could suffer thermal desorption before becoming stable. Hence, these approaches may be effective to avoid polycrystallization.

Figure 2 shows the PL spectra for (211) (a–c) and (100) (d–f) CdTe layers with different thicknesses from 5 μm to 20 μm. PL measurements are effective to evaluate not only impurities and their energy states, but also crystal defects and associated residual stress in crystals. Residual strain in the epilayer decreases the peak intensity of bound excitons, and broadens and shifts the peak position, while structural defects increase the intensity of deep-level emissions and broaden the peak widths.[11] In this sense, such measurements provide a relative measure of crystal quality, although absolute determination of defect density is difficult. Furthermore, the substrate pretreatment temperature, the growth temperature, as well as other growth conditions in this experiment were kept constant. Hence, possible impurities in the system such as Ga and As and their incorporation into the grown epilayer remained the same. Also, the formation of Cd vacancies (hence p-type property) due to its higher vapor pressure also did not change. The observed peak variation can therefore be attributed to the defect density and the degree of residual strain in the crystal. The spectra of the (211) CdTe layers consist of a neutral acceptor-bound exciton (A^0, X) line, neutral donor-bound exciton (D^0, X) line, and donor–acceptor pair (DAP) emission band.[12] The donor is believed to be residual iodine in the growth chamber, used for n-type doping, and the acceptor could be related to Cd vacancies. For (211) CdTe layers with thickness less than 20 μm, the (A^0, X) and (D^0, X) exciton lines were broad and weak, and the DAP bands were dominant. At CdTe thickness of 20 μm, on the other hand, the (A^0, X) line became sharp and dominant. These results indicate that the crystal quality of the (211) CdTe layers improved with their thickness, consistent with the results in Fig. 1. The emission energy of the (A^0, X) lines also increased with the thickness of the CdTe layer, as discussed in Fig. 3. On the other hand, (100) CdTe layers with thickness less than 20 μm showed broad and weak emissions in the exciton region but intense emissions in the DAP band, indicating lower crystal quality of (100) compared with (211) layers. In contrast to the above results, the (100)
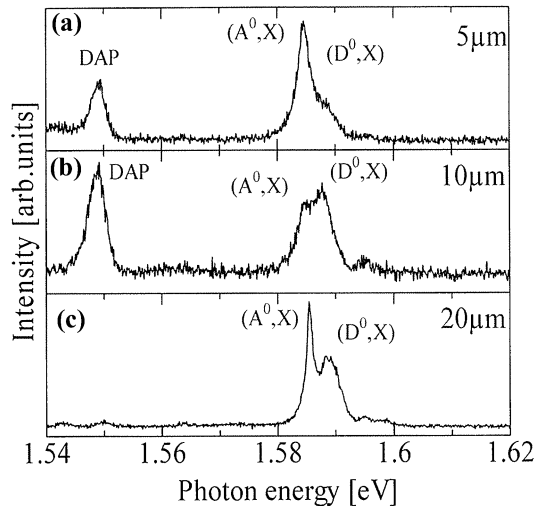
Fig. 2. PL spectra of grown (211) (a–c) and (100) CdTe layers (d–f) with thickness of 5 μm, 10 μm, and 20 μm.

Fig. 3. Variation of (A^0, X) emission energy as function of (211) CdTe layer thickness; dashed line shows (A^0, X) emission energy of bulk CdTe crystal.

CdTe layer with thickness of 20 μm showed a PL spectrum similar to that of the (211) layer. This indicates that a (100) CdTe layer with crystal quality comparable to that of the (211) layer was obtained at this thickness.

Figure 3 shows the variation of the emission energy of (A^0, X) line of the (211) CdTe layers with their thickness, while the dashed line shows the unstrained value for (A^0, X) for bulk CdTe crystal.[13] As explained above, the bound exciton emission energy strongly depends on the stress in the grown layer. In the epilayer under tensile stress, the emission energy of (A^0, X) peak will be lower than the unstrained value, but gradually approaches it if the strain relaxes. Figure 3 shows that the emission energy of (A^0, X) peak increased toward the unstrained value of bulk CdTe crystal with increasing CdTe thickness. This indicates that the tensile strain in the CdTe layer gradually relaxes with increasing CdTe thickness.
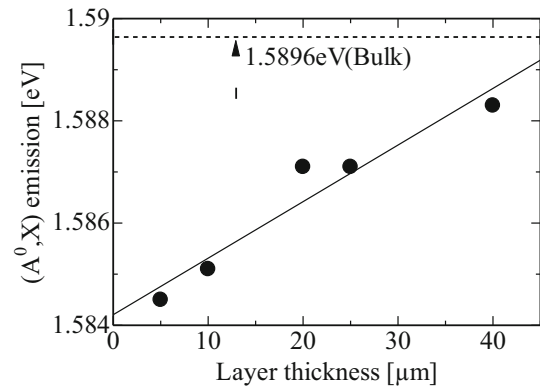
These experimental results show that the crystal quality of the (100) CdTe layers grown on (100) Si was lower than for (211) layers grown on (211) Si. To examine the effect of growth orientation on crystal quality, we also examined the DCRC FWHM values of (211) and (100) CdTe layers grown homoepitaxially on (211) and (100) CdTe substrates. The FWHM values of those CdTe substrates were below 30 arcsec. Growth of (211) and (100) CdTe layers was carried out in the same growth run. The FWHM values of the grown (211) CdTe layers were less than 90 arcsec, always being smaller than those of the (100) layers. These results indicate that the (100) layers contained higher density of crystal imperfections than the (211) layers. This is considered to be an inherent crystal quality characteristic which depends on the growth orientation.

We also examined the effect of the substrate surface properties on the crystal quality of the grown layers, by comparing the crystal quality of (100) CdTe layers grown in this experiments with that of (100) layers grown on (100) GaAs/Si.[7] The variation of the FWHM values of CdTe layers grown on (100) GaAs/Si is also shown in Fig. 1, being about 200 arcsec at CdTe thickness of 5 μm but about 70 arcsec for layers thicker than 20 μm. Furthermore, the PL results for CdTe on (100) GaAs/Si substrate showed a sharp, high-intensity (A^0, X) emission, with small defect-related peak.[7] These results show that the crystal quality of layers grown on GaAs/Si substrates was much better than that of layers grown in this experiment. This indicates that the crystal quality of the grown CdTe layers is strongly influenced by the surface properties of the substrate. The presence of an interfacial layer of either crystalline GaAs with orientation parallel to the substrate, or uniform coverage of the Si substrate with an atomic layer of arsenic as discussed below, results in high-quality epilayers.

We now discuss why the crystallinity of (100) CdTe grown on (100) Si is worse than that of (211) CdTe grown on (211) Si, and discuss ways to

improve it. It is well discussed in literature that CdTe predominantly grows in (111) direction on (100) Si substrate and suffers from double domains and twin formation.[9] Several attempts to obtain (100)-oriented growth on (100) Si directly have so far been unsuccessful. In this work, by carefully controlling substrate preparation and CdTe nucleation, we could obtain (100) CdTe on (100) Si. Here, we discuss the probable growth mechanism of this epitaxy in comparison with that of (211) CdTe on (211) Si. Our early investigation by cross-sectional transmission electron microscopy (TEM) showed that, although the crystallinity of those layers was not as good as our present crystals, the (211) CdTe/ (211) Si interface consisted of numerous GaAs clusters with random orientations (Unpublished work). CdTe grown on top of these clusters and their surroundings was not properly orientated, but CdTe grown in between clusters was orientated parallel to the Si substrate. As growth proceeded, this orientated CdTe overgrows the randomly orientated CdTe, resulting in improved crystallinity of the layer with increasing thickness. The origin of the clusters is thought to be thermally decomposed GaAs which randomly redeposits on the Si during substrate pretreatment. The orientated growth of the CdTe on Si between such GaAs clusters can be explained by formation of an interfacial layer of arsenic that allowed formation of a coherent interface. This growth mechanism is similar to that in molecular beam epitaxy (MBE) growth of CdTe/Si.[14] However, presence of atomic arsenic could not be confirmed by our TEM measurements at that time.

To investigate this further, we performed x-ray photoelectron spectroscopy (XPS) analysis of the GaAs-treated Si substrate. The results showed both Ga and As peaks along with Si peak signals. By analyzing the intensities of these peaks, the presence of GaAs clusters as well as one or two atomic layers of arsenic between them could be confirmed. This observation therefore supports the growth mechanism explained above. However, our current (211) CdTe epilayers exhibit much better crystal quality than the crystal used for the TEM analysis discussed above. This suggests that our current pretreatment condition suppresses randomly orientated GaAs cluster formation on (211) Si and promotes the formation of a uniform layer of atomic arsenic on the surface, though this requires further verification.

Hence, the following reasoning can be applied to explain the inferior crystal quality of (100) CdTe grown on (100) Si. We performed both (211) and (100) substrate treatments simultaneously in this study. However, it is very likely that this pretreatment condition was not adequate for the (100) Si substrate, as the properties and structure of these two surfaces are not similar. Hence, the surface coverage of atomic arsenic on the (100) Si substrate may be different from that on the (211) substrate,

leading to the observed difference in crystal quality. Hence, further optimization of substrate pretreatment conditions such as the temperature, the temperature ramping time during cooldown, etc. is needed to obtain uniform surface coverage of atomic arsenic and thereby growth of high-quality (100) CdTe on (100) Si.

Finally, we would like to comment on the properties of the CdTe epilayers on (100) GaAs/Si substrate. The high crystallinity of this growth can be explained by the presence of single-crystal GaAs with growth orientation similar to that of the Si substrate. Hence, subsequent growth on top of the orientated GaAs results in perfectly orientated CdTe with good crystal quality, as this growth is similar to CdTe growth on GaAs substrate. Although these grown epilayers show high structural quality, Ga and As outdiffused from the GaAs has detrimental effects on the electrical properties of the grown layer. Hence, CdTe grown on GaAs/Si substrate is not suitable for our x-ray and gamma-ray device applications.

CONCLUSIONS

The crystal quality of (211) and (100) CdTe layers grown on Si substrates was studied based on DCRC FWHM values and PL measurements. CdTe layers were grown by MOVPE on (211) and (100) Si substrates after the same substrates pretreatment. Grown (211) CdTe layers showed better crystallinity than the (100) layers. The crystallinity of the (100) CdTe layers was also compared with that of layers grown on GaAs/Si substrate. The results suggest that (100) layers with improved crystal quality could be obtained by optimizing the pretreatment of the Si substrate.

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