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X-RAY ANALYSIS OF ALPHA MERCURIC IODIDE CRYSTAL
STRUCTURE AND PROCESSING EFFECTS*

L. Keller^{***}, E.X. Wang and A.Y. Cheng^{***}

^{***}CAMET Research, Inc., Goleta, CA 93117

^{***}EG&G Energy Measurements Inc., Santa Barbara Operations, Goleta, CA 93117

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ABSTRACT

X-ray topography and rocking curve experiments were performed on α -mercuric iodide samples. As-grown crystals were examined for intrinsic defects and crystallinity. Orientation of certain defects depends on the direction of crystal growth. The propagation of as-grown crystalline features was documented. The extent of crystal damage introduced during various steps of device fabrication such as sawing, polishing, etching and contact deposition was explored. Coefficients of linear thermal expansion of $\alpha_{33} = 54 \pm 5 \cdot 10^{-6}/^{\circ}\text{C}$ along the tetragonal c-axis, $[001]$ direction and $\alpha_{11} = 11 \pm 4 \cdot 10^{-6}/^{\circ}\text{C}$ in the $[100]$ direction were measured.

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INTRODUCTION

Vapor crystal growth techniques have yielded the largest, most usable mercuric iodide crystals for room temperature X-ray and gamma-ray detector applications.¹ However line defects² and subgrain boundaries³ introduced during growth may contribute to poor detector performance. Furthermore, mismatches in thermal expansion between the crystal and its growth pedestal will cause stress within the crystal, especially during the cool-down phase after completion of crystal growth. Similarly, a mismatch between the evaporated metal contact and the crystal surface can produce a stress in the thin film resulting in poor adhesion of the film. Additionally, the softness of the HgI_2 crystal makes it prone to mechanical damage in the form of inelastic strains, plastic deformation and shearing that can be introduced during the various steps of detector fabrication. X-ray topography and rocking curves studies were conducted to investigate the extent of these effects.

EXPERIMENT

Asymmetric double crystal reflection topography⁴ has been employed to provide a qualitative assessment of imperfections present on as-grown and processed faces of HgI_2 samples. These studies can be considered a "surface" analysis of HgI_2 , because the 8.1 KeV ($\text{Cu-K}\alpha$) x-rays, only penetrate, depending on incident angle, 5-10 μm into the HgI_2 . Sets of topographs with the incident beam rotated by 90° , with respect to the normal of the plane of interest, were made. Thus, the contrast for linear defects is enhanced when the direction of defects is perpendicular to the diffraction plane. Note there is foreshortening of the topographs in the direction of the incident beam.

The determination of thermal expansion by XRD was carried out on a double crystal diffractometer in the nondispersive mode employing a 100 cut Ge

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monochromator and Cu-K α radiation. Both crystal samples and fabricated detectors were attached to zero-expansion ceramic plates and heated from room temperature to 60°C by a flow of heated N₂ gas. Measurements were not made until temperature equilibration was achieved.

RESULTS

As-grown Crystals

Virgin, as-grown, HgI₂ crystals show that there are inherent characteristics like line defects oriented along the $\langle 100 \rangle$ and $\langle 110 \rangle$ directions, "clear" or "hazy" regions and misoriented areas with a distinct boundary. Regions where optical micrographs show voids and lines of delineating can be linked to defects and strain regions on topographs. Multiple scratches due to general handling can be clearly distinguished. Additionally, by topographic examination of the top, middle (after sawing and polishing) and the bottom of 10 mm thick samples, it was determined that some distinct crystalline features are present in the crystal in the $[001]$ or c-direction for at least 10 mm.

A rectangular, single crystal block with edges along the $\langle 110 \rangle$ and $\langle 001 \rangle$ directions and dimensions of 10 x 12 x 12 mm³ was characterized for the surface "quality" of its as-grown and cut faces. While the (001) face was left intact, sawing and subsequent polishing were performed on the (110) and $(\bar{1}10)$ faces with 2 mm thick slices removed from each face. The (001) face topograph, Fig. 1 shows that nearly half of the face is not in reflection and produces no diffracted intensity. The misoriented portion is tilted away (a 5' tilt angle was determined by double crystal diffractometry) along a distinct boundary with no distinct crystallographic direction. The grain boundary intersects the (cut) (110) face and the (110) topograph, Fig. 2, clearly shows the dimensions of the misoriented region. The sharp boundary parallel to the c-plane suggests that the misoriented portion is structurally separated from the bulk. Additional parallel lines in the c-plane in fact indicate a lamellar structure or stacking of ~1 mm thick sheets along the c-plane.

The as-grown (001) face also exhibits an array of lines parallel to the $[110]$ direction. These defects, seen in high concentrations in "hazy" areas, develop along the $[001]$ direction and intersect the (001) plane and extend through the entire crystal in (110) "sheets" or "growth rings", are very likely the result of incremental crystal growth in the $[110]$ direction. Indeed, the $(\bar{1}10)$ topograph, Fig. 3, shows the expected "edge" view of these "sheets" of defects. In fact, the "sheets" or lines can be matched if the topographs in Figures 1 and 3 are positioned perpendicular to each other. The planar nature of these defects is further evidenced by rocking curve analysis. Traverse mapping of the $(\bar{1}10)$ face produced an average rocking curve width of $59 \pm 3^\circ$ compared to $27 \pm 2^\circ$ produced by the (110) face (which is co-planar with the direction of the line defect).

Sawing

Comparison between the initial surfaces and the newly formed, post-sawing surface, show the creation of strained areas at top and bottom edges of the sample in Fig. 4. These strained areas extend ~1-2 mm into the bulk and has been observed on a number of samples. Sawing of this particular sample was done with the string reciprocating along the vertical direction of the figure and cutting into the crystal from left to right. These strained areas could be attributed to the shearing action of the string, as it reciprocates back and forth, distorting the lattice of the HgI₂ material near the edges. The inside area of the crystal does not show this behavior. This is probably because the material is more rigid because it is supported by surrounding material and does

Figure 1. (001) Face of N8-19 Note the out of reflection area at bottom.

Figure 2. (110) Face of N8-19 (rotated by 90°), note dark portion.

Figure 3. (110) Face of N8-19 Note the vertical lines of defects.

Figure 4. N3-30 Sawn (001) Face. Strained areas on top and bottom.

not suffer lattice distortion. Edges on the left and right sides do not exhibit strain. The intense, vertical lines are caused by saw serrations.

Cleaving

A set of 2 crystals were cleaved and the four cleaved, unprocessed surfaces (two pairs of mirror surfaces were characterized) for surface damage on the (001) plane. For both crystals, the damage from the impact of the cleaving instrument can be clearly seen and the same region in the mirror surface is no longer in reflection as a result of bending. Irregular black and white contrast indicates that both surfaces are strained (extinction contrast). Striations on the lower portion of the surfaces are most probably the result of forced separation of the two crystal halves during the cleaving process.

Polishing

The first polish was done until the saw marks just disappeared. Rocking curves show that the crystallinity of samples can vary from FWHM of 25" to 50" over a 5 mm displacement. Occasionally, defects, aligned in the $\langle 100 \rangle$ or $\langle 010 \rangle$ directions, were introduced. Repolishing does not seem to introduce additional defects nor remove previously seen features, however, the rocking curves are more uniform. Because of the difficulty in repeatedly locating the X-ray beam at the same spot for subsequent rocking curves, it is not possible to make direct comparison of the same spot at different stages of processing.

Etching

Etching with KI did not seem to remove any of the defects seen after polishing. This leads to the conclusion that the defects introduced earlier were deeper than the average etch depth of $\sim 120 \mu\text{m}$. The utility of etching would be limited to cleaning the surface prior to contact deposition.

After Contact Deposition

The crystal topography is altered by evaporation of Pd films. Some prominent features within the crystal are retained while the rest is sufficiently jumbled to preclude interpretation. There appears to be some film stress in the evaporated Pd film, as occasionally films with peel or curl.

Thermal Expansion

The α_{11} 's are determined from the angular shift, $\delta\theta$, of the rocking curve as a function of temperature T:

$$\delta\theta = -\alpha \cdot \delta T \cdot \tan\theta \quad (1)$$

where θ is the Bragg angle and α is the coefficient of linear thermal expansion. A linear regression fit of numerous independent measurements yielded the thermal expansion coefficients of $\alpha_{33} = 54 \pm 5 \cdot 10^{-6}/^\circ\text{C}$ in the c or [001] direction and $\alpha_{11} = 11 \pm 4 \cdot 10^{-6}/^\circ\text{C}$ in the a or [100] direction. The degree of anisotropy defined as $A = (\alpha_{11}/\alpha_{33}) - 1$, was -0.80 . Table I shows that the α_{11} , of the latest HgI₂, is in good agreement with those obtained by others, however, the value for α_{33} is distinctly larger than those reported in the earlier literature.^{6,7} However, Gauthier & Nicolau⁶ studied solution grown crystals by XRD, while Haussühl & Scholz⁷ employed ultrasound techniques to investigate vapor grown crystals. Prokopovich's results⁸, from vapor growth of HgI₂ precipitated from acetone, deviate considerably from all others and the low anisotropy reported is attributed to low chemical purity of the HgI₂.⁶ Similarly, the trend of increasing α_{33} coefficient over time may indicate successive improvements in the purity of the HgI₂. Impurities are

often assumed to accumulate in open channels perpendicular to the c-axis. Thus, it appears that the thermal expansion along the c-axis is sensitive to the concentration of impurities contained within the unit cell. Verification of this hypothesis will have to await the development of reproducible analytical techniques for the HgI_2 matrix.

TABLE I: Recent Coefficient of Expansion Measurements

Author	Date	α_{11} ($10^{-6}/^\circ\text{C}$)	α_{33} ($10^{-6}/^\circ\text{C}$)	A
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This paper	1993	11 ± 4	54 ± 5	-0.80
Gauthier ⁶	1982	10 ± 1	46 ± 1	-0.78
Haussühl ⁷	1975	$10 \pm .3$	44 ± 1	-0.78
Prokopovich ⁸	1974	43 ± 2	69 ± 2	-0.38

A hysteresis effect was observed within every cycle of heating and cooling. Peak splitting indicates the presence of small angle grain boundaries and is probably due to plastic flow and deformation of the mercuric iodide at 65°C .

The high structural anisotropy of $\alpha\text{-HgI}_2$, $c_0/a_0 = 2.85$, is reflected in the strong directional dependence of its thermal expansion coefficients. If a crystal is grown with the c-axis, [001], vertical, the crystal is resting in its a-b plane and the α_{11} of $11 \pm 4 \cdot 10^{-6}/^\circ\text{C}$, is of the same order of magnitude as $\alpha = 3.3 \cdot 10^{-6}/^\circ\text{C}$ of the Pyrex glass used. However if the crystal is grown with the c-axis parallel to the pedestal, resting on its a-c plane, there is ~5X difference between the α_{11} and α_{33} and greater than one order of magnitude difference between α_{33} and Pyrex glass. This suggests defects and/or strain in the crystal region close to the growth pedestal and has been documented by an increased broadening of rocking curves.³ Mercuric iodide, in its a-b plane, appears to be a better match to evaporated Pd, $\alpha = 11 \cdot 10^{-6}/^\circ\text{C}$.

Various investigators^{6,9-11} suggest that deviations in HgI_2 stoichiometry will result in lattice parameter changes, however reported parameters^{9,10} do not show any clear correlations. Interestingly, the lattice parameters of 36 samples investigated by Nicolau & Rolland⁹ averaged to $a_0 = 4.372 \pm .002$ Å and $c_0 = 12.440 \pm .004$ Å and compares well with the NBS values¹² of $4.3693 \pm .0001$ Å and $12.4399 \pm .0004$ Å at 25°C for stoichiometric $\alpha\text{-HgI}_2$. Correlation is difficult because crystal parameter measurements¹³ are hampered by the mosaicity in most HgI_2 crystals, large uncertainties in stoichiometry determinations and the rigid demands for temperature control were probably not always satisfied. For example, a 3°C change in ambient temperature will result in a 0.002 Å change of c_0 .

CONCLUSIONS

As-grown, macro-defects such as large subgrains or crystal bending extend through millimeters of material and cannot be removed by polishing or deep etching. Strongly oriented bands which most likely are a result of incremental crystal growth are always present in as-grown as well as sawn surfaces. Selective etching appears to occur along these bands and it is speculated that stoichiometric variations make such chemical attack possible. String sawing strains the edges of samples but does not introduce damage to the interior. The cleaving of c-planes introduces a considerable amount of strain and can lead to macro-defects if the process is forced. Polishing appears to introduce specific, local defects but also restores the sample surface to crystalline uniformity. Etching does little, except to clean and prepare the immediate surface for contact deposition. The combined sawing, polishing and etching process generally lead to homogeneous surfaces with limited macro-defects. Major defects observed after this treatment are imperfections due to crystal

growth and therefore irreversible. Thus far it has not been possible to directly correlate differences in areal detector performance with topographical features and rocking curves.

The thermal coefficient of expansion of monocrystalline α - HgI_2 between 25°C and 65°C has been determined. The results indicate that strict temperature control is required for any determination of α - HgI_2 lattice parameters and that α_{33} may be linked to stoichiometry.

The refinement of HgI_2 crystal growth techniques at EG&G/SBO have resulted in more homogeneous crystals. Imperfections resulting either from growth or processing are readily localized against a more or less perfect bulk and therefore more likely to be identified and explained by x-ray diffraction methods.

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