

Characterization of (211) and (100) CdTe layers grown on Si substrates by metalorganic vapor phase epitaxy

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Abstract:

Crystal qualities of single crystal (211) and (100) CdTe layers grown on Si substrates have been evaluated. Respective CdTe layers were grown on (211) and (100) Si substrates by metalorganic vapor phase epitaxy. The same pretreatment procedure was applied to (211) and (100) Si substrates before the growth. CdTe layers of both orientations were grown in the same growth condition. Grown layers were examined by full-width at half-maximum values of double crystal X-ray rocking curve, and photoluminescence spectra at 4.2 K. (211) CdTe layers showed better crystallinities than those of (100) layers. Crystal quality of the (100) CdTe layers was also compared with that of the layers grown on an epitaxial (100) GaAs layer on Si substrate. The results suggest that an improvement of crystal quality of the (100) CdTe layers is expected by optimizing the pretreatment procedure of Si substrates.

Keywords: CdTe MOVPE, CdTe on Si, (211) CdTe, (100) CdTe

1. Introduction

We have been developing X-ray and gamma-ray detectors using single crystal (211) CdTe layers grown on (211) Si substrates 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 in the same procedure as that for the (211) CdTe layers, characterization of grown layers with other orientations had not been carried out. In this paper, we report our early investigation on (100) CdTe layers grown on (100) Si by MOVPE, and compare the crystal properties with that of the (211) layers, and also with the (100) CdTe grown on (100) GaAs/Si substrates.

2. Experimental details

Undoped (211) and (100) CdTe layers were grown on (211) and (100) n⁺-Si substrates at a growth temperature of 450 °C using diethyltelluride (DETe) and dimethylcadmium (DMCd) as precursors. A supply rate ratio of DETe to DMCd was kept constant at 3.0. The growth rate of CdTe layers was about 10 μm/h. Prior to the CdTe growth on Si substrates, a pretreatment of substrates was carried out to obtain single crystal and to avoid peel-off from the substrate. The pretreatment procedure is as follows; both (211) and (100) Si substrates were heated with GaAs pieces at a temperature of 900 °C for about 10 min to remove residual surface oxide. Then, substrates were cooled down gradually to around 550 °C to passivate surfaces with As and Ga. The 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. Thickness of CdTe layers was varied from 5 to 40 μm. After the growth of CdTe layers, post growth annealing typically at 700 °C for 90s was carried out to reduce the residual strain in the grown layers.⁶

Characterization of grown layers were carried out 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 an excitation wavelength of 488 nm and at the temperature of 4.2 K. Crystal quality of the (100) CdTe layers was also compared with that of the layers grown on (100) GaAs/Si substrates. The (100) GaAs/Si substrate had a 2 μm thick GaAs epitaxial layer on (100) Si substrates which had typical FWHM value of about 240 arc-s.⁷

3. Experimental results and discussion

Figure 1 shows variation of DCRC FWHM values of (211) and (100) CdTe layers with thickness of CdTe layers. In the figure FWHM values of (100) CdTe layers grown on (100)

GaAs/Si are also shown, which will be discussed later. The X-ray diffraction peak broadens due to the crystalline imperfections such as defects, threading dislocations, and twins in the grown layers as well as due to the intrinsic broadening of CdTe materials and wafer curvatures⁸. However, the later effects on the DCRC FWHM values is very low, 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 to 20 μm , and remained around 200 arc-s for the thickness from 20 to 40 μm . For the (100) layers, on the other hand, the FWHM values also decreased with thickness of CdTe layers. However, the FWHM values were larger than those of (211) layers, and the lowest value was 300 arc-s at the thickness of 20 μm .

(100) CdTe layers exhibited characteristics of polycrystallization when the layer thickness exceeded 30 μm , where the CdTe layers contained both (100) and (111) domains. Whereas the (211) CdTe layers were single domain independent of CdTe thickness. Growth of double domain (111) oriented CdTe layers on (100) Si have been reported in molecular beam epitaxy (MBE) where growth was carried out around 300 $^{\circ}\text{C}$.⁹ Growth of single crystal (100) CdTe layers on Ge/(100)Si substrates have been reported at growth temperature higher than 420 $^{\circ}\text{C}$ in MOVPE, however, the grown CdTe layers exhibited a mixture of (100) and (111) domains at lower growth temperature.¹⁰ Single crystal (100) CdTe growth in this experiment is considered due to high growth temperature of 450 $^{\circ}\text{C}$. The polycrystallization of (100) CdTe layers with increase of thickness may be caused by the lower surface migration of Cd and Te species on the (100) CdTe than that on the (211) surface. The lower surface migration promotes 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 decrease of growth rate should inhibit the island formation as the reactant species get more time to migrate over the substrate and also allows thermal desorption of unstable islands before they become stable. Hence this may be effective to avoid polycrystallization.

Figure 2 show variations of PL spectra with thickness of CdTe layers from 5 to 20 μm , where the top three figures (a-c) are for (211) and bottom three figures (d-f) for the (100) CdTe layers, respectively. PL measurement is effective to evaluate not only the impurities and their energy states, but also the crystal defects and associated residual stress in the crystals. A residual strain in the epilayer decreases the peak intensity of bound exciton, broadens and shifts the peak position, while the structural defects increase the intensity of deep level emissions and broaden the peak widths¹¹. In this sense, it provides a relative measure of the crystal quality though an absolute determination of the defect density would be 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, As and their

incorporation in the grown epilayer remains same. Also Cd-vacancy (hence p-type property) resulted due to its higher vapor pressure also does not change. Hence, the observed peak variation can be attributed due to the defect density and degree of the residual strain in the crystal. The spectra of (211) CdTe layers consist of neutral acceptor bound exciton line (A^0, X), neutral donor bound exciton line (D^0, X), and donor acceptor pair emission band (DAP)¹². The donor was thought to be residual iodine in the growth chamber which was used for n-type doping, and the acceptor could be related to the Cd vacancies. For (211) CdTe layers with thickness less than 20 μm , exciton lines of (A^0, X) and (D^0, X) were broad and weak, and emission from DAP bands was dominant. At the CdTe thickness of 20 μm , on the other hand, the (A^0, X) line became sharp and dominant. The above results indicate that the crystal quality of (211) CdTe layers improves with the thickness of CdTe layers, which is also consistent with the results shown in Fig.1. The emission energy of (A^0, X) lines also increased with the thickness of CdTe layers, which will be 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 and intense emissions in DAP band, which indicate lower crystal quality of (100) layers than that of (211) layers. In contrast to the above results, the (100) CdTe layer with thickness of 20 μm showed similar PL spectrum as that of the (211) layer. This indicates that (100) CdTe layer with crystal quality comparable to that of the (211) layer was obtained at this thickness.

Figure 3 shows variations of emission energy of (A^0, X) line of the (211) CdTe layers with thickness, where dashed line is unstrained value of the (A^0, X) from a bulk CdTe crystal¹³. 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 that of the unstrained value, but gradually comes closer if the strain relaxes. Fig. 3 shows the emission energy of (A^0, X) peak increased toward that of the unstrained value of the bulk CdTe crystal with increase of the CdTe thickness. This indicates that the tensile strain in CdTe layers gradually relaxes with increase of the CdTe thickness.

The above experimental results show that the crystal quality of grown (100) CdTe layers on (100) Si is lower than those of the (211) layers on (211) Si. To examine the effect of growth orientation on the crystal quality, we also examined DCRC FWHM values of homo-epitaxially grown (211) and (100) CdTe layers on (211) and (100) CdTe substrates. The FWHM values of those CdTe substrates were less than 30 arc-s. The growth of (211) and (100) CdTe layers was carried out in the same growth run. The FWHM values of grown (211) CdTe layers were less than 90 arc-s, and were always smaller than those of the (100) layers. These results indicate that the (100) layers contain higher density of crystal imperfections than the (211) layers. This was considered as an inherent characteristic of crystal quality which depends on growth orientation.

We also examined effect of surface property of substrates on the crystal quality of grown

layers. We compared the crystal quality of (100) CdTe layers grown in this experiments with that of the (100) layers grown on (100) GaAs/Si.⁷ Variation of FWHM values of CdTe layers grown on (100) GaAs/Si is also shown in Fig. 1. As shown in the figure, FWHM values of layers grown on GaAs/Si substrates were around 200 arc-sec at the CdTe thickness of 5 μm , and about 70 arc-sec for layers thicker than 20 μm . Furthermore, the PL results from the CdTe on (100) GaAs/Si substrate showed a sharp and high intensity (A°, X) emission, with small defect related peak⁷. These results show that crystal quality of layers grown on GaAs/Si substrates are much better than that of layers grown in this experiments. This indicates that the crystal quality of grown CdTe layer is influenced strongly by the surface property of the substrate. Presence of interfacial layers of either crystalline GaAs with orientation parallel to the substrate or uniform coverage of Si substrate with atomic layer of arsenic as discussed below produce high quality epilayers.

We would like to discuss further why the crystallinity of the (100) CdTe grown on (100) Si is poorer compared to that of (211) CdTe on (211) Si, and discuss ways to improve them. It is well discussed in the literature that CdTe predominantly grows in (111) direction on (100) Si substrates and suffers from double domains and twin formations⁹. Several attempts to obtain (100) orientated growth on (100) Si directly have so far been unsuccessful. In this work by carefully controlling the substrate preparation and the CdTe nucleation we could obtain (100) CdTe on (100) Si. Here we discuss the probable growth mechanism of this epitaxy comparing it to that of the (211) CdTe/(211)Si. Our early investigation of (211) CdTe/(211)Si interface using cross-sectional transmission electron microscope (TEM), though the crystallinity of those layers was not as good as our present crystals, showed that the interface consists of numerous GaAs clusters with random orientations¹⁴. The CdTe grown on the top of these clusters and their surroundings were not properly orientated, however, CdTe grown in between those clusters were orientated parallel to the Si substrate. As the growth proceeds this orientated CdTe overgrows the random orientated CdTe resulting improvement in crystallinity of the layer with the thickness. The origin of the cluster was thought to be thermally decomposed GaAs which randomly redeposits on the Si during substrate pretreatment. The orientated growth of CdTe on Si in between those GaAs clusters could be explained by formation of an interfacial layer of arsenic that allowed the formation of a coherent interface. This growth mechanism is similar to that of a molecular beam epitaxy (MBE) growth of CdTe/Si¹⁵. However, presence of atomic arsenic could not be confirmed by our TEM measurement at that time.

In order to investigate it further, we performed an XPS analysis of the GaAs treated Si substrate. The XPS exhibited both Ga and As peaks along with Si peak signals. By analyzing these peak intensities the presence GaAs clusters as well as presence of 1 to 2 atomic layers of arsenic in between those clusters could be confirmed. Hence this observation supports the above explained growth mechanism. Our current (211) CdTe epilayers however exhibit much better

crystal quality than that of the crystal used for above discussed TEM analysis. This suggests our current pretreatment conditions suppresses the randomly orientated GaAs cluster formation on (211) Si and promotes a uniform layer of atomic arsenic formation on the surface, though it needs further verifications.

Hence the following reasoning could be applied to explain the inferior crystal quality of (100) CdTe growth on (100) Si. We performed both (211) and (100) substrate treatments simultaneously in this study. However, it is very likely that pretreatment conditions for (100) Si substrate is not adequate as the properties and structures of these two surfaces are not similar. Hence surface coverage of atomic arsenic of the (100) Si substrate may be different than that of the (211) substrate leading to difference in crystal quality. Hence further optimization of substrate pretreatment conditions such as temperature, as well as temperature ramping time during cool down, etc is needed to attain a uniform surface coverage of atomic arsenic in order to obtain high quality (100) CdTe on (100) Si.

Finally we would like to comment on the properties of CdTe epilayers on (100) GaAs/Si substrates. The high crystallinity of this growth could be explained due to the presence of single crystal GaAs with growth orientation similar to the Si substrate. Hence subsequent growth on the top of the orientated GaAs results perfectly orientated CdTe with good crystal quality, as this growth is similar to that of CdTe growth on GaAs substrates. Though the grown epilayers are of high structural quality, however, Ga, As out-diffused 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, gamma ray device applications.

4. Summary

Crystal qualities of (211) and (100) CdTe layers grown on Si substrates have been studied by FWHM values of DCRC, and PL measurements. CdTe layers were grown on (211) and (100) Si substrates by MOVPE after a pretreatment of Si substrates. Grown (211) CdTe layers showed better crystallinities than those of the (100) layers. Crystallinity of (100) CdTe layers were also compared with layers grown on GaAs/Si substrates. The results suggest that an improvement of crystal quality of (100) layers is expected by optimizing the pretreatment of Si substrates.

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Figure captions:

Fig. 1 Variation of FWHM values of DCRC measurements for (211) and (100) CdTe layers as a function of thickness of CdTe layers. Solid circles represent data for (211) layers, and open circle for (100) layers. Solid triangles represent data for (100) layers grown on (100) GaAs/Si substrates.⁷

Fig. 2 PL spectra of grown CdTe layers with thickness of 5, 10, and 20 μm . (211) CdTe layers (a-c), and (100) CdTe layers (d-f).

Fig. 3 Variation of (A^0 , X) emission energy as a function of thickness of (211) CdTe layers. Dashed line shows (A^0 , X) emission energy of bulk CdTe crystal.

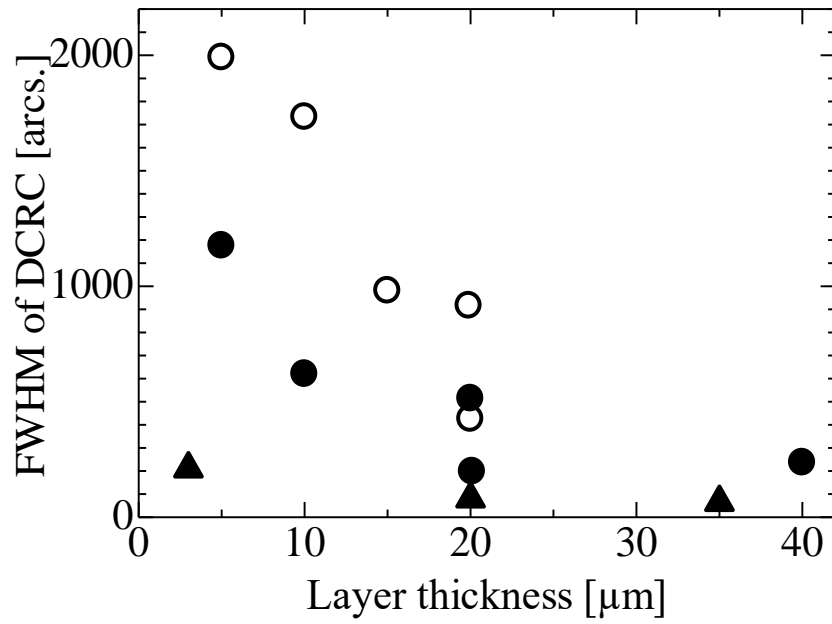


Fig. 1
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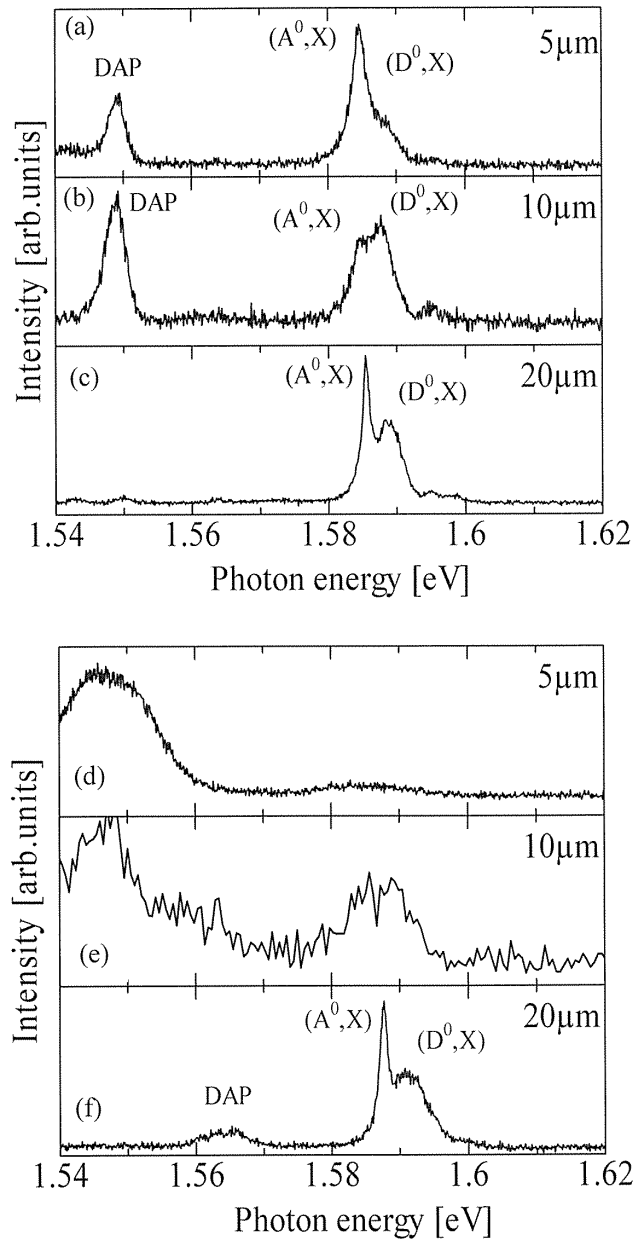


Fig. 2
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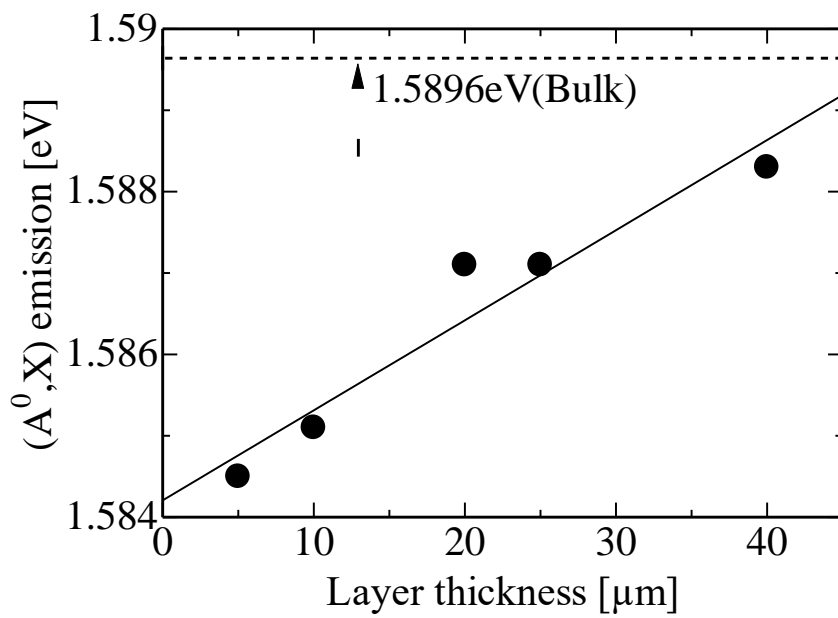


Fig. 3
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