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Descending Infrared Transmission Spectra of CdZnTe Substrates Due to Surface Roughness

E. Selvig[1], K.O. Kongshaug, R. Haakenaasen, T. Lorentzen and T. Brudevoll

FFI – Norwegian Defence Research Establishment, P.O. Box 25, NO-2027-Kjeller, Norway

[1]e-mail: espen.selvig@ffi.no

Phone: +47 63807335, Fax: +47 63807212

ABSTRACT

(111)B-oriented $Cd_{0.96}Zn_{0.04}Te$ substrates with rough surfaces have been found to have infrared (IR) transmission spectra which decrease rapidly in intensity as the photon energy increases. The rough surfaces were produced by Everson etching or rough polishing. The descending spectra could be qualitatively described by an equation found in the literature. Flat low intensity IR transmission spectra were found to be due to a combination of free carrier absorption and rough surfaces. The B-side of the substrate is the growth side. By etching the A-side of the substrate only we found that the black layer formed by the Everson etch on this side introduces two features in the IR transmission spectra: a dip at approx. 625 cm^{-1} and a special kind of ascending IR transmission spectrum: The ascending spectrum increases from approx. 65% at 500 cm^{-1} up to 72.5% at the highest wavenumbers around 4000 cm^{-1}. There is a correlation between the dip and the ascending spectrum: Six out of the seven spectra with largest dip have the highest transmission at 4000 cm^{-1} suggesting a common origin.

Key words: CdZnTe, IR transmission spectra, surface roughness, Everson etch

INTRODUCTION

CdZnTe is used for gamma-ray detectors as well as substrates for epitaxial growth of HgCdTe. Infrared (IR) transmission spectra are useful as they can reveal type and concentration of carriers from dopants/impurities due to free carrier absorption (FCA).[1,2] FCA results in spectra that increase in intensity with the wavenumber and are called 'ascending spectra'.[3] In our $Cd_{0.96}Zn_{0.04}Te$ substrates, however, we have also observed another type of spectra; descending spectra. In the literature these descending spectra have been related to dislocations.[3] We propose an alternative interpretation of these spectra which involves rough substrate surfaces. Te precipitates have also been reported to affect transmission spectra.[4,5] We have plotted typical spectra in Fig. 1.

We have characterized as-delivered CdZnTe substrates with roughly polished surfaces and substrates that have been Everson etched resulting in rough surfaces. The descending IR transmission spectra appear in substrates with rough surfaces. In substrates without FCA polishing the rough surfaces resulted in spectra that were flat with high intensity. We have compared our results to a theoretical equation for transmission through rough surfaces.[6]

EXPERIMENT

Substrate 1 was an as-delivered (111)B-oriented 30 mm × 30 mm CdZnTe substrate and both sides were mirror-like. The rms roughness (R_q) of the growth side and backside was 27.2 nm and 15.2 nm, respectively. The roughness was measured using an Alpha-Step 500 Surface Profiler using the following equation:

$$R_q = \sqrt{\frac{1}{N}\sum_{i=1}^{N} y_i^2} \tag{1}$$

where y_i is the deviation from the center line of the surface profile and N is the number of measured points on the surface. The profiles we measured were 500 μm long.

IR transmission spectra were recorded in a 6 × 6 grid pattern in a Perkin Elmer Spectrum GX FTIR. The spectra were relatively flat decreasing only slightly from 66.2 to 65.0% in the wavenumber range 500 - 4000 cm^{-1} (2.5 - 20 μm) (Fig. 2a). Both sides of the substrate were then etched in an Everson etch for 2.5 minutes, rinsed in DI water and blown dry with N_2.[7] The Everson etch is a polarity etch which affects the growth side and backside differently. Etching the Te-terminated B-side (growth side) results in etch pits around points where dislocations intersect the surface, whereas the CdZn

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terminated A-side (backside) turns black. After etching the transmission spectra were of the descending type and the spectra showed a dip at approx. 625 cm^{-1} (Fig. 2b). The different greyscale (colours) in the spectra correspond to different positions on the substrate surface. The dip and descending spectra were clearly due to changes at the surfaces introduced by the etch. The average roughness on the growth side was 134 nm and 39 nm on the backside. The etch pit density (EPD) was evaluated using optical microscopy (magnification 100) and found to vary from 1×10^{4} to high 10^{6} cm^{-2}.

In order to determine from which side of the substrate the dip at 625 cm^{-1} and the descending spectra originated we polished the growth side of the substrate only. We used 0.05 μm alumina powder to remove 40 μm on the growth side resulting in a mirror-like surface ($R_q =$ 0.02 μm). Transmission spectra were recorded in a 6 × 6 grid pattern. The transmission spectra were no longer descending, but slightly ascending from 65% at 500 cm^{-1} upto 68% at 4000 cm^{-1} (Fig. 2c). We call these ascending spectra "the second type of ascending spectra" as there is another type of ascending spectra due to free carrier absorption as shown in Fig. 1. The dip at 625 cm^{-1} was still present. This shows that the descending spectra originated at the growth side of the substrate, and that the dip and the second type of ascending spectra originated at the blackened backside.

The backside was then polished and 60 μm was removed resulting in a mirror-like surface and a roughness of 0.02 μm. This resulted in flat transmission spectra at 65% (Fig. 2d), and the dip at 625 cm^{-1} was gone. This further confirmed that the dip and the second type of ascending spectra originated at the blackened backside.

Another substrate (Substrate 2) which had been similarly Everson etched on both sides showed descending spectra, and some spectra that were ascending at low wavenumbers and relatively flat above 1000 cm^{-1} (Fig. 3a). The spectra with the highest intensities also showed a dip in transmission at approx. 625 cm^{-1}. The EPD was evaluated to 2.8×10^{4} – 2.2×10^{5} cm^{-2} using optical microscopy (magnification 20). The growth side of this sample was then polished using 0.05 μm alumina powder removing 60 μm of the substrate to create a mirror-like surface. This had the following effect on the transmission spectra: The descending and the low flat transmission spectra disappeared, and only high flat transmission spectra, ascending spectra (FCA) and the second type of ascending spectra were observed (Fig. 3b). The latter ascending spectra increased from 65.5 % at 500 cm^{-1} and up to 72.5% at 4000 cm^{-1}. The dip was still present in the spectra. These results are consistent with the results from substrate 1.

We then polished the backside and observed that the dip and the second type of ascending spectra (> 66%) disappeared (Fig. 3c): The spectra with transmission above 66% at 4000 cm^{-1} were replaced by high flat transmission spectra at 65%. These results are also similar to the ones from substrate 1.

Transmission spectra with FCA due to holes were observed before and after polishing (Figs. 3 a-c) showing that FCA was not surface related. A contour map of the transmission at 500 cm^{-1} shows that the FCA is localized to a corner of the substrate (Fig. 4).

To further examine the effect of surface roughness we measured the transmission spectra of an as-delivered substrate from another vendor (Substrate 3). This substrate had mirror-like growth side (R_q = 19 nm) and a backside that was roughly polished (R_q = 267 nm). The transmission spectra which were recorded in a 5 × 5 grid pattern on the substrate surface were exactly equal and of the descending type (Fig. 5a). The rough backside of the substrate was then polished to a roughness of R_q = 12 nm. The resulting transmission spectra were all flat with high intensity at approx. 65% (Fig. 5b).
We then etched the growth side of the substrate for 2.5 minutes in an Everson etch. Transmission spectra are shown in Fig 5c. The transmission spectra are slightly decreasing in intensity as the wavenumbers increase. This is probably due to etch pits.

Transmission microscopy was performed on this substrate to image the etch pits (Fig. 6a), using photons with wavenumbers in the range 8900 – 12800 cm^{-1}. The range was limited by the silicon camera chip and absorption in the substrate. The star-shaped ensembles of dislocations are due to Te-rich particles as described in Xu et al.[8] These ensembles are distributed evenly across the surface with a density of 435 cm^{-2}. Between these ensembles there is a background etch pit density of 1.1×10^{5} cm^{-2}. The EPD was evaluated using optical microscopy (magnification 20).
The backside of the substrate was etched for 2.5 minutes in an Everson etch. The backside was only slightly darker after etching and the transmission spectra remained as in Fig. 5c. We therefore etched for another 3 minutes until the backside turned black. The transmission spectra turned into the second type of ascending spectra we observed in substrates 1 and 2 which we attributed to the blackened surface (Fig. 5d). A much weaker dip at 625 cm^{-1} was observed in the transmission spectra from this sample.

RESULTS AND DISCUSSION

Surface Roughness and Descending Spectra

We have studied substrates with rough surfaces due to rough polishing or etching: A substrate with flat transmission spectra was Everson etched resulting in an increased surface roughness of 134 nm and the transmission spectra turned into descending spectra (Fig. 2a-b). And by polishing the rough surfaces of both Everson etched and roughly polished substrates the descending spectra disappeared (Figs. 2b-c, 3a-b, 5a-b). This shows that the descending spectra are associated with the substrate surface.

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The transmission microscopy image of a star-shaped-ensembles of etch pits (Fig. 6a), revealed by the Everson etch, show black etch pits. This demonstrates that etch pits transmit little or no photons. The surface profile through one of these ensembles is shown in Fig. 6b and clearly shows that they are associated with roughness. I.e. the Everson etched surface is associated with increased roughness that causes lower transmission levels.

Previously, descending spectra have been related to dislocations.[3] The present study shows that the dislocation-revealing etch introduces etch pits which result in roughness. This roughness results in the descending spectra. Descending spectra need not be evidence for etch pits but can also be caused by a roughly polished surface (Fig. 5a). A model for IR transmission spectra due to surface roughness is presented in the next section.

The low-intensity spectra in Fig. 3a are relatively flat. However, after polishing the rough surface, these spectra were replaced by spectra dominated by FCA (Fig. 3b). This shows that the flat low intensity spectra were due to a combination of surface roughness and FCA. The FCA in this substrate was due to absorption by holes as determined from the shape of the transmission spectra.[1] Secondary ion mass spectrometry (SIMS) measurements indicated Na impurities which could have been a source for the free carriers and thereby the FCA. The Na concentrations were in the high 10^{14} cm^{-3} but this was not enough to explain the low transmission intensities. We believe that the main source of the holes was Cd vacancies.

A Model for IR Transmission through Rough Surfaces

A model for IR transmission through a sample with a Gaussian distribution of surface roughness was presented by Filinski (neglecting multiple reflections)[6]:

$$T = (1 - R)^2 \cdot \exp(-\alpha_{eff}\, d) \tag{2}$$

where R is reflectance of the smooth surface, d is the thickness of the sample and the effective absorption coefficient, α_{eff}, is :

$$\alpha_{eff} = \alpha_0 + \alpha_{SC} = \alpha_0 + \frac{1}{d}\left(\frac{2\pi R_q (n - n_0)}{\lambda_0}\right)^2 \tag{3}$$

where α_0 is the bulk absorption coefficient, α_{SC} describes loss of photons due to scattering at the rough surface, R_{q} is the rms value of the surface roughness, n is the refractive index of the material with the rough surface, $n_0 = 1$ (air), and λ_0 is the wavelength in air. The scattering described by Eq. 3 considers interference between photons at normal incidence to a flat surface with flat indents (piecewise flat

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surfaces at different heights). I.e. the photons are always normal to the air/material interface. The equation does not take into account losses due to refraction at non-normal surfaces which causes photons not to reach the detector.

It is clear from Eq. 3 that photons with longer wavelengths than $2\pi R_q$ $(n - n_0)$ will to a much lower extent be affected by the surface roughness than shorter wavelengths. Measured transmission spectra for different surface roughnesses are plotted together with calculated spectra (Eq. 2) in Fig. 7. We have used spectra from roughly polished substrates as these are more uniform in roughness so the exact position of the roughness measurement is not so critical. The equation fairly well describes the shape of the descending transmission spectra.

Dip in Transmission and the Second Type of Ascending Spectra

We have found that the dip at 625 cm^{-1} and the ascending spectra with $T(4000\ cm^{-1}) > 66\%$ originated at the blackened A-side, after Everson etching. Furthermore, there is a correlation between the dip at 625 cm^{-1} and the ascending spectra with $T(4000\ cm^{-1}) > 66\%$ (Fig. 3b); six out of the seven spectra with largest dip have the largest transmission at 4000 cm^{-1} further confirming their common origin. A spectrum similar to the second type of ascending spectra in Fig. 3b can be found in Fig. 2a in Yujie et al.[4] In that study it was reported that samples displaying this type of spectrum was free of Te precipitates. In the present study, however, the presence of such spectra is a surface effect.

A similar dip in the transmission spectra was observed in a descending spectrum in another study but in that study the dip was located at approx. 1370 cm^{-1}, probably due to different surface chemistry because they used other etchants: E (HNO_3 : deionized water : K_2CrO_7 (10 ml : 20 ml : 4 g)) and E_{Ag} (E solution : $AgNO_3$ (10 ml : 0.5 mg)).[3] The Everson etch that we used in this study is 48% HF : 65% HNO_3: 88% lactic acid (6 ml : 24 ml: 150 ml). Burgess et al. found that Everson etching Cd resulted in a black surface layer, whereas Everson etching Te did not result in a black surface.[9] They suggested that the black layer was $(Cd(H_2O)_6)^{2+}$ or a similar complex.

Descending Spectra from LPE-grown HgCdTe Layers

Descending spectra have also been observed from some of our LPE-grown HgCdTe layers. In the final stage of HgCdTe growth the Te-rich melt is poured off the sample. Sometimes some melt sticks to the sample as shown in Fig. 8a (lower right corner, and upper right corner, near position 119). The descending spectrum in Fig. 8b (position 11) is recorded through this melt. The spectrum is descending because the residual melt has a high surface roughness; in the range 300 – 850 nm. The

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spectrum at position 119 is flat but at lower intensity. The residual melt at this position is much thicker and the part of the FTIR beam that hits the melt is 100% blocked. The spectrum consists of the part of the beam that passed outside the residual melt. The low transmission in some of the other spectra (< 54%) is due to free carrier absorption in the substrate.

CONCLUSIONS

We have shown that descending IR transmission spectra are due to surface roughness induced by either Everson etching or rough polishing. IR transmission spectra which were flat with low intensity were shown to be a combination of descending spectra due to surface roughness and ascending spectra due to free carrier absorption. An equation for IR transmission through a sample with a rough surface describes the shape of the descending transmission spectra fairly well.

The black layer formed on the A-side of CdZnTe substrates during Everson etching was shown to result in transmission spectra which increase from approx. 65% at 500 cm^{-1} up to 72.5% at 4000 cm^{-1}. This increase in transmission was correlated with a dip in the transmission at 625 cm^{-1}.

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FIGURES

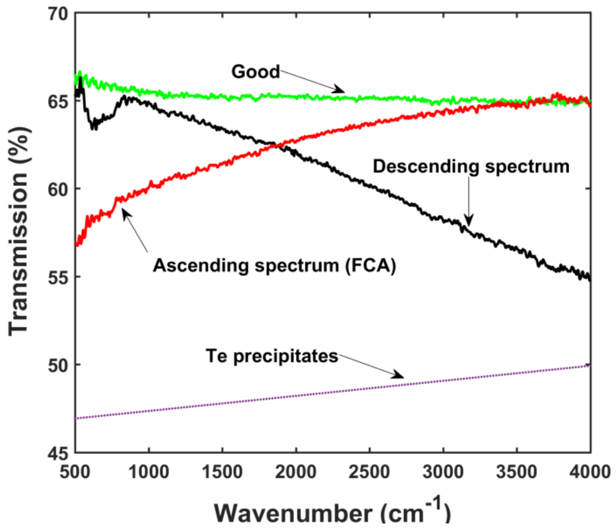

Fig. 1. Typical IR transmission spectra of CdZnTe. The spectrum of CdZnTe with Te precipitates is indicated as a straight line (based on spectra in refs. 4 and 5 as we have measured no such spectra).

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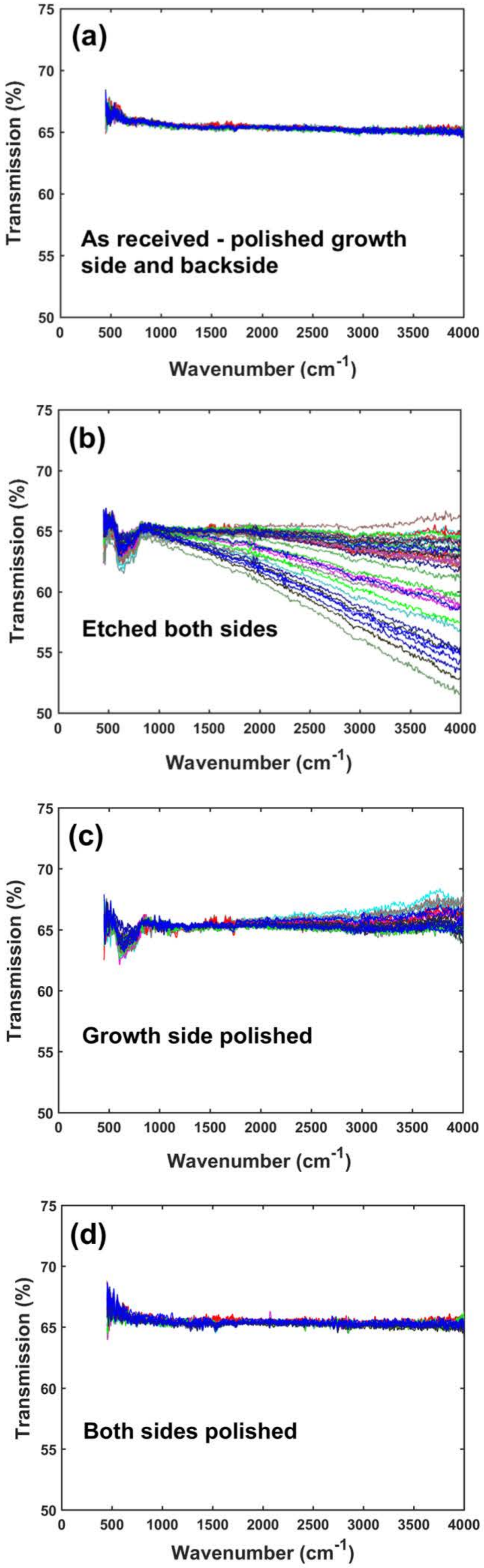

Fig. 2. IR transmission spectra recorded in a 6 × 6 grid from substrate 1 (a) As received, mirrorlike surfaces. (b) After Everson etching of both sides. (c) After polishing the growth side. (d) After polishing the backside.

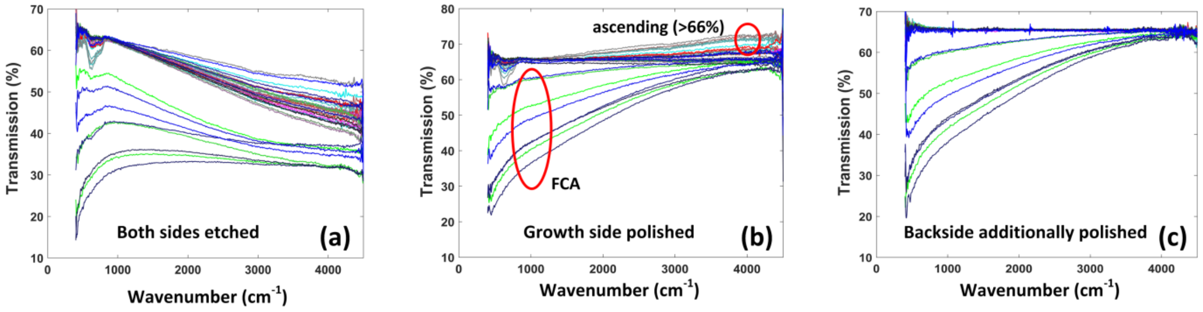

Fig. 3. IR transmission spectra from substrate 2. (a) Both sides Everson etched showing descending spectra. (b) Growth side polished; showing two types of ascending spectra. (c) Backside additionally polished; only high flat spectra and some showing FCA. No dip.

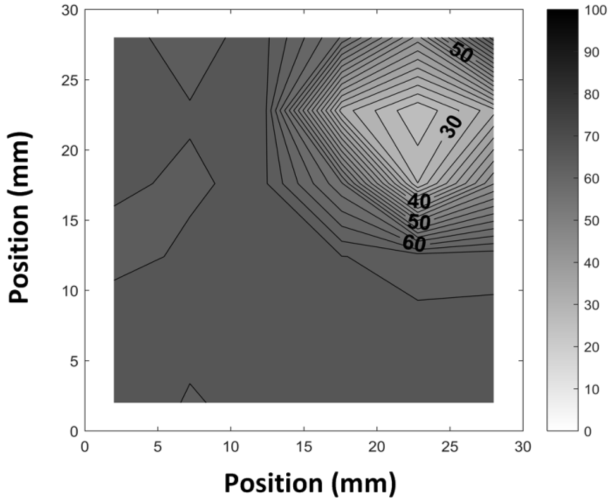

Fig. 4. Contour map of the transmission intensity at 500 cm^{-1} in the 30 × 30 mm^2 substrate 2 with both sides polished. The FCA is localized to the upper right corner.

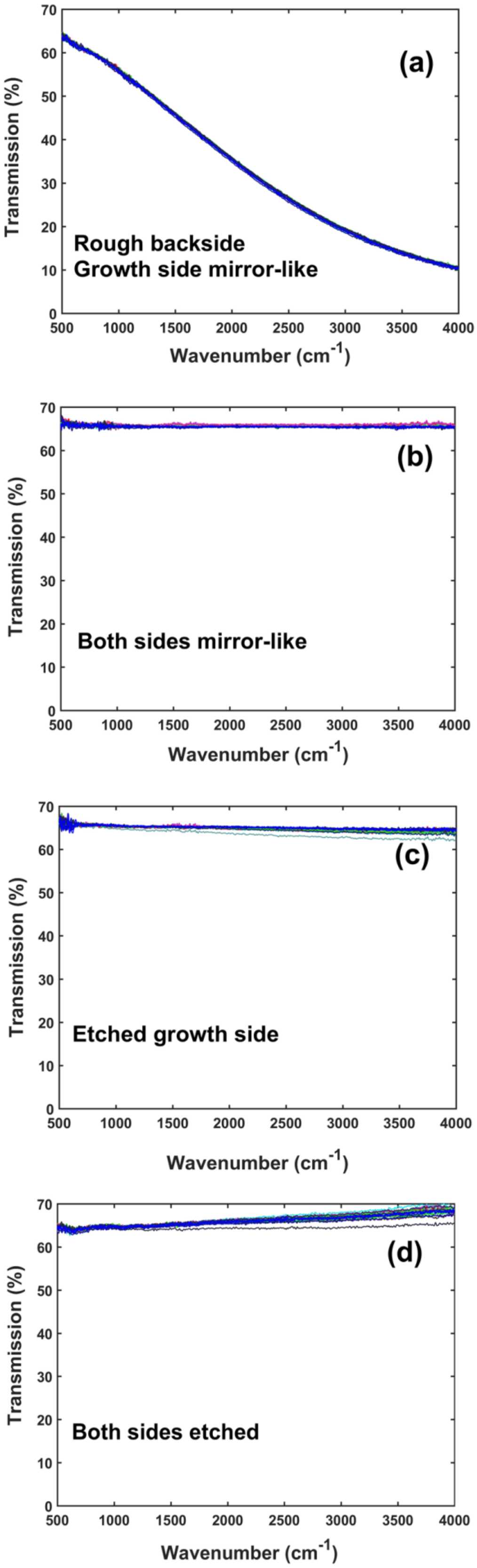

Fig. 5. IR transmission spectra recorded in a 5 × 5 grid across substrate 3. (a) As-delivered: Mirror-like growth side and rough backside. (b) Polished: Both sides are mirror-like. (c) After Everson etching the growth side. (d) After Everson etching the backside.

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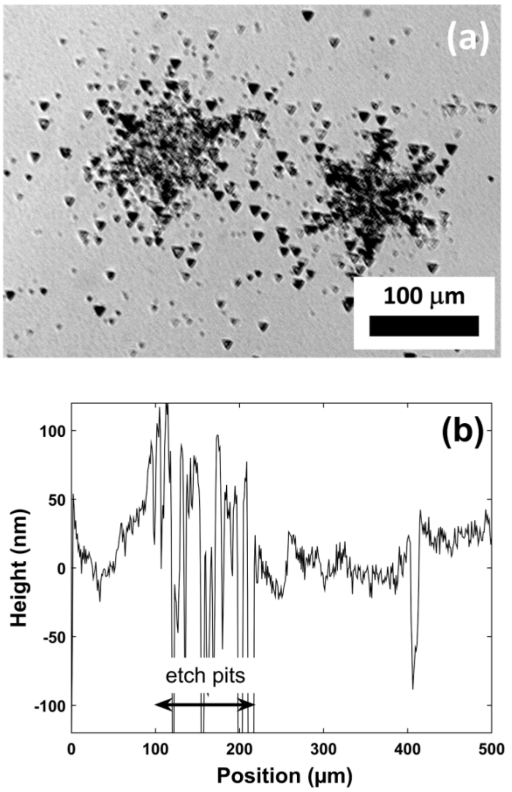

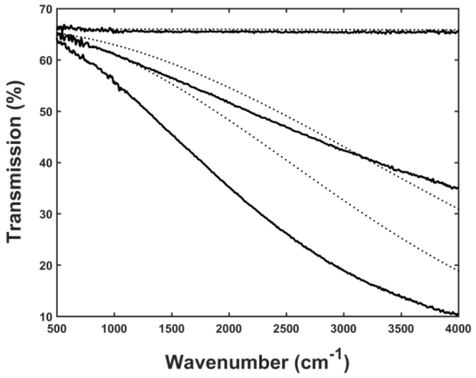

Fig. 6. (a) IR transmission micrograph of a star-shaped ensemble of etch pits after Everson etching, and (b) a surface profile across one ensemble (100 – 220 µm).

Fig. 7. Experimental (continuous lines) and calculated (dotted) IR transmission spectra (Eq. 2) for a CdZnTe substrate with one smooth surface and one rough surface. From top to bottom R_q = 0.012, 0.21 and 0.27 µm.

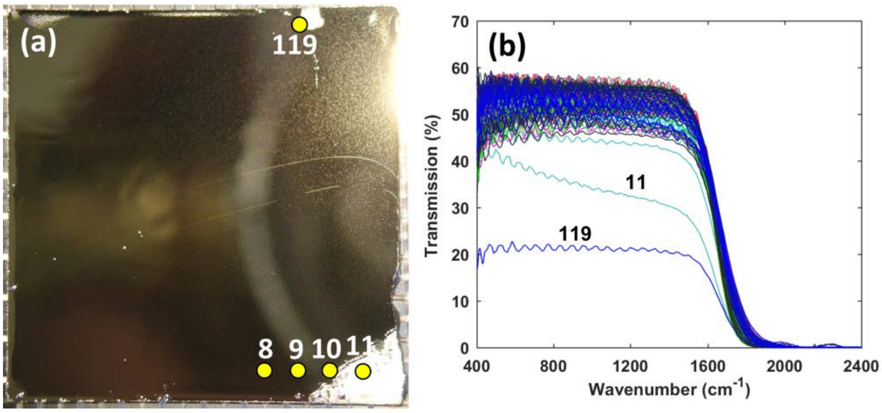

Fig. 8. (a) LPE-grown HgCdTe layer (x = 0.23) on a CdZnTe substrate with some residual Te-rich melt on the surface (lower right corner and close to position 119 in upper right corner). The numbers indicate where some of the spectra were recorded. (b) Transmission spectra from a HgCdTe layer on CdZnTe measured in an 11 × 11 grid.

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