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Critical Thickness of ZnTe on GaSb(211)B

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An important parameter for heteroepitaxial material systems is the critical thickness h_c. To date, for the material system ZnTe on GaSb, agreement between experimental and theoretical values of h_c has been poor. In this paper, we present results of an experimental study of h_c for ZnTe layers on GaSb(211)B substrates based on a combination of high-resolution x-ray diffraction and photoluminescence measurements. Our experimentally determined h_c value of 350 nm to 375 nm agrees well with the models of Cohen-Solal and Dunstan.

Key words: ZnTe, GaSb, molecular beam epitaxy, critical thickness, x-ray diffraction, photoluminescence

INTRODUCTION

For heteroepitaxy of metal or semiconductor materials an important characteristic is the critical thickness h_c of the epilayer. Below h_c, the layer is pseudomorphic to the substrate and no misfit dislocations form. Above h_c, the layer assumes its bulk lattice parameter and misfit dislocations and their threading segments form to relieve strain.

ZnTe is an emerging material of interest for photovoltaic applications and as a buffer layer for HgCdTe or HgCdSe. ZnTe has been deposited on a variety of substrates, including Si, InP, InAs, GaAs, and GaSb.[1,2] Not unexpectedly, the full-width at half-maximum (FWHM) values of Bragg reflections in x-ray diffraction (XRD) spectra are found to be lower for ZnTe on substrates with lower lattice parameter mismatch: 33 arcsec for ZnTe/GaSb (0.13% mismatch) compared with 45 arcsec for ZnTe/GaAs (7.3%). Moreover, intensity of photoluminescence from ZnTe at 2.26 eV has been found to be stronger for ZnTe/GaSb than for ZnTe/GaAs.[1]

There are currently only two reports of experimentally determined values for h_c of ZnTe/GaSb, both of which were for layers deposited by metal-organic vapor-phase epitaxy (MOVPE) on substrates with (100) orientation. Upper limits of 180 nm and 800 nm were derived from optical and x-ray diffraction measurements.[3,4] However, there are currently no studies of the critical thickness of ZnTe/GaSb grown by molecular beam epitaxy (MBE) and none for the (211) orientation. The (211)B orientation is of particular interest for MBE growth of HgCdTe or HgCdSe deposition, as it has been found to suppress the formation of twin-related hillocks which are prevalent when the (100) orientation is used.[5]

Herein we present results for ZnTe layers deposited by molecular beam epitaxy (MBE) to various thicknesses on GaSb(211)B substrates. We chose this orientation because a near-term use for this ZnTe/GaSb system is as a composite substrate for MBE of HgCdSe for infrared detector applications. We derive a value for critical thickness based on high-resolution x-ray diffraction (HRXRD) and photoluminescence (PL) measurements. In the HRXRD measurements, the FWHM of 422 reflections from ZnTe as well as the separation between ZnTe and GaSb peaks were analyzed to yield a value for h_c. Since the 422 reflection is a symmetric reflection, it probes the out-of-plane lattice parameter and hence can be used to determine strain in pseudomorphic layers. For a similar material system—ZnSe on GaAs—the HRXRD FWHM method has been found to be more sensitive than the strain method.[6] PL spectra were analyzed and confirmed the assignment of h_c that was derived from HRXRD. Finally, threading dislocations in relaxed ZnTe were observed directly in PL images acquired from these layers.

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THEORETICAL CONSIDERATIONS

Several authors have formulated models to estimate the critical thickness in heteroepitaxy systems. The model of Matthews–Blakeslee has been applied extensively to mismatched systems.[7–9] Firstly, they assume that there are pre-existing threading dislocations from the substrate which can elongate to form misfit dislocations in the epilayer. Their force balance model then assumes that the critical thickness occurs when the misfit strain force (which elongates the threading dislocation) matches the tension force (which opposes the elongation) found in a pre-existing line dislocation. Above the critical thickness, the force of the misfit strain exceeds that of the tension force, destroying the coherency that previously existed at the interface and creating additional dislocations.

In this model, the critical thickness is given by

$$h_c = \frac{b(1 - \nu\cos^2\alpha)}{8\pi f_m(1+\nu)\cos\beta}\left[\ln\left(\frac{h_c}{b}\right)+1\right], \quad (1)$$

$$b = \frac{1}{2}a_l\langle 110\rangle, \quad (2)$$

$$f_m = \frac{a_l - a_s}{a_s}, \quad (3)$$

where h_c is the critical thickness (Å), $\boldsymbol{b}$ is the Burgers vector (Eq. 2), ν is the Poisson's ratio, α and β are the angles between the dislocation line and the Burgers vector, f_m is the misfit parameter (Eq. 3),[10] a_l is the epilayer lattice parameter, and a_s is the substrate lattice parameter. Assuming that the misfit dislocations are of the 60° type ($\alpha = \beta = 60°$), and lattice parameters are a_{ZnTe} = 6.1039 Å and a_{GaSb} = 6.0959 Å,[3] the value of critical thickness is 115 nm.

Cohen-Solal et al.[11] chose a simpler model where misfit at a heteroepitaxial interface is accommodated by a combination of misfit strain and misfit dislocations. The energy is then calculated using Keating's valence force approximation to yield the following semi-empirical expression:[10,11]

$$h_c = A * f_m^{-3/2}, \quad (4)$$

where A^* is an adjustable parameter. Cohen-Solal et al. determined that A^* is approximately 0.15 for zincblende semiconductor systems with misfit of less than 8%. As the ZnTe/GaSb system has a misfit of only 0.13%, we chose to adopt Cohen-Solal's estimate of 0.15 for A^*, in which case Eq. 4 yields a value of h_c = 316 nm.

Instead of using energy-minimization arguments, Dunstan et al.[12] proposed a geometrical model to estimate the critical thickness. They assume that a misfit dislocation will not form if the strain is less than $\boldsymbol{b}/md$, where $\boldsymbol{b}$ is the Burgers vector, d is the film thickness, and m is between 1 and 2. In this model, the critical thickness is given by

Table I. Summary of model calculations of the critical thickness values for ZnTe on GaSb

Model	Calculated h_c (nm)	Ref.
Matthews-Blakeslee	115	This work
Matthews-Blakeslee	240	[13]
Cohen-Solal	316	This work
Cohen-Solal	460	[3]
Dunstan	329	This work
Dunstan	330	[3]

$$h_c = \frac{b}{f_m}, \quad (5)$$

which yields a value of 329 nm for the ZnTe/GaSb system. A summary of critical thickness values for the various models is given in Table I.

EXPERIMENTAL PROCEDURES

ZnTe layers were deposited in a DCA MBE system. A 400 g SUMO cell provided a source for elemental Zn, while elemental Te_2 was provided from a Veeco valved cracker cell. GaSb substrates with (211)B orientation were purchased from Intelligent Epitaxy Technology, Inc. After removing the oxides from the wafer surface by exposing them to atomic hydrogen for 20 min at temperature of 400°C, the substrates were transferred to the growth chamber under vacuum. A form of migration-enhanced epitaxy was employed to nucleate the ZnTe epilayers. The Zn and Te beam equivalent pressures (BEP) were 2.6×10^{-7} torr and 4.1×10^{-7} torr, respectively. With the substrate temperature at 320°C, the surface was exposed to Zn for 60 s followed by a sequence of ten periods of alternating exposures of Zn and Te simultaneously for 5 s and followed by Zn exposure for 60 s. The initial Zn pre-exposure is to minimize the formation of Ga_2Te_3 phase between the GaSb and ZnTe interface.[13] The alternating sequence of Zn with Te and Zn only was chosen because a similar sequence was shown to result in high-quality ZnSe on GaAs(100).[14] ZnTe layers were subsequently deposited to thicknesses in the range from 50 nm to 2000 nm by conventional MBE where both the Zn and Te shutters were simultaneously opened for the remaining growth time.

HRXRD measurements were made using a Bede D1 system under triple-crystal configuration and copper $K_{\alpha 1}$ x-ray line with wavelength of 1.54056 Å. There is an instrumental broadening of ~18 arcsec in the XRD system. All HRXRD measurements were performed with the sample at room temperature. Bede RADS software was used to simulate the HRXRD data.

Micron-scale photoluminescence (μPL) was performed using the 488 nm line from an Ar-ion laser as the illumination source through a microscope

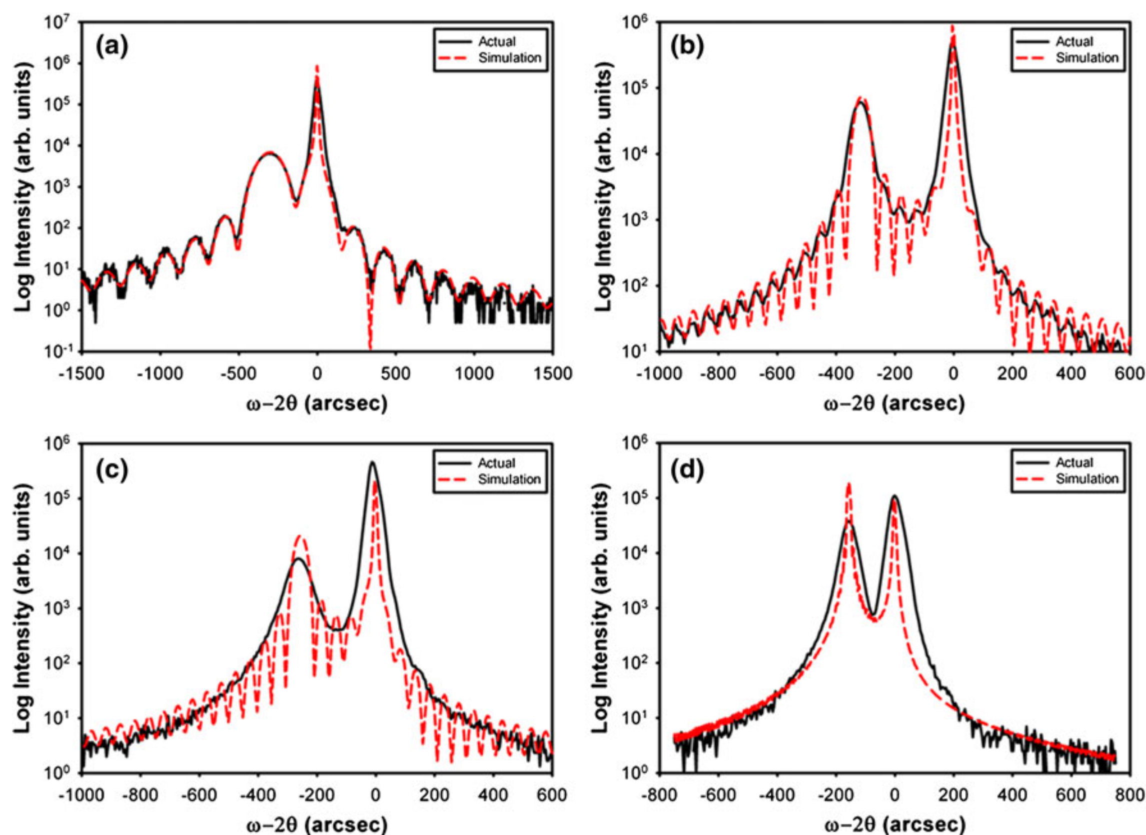

Fig. 1. HRXRD ω–2θ measurements of ZnTe grown for (a) 100 nm, (b) 350 nm, (c) 375 nm, and (d) 2100 nm.

with a 20× objective. The size of the excitation spot on the layer was approximately 35 μm. Luminescence spectra were obtained with a double-pass 1-m monochromator coupled to a thermoelectrically cooled InGaAs photomultiplier tube. Images of luminescent intensity were acquired with a high-sensitivity Si charge-coupled device (CCD) camera.

RESULTS

Figure 1 shows HRXRD spectra for four ZnTe layers with thickness values ranging from 100 nm to 2100 nm. At thicknesses below 350 nm, there are clear thickness fringes—an indication that the crystallographic quality of the layers is excellent. For values greater than 350 nm, the thickness fringes disappear, an indication that crystal quality has decreased. A simulation performed on these spectra gives a best fit when the target thickness for the MBE deposition is used as a parameter.

Figure 2 plots FWHM values versus layer thickness. Below 350 nm, there is a clear log–log relationship between FWHM value and layer thickness. This is consistent with a finite thickness analysis of pseudomorphic layers which yields a log to negative log relationship between FWHM value and layer thickness.[6] Between 350 nm and 375 nm, the FWHM value increases abruptly from 57.7 arcsec to 71.7 arcsec. This change coincides with the

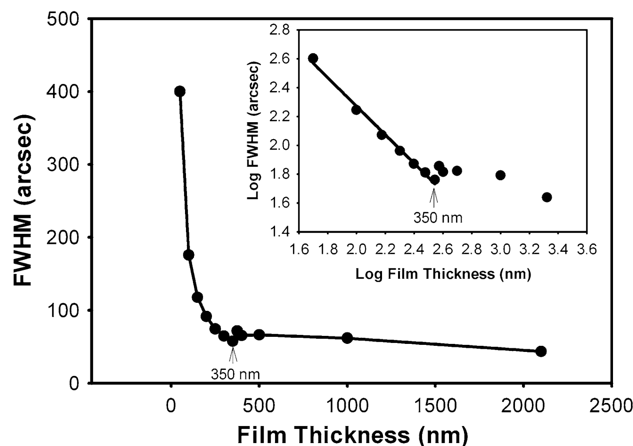

Fig. 2. FWHM of the ω–2θ ZnTe(422) peak at different thicknesses. Inset shows the same plot on a log–log scale.

disappearance of the HRXRD fringes. From this abrupt change, we conclude that the critical thickness value is between 350 nm and 375 nm. Above 375 nm, the FWHM starts to decrease again with a much reduced thickness dependence, with the lowest FWHM measured to be 43.6 arcsec for the thickest layer.

An independent estimate of h_c can be obtained by measuring the strain in the epilayer. Below the

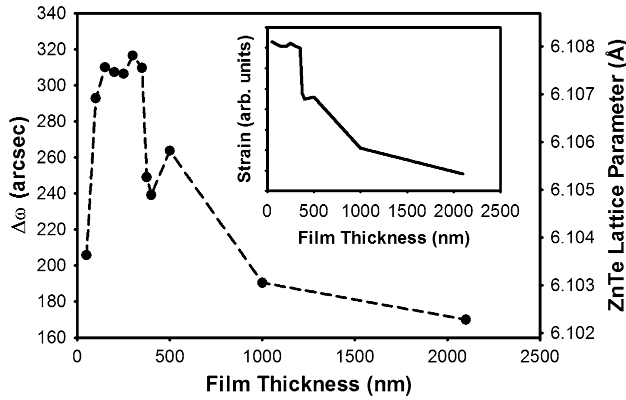

Fig. 3. HRXRD of the peak separation between ZnTe(422) and GaSb(422) ω–2θ peaks and the measured out-of-plane lattice parameter for ZnTe of different epilayer thicknesses.

critical thickness, the layer is pseudomorphic to the substrate and the strain will be maximum. (For ZnTe on GaSb, this strain is compressive in plane and tensile out of plane.) Above the critical thickness, the layer relaxes and the strain is expected to decrease. The amount of out-of-plane strain is reflected in the separation between epilayer and substrate peaks in the HRXRD spectrum. Figure 3 plots the separation between ZnTe and GaSb peaks as a function of layer thickness. With the exception of the 50-nm layer, for layers with thickness below 350 nm the separation is at a maximum and fairly constant. Above 350 nm, the separation decreases rapidly, reaching a value of 170 arcsec at 2100 nm. This value is less than the value of 213 arcsec calculated from bulk ZnTe and GaSb lattice parameters. The inset to Fig. 3 shows the relative strain values that were obtained from Bede RADS simulations. Relative values are given because the absolute value of the strain was found to be quite sensitive to the bulk lattice constants chosen as input to the simulation.

Even if an epitaxial layer is fully relaxed at growth temperature, residual strain will occur during cooldown if the thermal expansion coefficients of layer and substrate are not the same.[3,4,15] We calculated an expected value of 6.101 Å for a fully relaxed ZnTe layer at growth temperature upon cooling to room temperature following a standard approach[16,17] of estimating the thermal mismatch strain using elastic properties for ZnTe[18] and the appropriate strain ratio for the (211) orientation.[19] Comparison with the measured values in Fig. 3 suggests that either the (211)B layers are not fully relaxed at the largest thickness of 2100 nm or additional relaxation through dislocation generation is occurring during cooldown due to differences in the thermal expansion coefficient.

Strain in an epilayer also manifests itself as a shift in the position of a peak in a PL spectrum. Figure 4 shows representative PL spectra for three of the layers discussed above. They consist of a

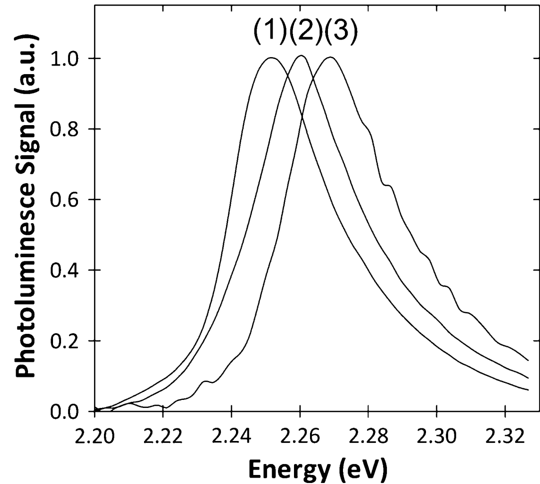

Fig. 4. Spectral PL of epilayers with thicknesses of (1) 2.1 μm, (2) 1.0 μm, and (3) 200 nm.

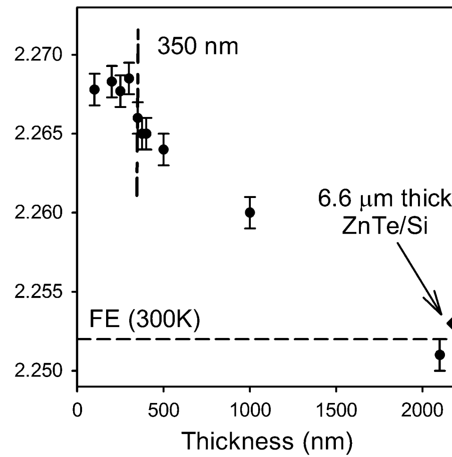

Fig. 5. Variation of PL peak energy with ZnTe layer thickness. The PL peak energy measured for a 6.6-μm-thick ZnTe/Si sample is also indicated for comparison.

single peak with FWHM value of about 39 meV. The ZnTe/GaSb epilayer PL peak position is fairly constant at about 2.268 eV for layers up to about 350 nm, whereupon it begins to shift to lower energy (Fig. 5). As was the case for the data derived from x-ray measurements shown in Fig. 3, a change occurs for layer thicknesses of about 350 nm. The location of the peak continues to decrease with increasing layer thickness, with an apparent stabilization at 2.253 eV, a value lower than the ~2.260 eV observed for ZnTe epilayers on a variety of substrates.[1] Note the agreement in the energy of the PL peak for a 2.1-μm-thick ZnTe/GaSb and a 6.6-μm ZnTe/Si sample (provided courtesy of Dr. Yuanping Chen of the US Army Research Laboratory) in Fig. 5.

Localized sample heating was ruled out as the origin of this discrepancy in peak energies by varying the incident laser power by a factor of ten

with no detectable shift in energy. Based on results of other studies of the effects of strain on ZnTe PL,[16,17] the residual thermal expansion mismatch strain in the layer is not of sufficient magnitude to result in this lower energy (and should be comparable to other growths on GaSb).

Identifying the origin of the PL peak energy is beyond the scope of this critical thickness study. Other laboratories have, however, investigated the complex nature of room-temperature PL in II–VI materials, and have presented evidence that the PL is often a mixture of band-to-band and excitonic transitions.[20] An earlier study of high-quality homoepitaxial ZnTe suggests that the predominant mechanism for PL emission is the first excited state of the free exciton (FE) up to temperatures as high as ~250 K.[21] Extrapolating their measurements indicates that a 300-K FE PL signature should occur at 2.252 eV. This energy is indicated by the horizontal dashed line shown in Fig. 5. By using the FE binding energy of ~13 meV, they arrive at a bandgap energy of 2.265 eV. If this is the correct bandgap energy of ZnTe at 300 K, then the strain present in the layers thinner than the critical thickness can easily account for the shift to higher energies. It is interesting to note that the location of the PL peak for emission from the thicker ZnTe samples in our study is consistent with the projected 300-K FE energy. Perhaps, similar to what Giles et al.[16] observed for CdTe, the 300-K PL emission in high-quality ZnTe is highly excitonic in nature.

Finally, we present direct evidence for the presence of threading dislocations that accompany the relaxation of ZnTe of thickness exceeding h_c. Figure 6a–c shows panchromatic μPL images taken at room temperature from three ZnTe layers of different thicknesses. Layers with thickness of 350 nm or less exhibited a bright uniform PL image with only a few discernible nonradiative features. By counting these features in a number of micrographs similar to that of Fig. 6a, we estimate an upper limit on the value of dislocation density to be $\sim 1 \times 10^5$ cm^{-2}. Nonradiative features are evident in Fig. 6b for a layer with thickness of 400 nm, and are quite pronounced in Fig. 6c for a layer with thickness of 1 μm. We attribute these nonradiative features to threading dislocations in the ZnTe layer. We take their appearance to be an indication that the thickness has exceeded h_c. A value of 1×10^5 cm^{-2} is not unreasonable for a layer pseudomorphic to a

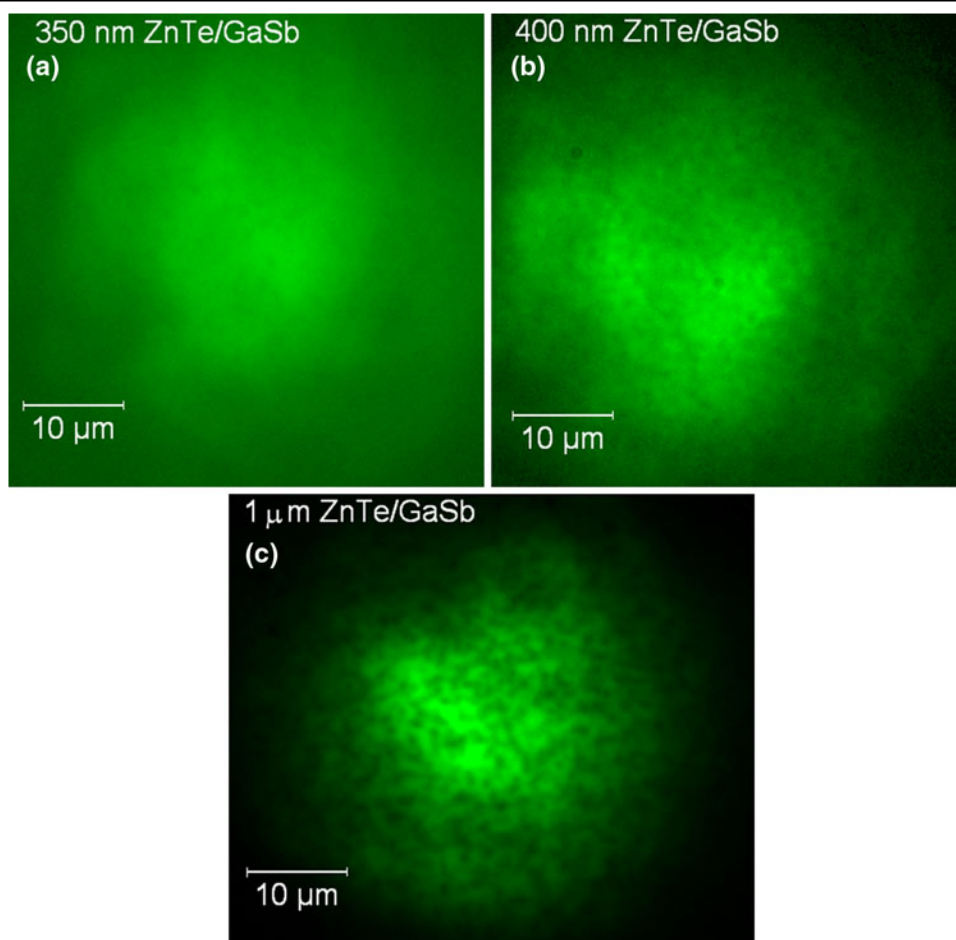

Fig. 6. Microphotoluminescence images of films grown to (a) 350 nm, (b) 400 nm, and (c) 1 μm. The illuminated area is approximately 1140 μm^2.

GaSb substrate with etch pit density values quoted by the vendor to be below 1×10^4 cm^{-2}. We estimate a value of 10^6 cm^{-2} for the dislocation density in the layers that are relaxed.

CONCLUSIONS

An analysis of HRXRD spectra for ZnTe layers deposited by MBE on (211)B GaSb substrates, based either on FWHM values or on the separation of the diffraction peaks, gives a value between 350 nm and 375 nm for h_c. This is in good agreement with theoretical predictions of 316 nm and 329 nm, using the Cohen-Solal and Dunstan models, respectively. Layers with thickness below h_c are pseudomorphic to the GaSb substrate, have low dislocation densities, and are highly strained and of high quality as indicated by the presence of XRD thickness fringes and reasonably low FWHM values. For thickness values greater than h_c, fringes in the HRXRD spectra vanish and there is a dramatic decrease in the strain in the layer. This value of h_c is confirmed by measurements of the variation in the energy of PL peaks. Direct evidence for dislocations in layers that exceed h_c is found in the nonradiative features that appear in μPL images.

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