Studies of phase segregation in $Cd_{1-x}Zn_xTe$ using surface photovoltage spectroscopy

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$Cd_{1-x}Zn_xTe$ wafers used for x-ray detector arrays have been failure analyzed using x-ray diffraction, x-ray electron spectroscopy (XPS), energy dispersive spectroscopy (EDS), and surface photovoltage spectroscopy (SPS). The last shows ZnTe segregation in failed pixels while the precipitant phase is too small to be observed by the other techniques. The Zn concentration, measured using EDS and XPS, was higher than that deduced from SPS data, confirming the conclusion. The segregation can be revealed only by SPS since it is sensitive to the electronic structure and thus to x in each phase while the other techniques average x over their measurement volume. © *2002 American Institute of Physics.* [DOI: 10.1063/1.1493230]

The ternary alloy $Cd_{1-x}Zn_xTe$ (CZT) is widely used as a base material for x-ray detectors and other devices.[1,2] Appropriate detector performance is achieved by obtaining wafers with a uniform Zn concentration and a single crystalline zinc blende phase. The homogeneous zinc blende phase, which exists for any Zn concentration above 300 °C (when the Te concentration is 50 at. %) separates at lower temperatures into two phases. The two zinc blende phases are denoted by α and α', which refer to ZnTe-rich and CdTe-rich solid solutions, respectively.[3] Thermodynamic calculations[4] and experimental results[3,5] show that this solid phase miscibility gap in CZT exists at room temperature for almost any Zn concentration. Thus, phase segregation is expected due to the slow cooling rate, normal during crystal growth.[5]

In actual applications of CZT-based devices, phase inhomogeneity is known to cause inferior performance. Besides accurate determination of the Zn concentration, a clear indication of the single-phase structure of the base material is crucial. Conventionally, the former is performed using energy dispersive spectroscopy (EDS), x-ray electron spectroscopy (XPS), etc., while the latter is carried out using x-ray diffraction (XRD). Recently, we have shown the power of surface photovoltage spectroscopy (SPS)[6] in accurately determining the Zn concentration by obtaining the exact band gap of the alloy.[7] The relation between the band gap, E_g, and the Zn part in the cation concentration (normalized to 1) x has been formulated by Tobin *et al.*[8]

$$E_g = 1.5045 + 0.631x + 0.128x^2, \tag{1}$$

where 1.5045 eV is the band gap of CdTe.

In this letter, we show that SPS is also capable of yielding information about the phases of the actual detector base material and acts as a quality control tool.[9,10] Since SPS can easily detect band-to-band transitions, it proves to be highly sensitive to phase inhomogeneities (such as ZnTe segregated in the CZT alloy bulk or at its surface). These may avoid detection by conventional techniques, such as XPS and EDS, due to their inability to distinguish between Zn in the alloy and Zn in ZnTe. In addition, the lattice parameter is related to the band gap, allowing precipitate detection using XRD. However, this technique is limited to a certain size of segregated precipitants. In the past, SPS was employed to characterize the electronic structure of CdSe quantum dots[11] and proved to be sensitive to nanoscale particles. Performing SPS on CZT x-ray detectors with poor response indicates a second phase, identified as ZnTe. The indications are presented and discussed in view of results by complementary techniques following experimental data, presented in next.

The $Cd_{1-x}Zn_xTe$ samples were provided by Imarad Imaging Systems Ltd., Israel. The crystals were grown using a modified horizontal Bridgman technique without thermal posttreatment. All the surface photovoltage (SPV) spectra of $Cd_{1-x}Zn_xTe$ were measured as received in ambient temperature using a vibrating Au Kelvin probe (2.5 mm in diameter) arrangement (Delta-Phi Electronik, Germany). A spectrometer with a double monochromator (McPherson Inc., Chelmsford, MA) provided monochromatic incident light with a resolution of about 0.2 nm. The scan step of 2 nm yields an energy error of several meV. The CZT samples were divided into $16\times16=256$ pixels, each 2.5×2.5 mm^2, arranged such that pixel number 1 is the top left one and number 256 is the bottom right one. The manufacturer marked the pixels "bad" and "good" according to a nuclear spectroscopy test. The pixels were measured using SPS with 2 nm steps and 2 s dwell time. Similar results were obtained with 10 s dwell time. The SPS spectra were taken in the wavelength range from 1250 to 450 nm, similar to in a previous paper,[7] which dealt with surface states of CZT samples.

Comparison of the SPS results to conventional measurements was carried out by several techniques: XRD for phase identification and lattice parameter evaluation, using an x-ray powder diffractometer (Scintag, Switzerland); XPS, using a 5600 multitechnique system (PHI, Minneapolis, MN) in an UHV system (2×10^{-10} Torr base pressure) with an Al $K\alpha$ monochromated source (1486.6 eV) and a hemispherical analyzer (slit aperture 0.8 mm in diameter); and EDS, for

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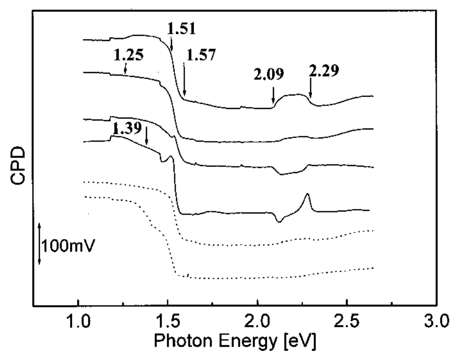

FIG. 1. CPD as a function of the photon energy measured at different surface positions of a CZT sample. The dotted (solid) curves were obtained from good (bad) pixels. Several transitions are marked.

Zn concentration, using a Link detector (Oxford, UK) combined with a scanning electron microscope (JEOL 6300).

Figure 1 shows the contact potential difference (CPD) spectra obtained from several pixels (good, dotted curves and bad, solid curves) of several CZT samples. The spectra are vertically shifted for clarity. The main slope change is the band-to-band transition located at about 1.57 eV. The illumination causes a decrease in the CPD value (with respect to an Au probe), i.e., flattening of the upward band bending at the surface, which indicates an n-type material. The band-to-band transition signal starts at about 1.51 eV, possibly due to the band tail effect.[12–14] Additional subband gap features are seen at 1.25 and 1.39 eV (the latter is harder to observe). These features have been assigned to surface states: an acceptor-like surface state 1.25 eV below the conduction band minimum and a donor-like surface state 1.39 eV above the valence band maximum.[7] The abrupt "jumps" are due to filter changes.

All the bad pixels show two superband gap transitions, at 2.09 and at 2.29 eV. These transitions are much smaller, and mostly nonexistent, in the spectra of the good pixels. Since these features do not appear in all spectra, the possibility of associating them to transitions from other valence bands or to a higher valley in the conduction band is eliminated. ZnTe has a band gap of 2.26 eV, which is in a good agreement with the 2.29 eV transition. Thus, it may be related to a ZnTe phase in the CZT matrix. The difference in band gap value may be due to Cd atoms dissolved in the ZnTe phase or to a "blueshift" induced by quantum confinement of the nanosized particles of the ZnTe phase. The existence of this ZnTe phase is not unexpected in view of the phase separation, segregation, and precipitation implied in the introductory paragraph and will be elaborated on later.

The origin of the 2.09 eV transition is unclear. Any possible oxide phase, such as TeO_2, CdO or ZnO, does not fit the energy of this transition. Surface oxidation creates surface states that appear in the subband gap region, as mentioned earlier. Ruault *et al.*[5] found some isolated spots, randomly scattered in the electron diffraction pattern of an as-grown CZT crystal. They identified them as $CdTeO_2$ related, since oxidation may occur during crystal growth. Thus, the 2.09 eV transition may be related to $CdTeO_2$ or to a subband gap transition in the ZnTe phase. In XRD of both good and bad pixels in the CZT samples there is no evidence of the α' phase. Only CdTe peaks appear, slightly shifted due to the

TABLE I. Zn concentration x of a CdZnTe sample determined by SPS at different surface positions.

Pixel No.	Band gap ± 0.005 (eV)	$x \pm 0.009$
16 (B)	1.551	0.072
28 (B)	1.547	0.066
36 (G)	1.552	0.074
107 (G)	1.549	0.069
148 (B)	1.553	0.075

dissolved Zn. Apparently, the precipitates are too small to be detected by the diffraction experiment. Despite the large lateral size of the Kelvin probe, it succeeds in detecting the precipitates due to its sensitivity to their electronic structure.

Most of the SPS measurements, which show the two transitions at 2.09 and 2.29 eV, indicate a positive slope for the former and a negative slope for the latter (n-type precipitates). Few pixels show p-type precipitates and a negative slope at 2.09 eV (as seen in Fig. 1). The semiconductor type may be determined by the stoichiometry in the precipitant phase.[15,16]

From the CPD spectra we calculated x using the tangent intersection technique[7] to determine the alloy band gap. The values of the band gap obtained are between 1.55 and 1.57 eV depending on the specific wafer. They correspond to x values from 0.07 to 0.10. The band gap and x values are quite similar within a wafer, showing good uniformity in the plane perpendicular to the growth direction.[17–19] It should be noted that SPS determines the band gap of the α' phase and thus the x calculated is for that phase only.

The value of x for the $Cd_{1-x}Zn_xTe$ sample was also measured using XRD and EDS. The lattice parameter obtained by XRD was 6.4329 ± 0.00003 Å, yielding $x = 0.12$ in good agreement with the Zn concentration measured by EDS, 6.0 at. %, while x measured using SPS yielded a value of 0.10. SPS yields consistently lower x values than EDS and XRD.

SPS results were also compared to XPS results at different pixels of another sample. Table I shows typical SPS values from various pixels, which yielded an average value of 0.07, irrespective of whether the pixel was bad, marked (B), or good, marked (G). The XPS results average about 2 at. % higher for the bad compared to the good pixels. The two types of pixels reflect a variation in x, which increases towards the rim of the wafer due to the specific growth process.

Comparison of the SPS and the XPS results shows a correlation between the existence of the 2.29 eV transition in the CPD spectra and higher values of x in the XPS data, both obtained in bad pixels. Good pixels are distinguished by the absence of that transition in their spectra while their x values, measured by XPS, are lower and closer to those of the SPS data. The salient point is that SPS is sensitive to the electronic structure and thus to x in each phase, individually, even if its grains are on a nanoscale size, while XPS, EDS and XRD average the Zn concentration over their measurement volume. Thus, only SPS could show that each pixel contains mainly the CZT (α') phase with a similar x value and a different amount of segregated ZnTe phase. The latter

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precipitates are due to changes in x caused by the crystal growth process. A nonuniform cooling rate followed by a nonflat solidification front are the main causes of the x profile in the plane perpendicular to the growth direction.

The correlation between SPS and other data with device performance on the different pixels leads to the conclusion that bad pixels have stronger ZnTe segregation compared to good pixels. Since conventional techniques yield an average value for the Zn concentration they may lead to wrong x determination. However, SPS emerges as capable of providing x values for each phase and of identifying the phases in very small grains that escape detection by XRD. It is thus very suitable as a failure analysis tool as well as for in-line quality control monitoring.

It is important to note that bulk phase separation may not be the only process occurring. Te precipitates have been previously observed, mostly at CZT grain boundaries.[20] To distinguish between the bulk and the surface mechanisms, a sample was etched by 1% Br_2/CH_3OH solution. This etching increases the TeO_2 surface state[21–23] and depletes the CdZnTe of Zn.[7] The superband gap spectral features remained after etching, showing that it was mostly bulk segregation.

In conclusion, surface photovoltage spectroscopy has been found to be an effective experimental tool that can indicate phase segregation in $Cd_{1-x}Zn_xTe(111)$ alloys. Phase segregation is indicated in SPS spectra, even if it occurs in very small particles which escape observation by XRD. The sensitivity of SPS to the electronic structure provides more accurate estimation of x than conventional bulk- or surface-sensitive techniques, which average the Zn concentration, potentially leading to erroneous results.

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