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HgZnTe-based Detectors for LWIR NASA Applications

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HgZnTe has become of growing interest in recent years for IR detector applications because of the promise of equivalent performance but with greater producibility and reliability than HgCdTe-based detectors. The substitution of Zn for Cd in a dilute alloy with HgTe was predicted by Arden Sher et al (J. Vac. Sci. Technol. A 3(1), Jan/Feb 1985, pp. 105-111) to give a material with greater mechanical hardness along with other advantageous properties for IR detectors. Over the past four years, our group and others have grown and characterized HgZnTe and shown that it indeed has increased microhardness, lower Hg diffusion rates and equivalent crystal quality, electrical and optical properties as compared with HgCdTe. Other advantageous properties including higher Hg vacancy formation energies, sharper exciton line, and reduced Te antisite formation have been predicted and/or measured. Triboulet and coworkers in France have fabricated diodes from bulk-grown HgZnTe and have seen greater bake stability for these devices as compared with their HgCdTe diodes. We report here today on test results on our first lot of VLWIR HgZnTe photoconductors using the HIT approach developed for HgCdTe.

Our initial goal on this program was to grow and characterize HgZnTe and determine if it indeed had the advantageous properties that were predicted. We grew both bulk and liquid phase epitaxial HgZnTe and collaborating with SRI and Stanford we determined that HgZnTe had the following properties: 1) microhardness at least 50% greater than HgCdTe of equivalent bandgap, 2) Hg annealing rates of at least 2 - 4 times longer than HgCdTe, and 3) higher Hg vacancy formation energies. This early work did not focus on one specific composition (x-value) of HgZnTe since NASA was interested in HgZnTe's potential for a variety of applications. Since the beginning of 1989, we have been concentrating, however, on the liquid phase growth of VLWIR HgZnTe (cutoff ≈ 17 μm at 65K) to address the requirements of the Earth Observing System (Eos).

Since there are no device models to predict the advantages in reliability one can gain with increased microhardness, surface stability, etc., one must fabricate HgZnTe detectors and assess their relative bake stability (accelerated life test behavior) as compared with HgCdTe devices fabricated in the same manner. Fabrication of HgZnTe devices only became feasible for us in 1989 as we were able to reduce Te melt retention on the surface of our layers and obtain a reasonable yield of device quality layers. We have chosen to fabricate HIT detectors as a development vehicle for this program because high performance in the VLWIR has been demonstrated with HgCdTe HIT detectors and the HgCdTe HIT process should be applicable to HgZnTe. HIT detectors have a significant advantage for satellite applications since these devices dissipate much less power than conventional photoconductors to achieve the same responsivity.

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Our first lot of HgZnTe HIT photoconductors exhibit high performance with cutoffs greater than 18 μm. We have performed initial radiometric testing at 30K and 80K and have achieved peak D* of 6×10^{10} cm$\sqrt{Hz}$/W at 30K which is within a factor of two of BLIP for the background level used (3×10^{16} ph/cm^2/sec). Peak responsivites at 80K of 3×10^4 V/W have been measured which are comparable with those typically seen for conventional HgCdTe photoconductors. These results are very exciting especially in view of the fact that this is our first lot of HgZnTe devices. Parameters of the starting material which may have limited performance of this first lot will be discussed. Also to be discussed are our plans to continue this year to refine the material parameters (thickness, cutoff, etc.) to achieve higher performance with our second lot to be processed in June.

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Innovative LWIR Detector Workshop
April 25, 1990

Sponsored by NASA/Langley (W. E. Miller, Technical Monitor)

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Outline

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- **Why HgZnTe?**
- **Early Program Results**
- **1989 Materials Improvements**
- **First HgZnTe PC Results**

HgZnTe Offers Many Potential Advantages for LWIR Applications

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- HgZnTe offers same performance as HgCdTe but potentially with:
  - Greater stability against thermal and mechanical degradation
    - Short ZnTe bond
- Specific advantages predicted and/or measured:
  - HgZnTe mechanically harder (at least 50% for same bandgap)
    - Lattice matches to tougher substrate (20% CdZnTe)
  - Slower Hg diffusion (annealing data)
  - Larger Hg vacancy formation energies predicted
  - Greater bake stability of HgZnTe diodes (French data)
  - Concentration fluctuations suppressed - large binary lattice mismatch
    - Measured uniformity greater for THM HgZnTe vs HgCdTe
    - Exciton line is very sharp
  - Higher m* for same bandgap (15% for .1 eV)

EARLY PROGRAM RESULTS

NASA Has Funded HgZnTe At SBRC Since 1986

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- NASA's main concern is device stability in satellite FPAs
- Began as coordinated program with SRI, Stanford:
  - SRI: Theory
  - Stanford: Hardness, Diffusion Measurements
  - SBRC:
    - Bulk HgZnTe Growth (SSR & ZM)
    - Bulk CdZnTe Growth (20% Zn for lattice matched substrates)
    - HLPE HgZnTe
    - Phase Diagram - Liquidus Measurements
    - Materials Characterization/Device Science
- Current goal is development for VLWIR EOS applications
  - 17 μm at ≥ 65 K
- Other HgZnTe work in France, Israel, Poland, Pittsburgh

Growth of HgZnTe is Difficult

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- Initial goals to see if HgZnTe could be grown and had promised properties
- Issues concerning HgZnTe growth:
  - Low Zn solubility in Hg or Te-rich melt - much lower than Cd
    - Lowest in Hg melt
    - Same issues with Te-melt growth as for HCT (melt retention)
  - High segregation coefficient of Zn in Te-rich melt
    - 3.5 times that of Cd
    - Tends to increase layer grading
  - HgTe-ZnTe lattice mismatch large - 6% vs 0.3% for HgTe-CdTe
- Both bulk and epitaxial HgZnTe were goals for the program

All Early Program Goals Met

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- Early focus of program on material issues
  - Can we grow HgZnTe?
  - Does it have predicted advantageous properties?

- In first year of program, growth goals achieved:
  - Successful bulk growth of HgZnTe (x = 0.16) of high quality - required for structural characterization
    - Mechanical hardness
    - Photoemission
  - Successful bulk growth of $Cd_{.8}Zn_{.2}Te$ with high crystal quality - required for lattice-matched substrates
  - Successful growth of HLPE HgZnTe ($.11 \le x \le .24$)
    - Good compositional uniformity/crystal quality

Many HLPE HgZnTe Properties Similar to LPE HgCdTe

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- In first year, demonstrated that compared with LPE HgCdTe, HLPE HgZnTe has comparable:
  - Crystal quality
  - Vertical and lateral compositional uniformity
  - Low impurity densities (in annealed wafers)

- Experimentally and theoretically showed that HLPE HgZnTe has:
  - Comparable carrier lifetime with good lateral uniformity
  - Comparable electron mobility (μ) and predicted factor of two smaller hole μ

- Valence band offest measured in bulk HgZnTe by photoemission
  - Smaller than in HgCdTe ($\approx$ 200 meV vs 350 meV)

First Year Work Shows Advantages of HgZnTe

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- Both bulk and epitaxial HgZnTe found at least 50% harder than same E_G HgCdTe
  - Knoop microhardness measurements, nanoindenter
- Hg in-diffusion rate at least 2 - 4 times slower for HgCdTe
  - Annealing experiments
- Larger Hg vacancy formation energies predicted
  - HgZnTe should be more stable against Hg loss
- Larger electron m* predicted
  - Reduced tunneling

HARDENING OF ALLOY DUE TO Zn DEMONSTRATED BY MICROHARDNESS MEASUREMENTS

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MATERIAL	KHN	OTHER MATERIALS	KHN
$Hg_{0.84}Zn_{0.16}Te$	45.9	$Cd_{0.80}Zn_{0.20}Te$	78.5
$Hg_{0.90}Zn_{0.10}Te$	38.0	$Cd_{0.96}Zn_{0.04}Te$	46.3
$Hg_{0.80}Cd_{0.20}Te$	31.6	CdTe	36.1

KHN = KNOOP HARDNESS NUMBER

- **THEORETICAL FOUNDATION — SRI**
  - **HARDNESS DETERMINED BY ENERGY REQUIRED TO FORM PAIRS OF DISLOCATIONS, E_{PD}**
    - **$E_{PD} \sim 1/d^{10} \rightarrow d$ = CATION-ANION BOND LENGTH**
  - **$d_{ZnTe}/d_{CdTe} \simeq 0.94$ ($d_{HgTe}/d_{CdTe} \simeq 1$)**
  - **SMALLER ZnTe BOND LENGTH INHIBITS DISLOCATION FORMATION AND PROPAGATION**

Concentration Fluctuations Probably Suppressed in HgZnTe

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- Large lattice mismatch between HgTe and ZnTe favors uniform composition
    - Negligible mismatch between HgTe and CdTe
- Evidence of greater compositional uniformity in HgZnTe exists (Triboulet):
    - THM ingot uniformity
    - Sharpness of exciton line
    - Excellent diode cutoff uniformity
- Greater compositional uniformity offsets larger dE_g/dx in HgZnTe
    - Bowing in E_g vs x also reduces dE_g/dx at long wavelengths:
        - dE_g/dx = 2.1 eV for HgZnTe ;
          = 1.9 eV for HgCdTe
          (at E_g = 0.1 eV or 12.4 μm)

SAT in France Has Produced LWIR HgZnTe Diodes

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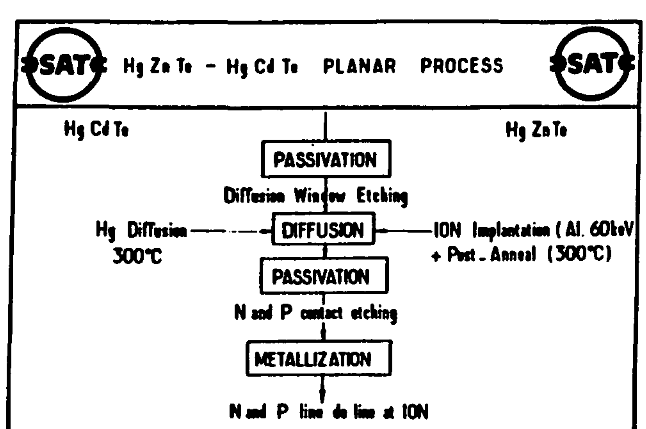
- SAT achieved comparable diode performance to HgCdTe with bulk HgZnTe and modified SAT process:
    - 14.35 μm performance was achieved with <u>implanted</u> HgZnTe



French Data Implies Greater HgZnTe Diode Bake Stability

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- Maximum temperature of vacuum bake before degradation is higher for HZT
- Evaluation of bake data requires details of separate processes for HCT and HZT

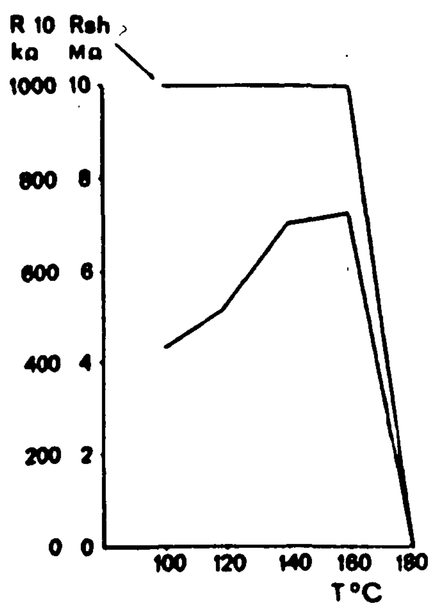

Figure 3. Variation of the shunt (Rsh) and R(- 10 mV) resistances during the thermal test under vacuum.

These performances of MZT are comparable to those of their MCT counterparts.

Over eight hundred elements have been submitted to thermal test to assess their reliability, under the following conditions of vacuum heating :

(100°, 96 h) + (120°, 96 h) + (140°, 96 h) + (160°, 96 h) + (180°, 96 h).

The great majority of the diodes display results as in figure 3. The shunt resistances are limited to 10 MΩ because of the precision of the measurements under automatic points. R (- 10 mV) increases during the first stages of heating before falling, together with Rsh, after the last heating at 180°C. These results express well a very significant improvement in stability compared to MCT diodes of the same cut-off wavelength.

6. CONCLUSIONS

This study demonstrates clearly that the fundamental advantages predicted for MZT over MCT are now confirmed by many relevant experimental results. The reliability of the photodiodes together with their high performances make now MZT the successor designate of MCT for IR detection. The ready ability for MZT to be processed in existing MCT manufacturing facilities can be also considered to be a determining advantage.

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RECENT PROGRESS

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1989 Goal to Achieve/Process Device Quality VLWIR HgZnTe

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- Focused on obtaining device quality VLWIR HgZnTe in 1989
  - Shifted to VLWIR (λ_{co} $\geq$ 16 µm @ 80K) from LWIR
- Goals were to routinely achieve:
  - Good surface morphology - reduce melt retention
  - Desired electrial properties
  - High optical transmission below gap
  - Good carrier lifetimes
  - Cutoff, thickness in desired range
- Device goal was to process/test one lot of HgZnTe Common Module
- Use Trapping Mode approach demonstrated for VLWIR HCT

CURRENT GROWTH PARAMETERS

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- GROWTH TECHNIQUE: Te MELT LPE, HORIZONTAL SLIDER
- TEMPERATURE RANGE: 462 - 455° C
- MELT COMPOSITION: 14 g Te, .07 g ZnTe, SEPARATE Hg SOURCE
- COOLING RATE: 0.1° C / MINUTE
- SUBSTRATES: CdTe, $Cd_{.96}Zn_{.04}Te$, $Cd_{.80}Zn_{.20}Te$ (NOMINAL)
- SIZE: 1 X 1 INCH
- X-VALUE RANGE: X = .12 - .18

HgZnTe LPE Growth Improved Dramatically in 1989

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- Layer Yield Historically Lowered by:
  - Te Melt Retention
  - Strong Composition/Thickness Dependence on Temperature
    - High Zn Segregation
- Sources of Recent Improvement (VLWIR HgZnTe, $x \approx 0.14$):
  - Reduced O_2 Contamination
  - Substrate Screening
  - Use of Lower Zn% Substrates
  - Improved Temperature Control

HgZnTe PC Lot 1 Testing

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HgZnTe PC Lot 1 Testing Overview

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- Several wafers tested at both 80K and 30K with:
  - 800K blackbody, 30° FOV
  - Background Flux = 3×10^{16} photon/cm^2 /sec
- 80K results:
  - Blackbody D* ≈ 5×10^{9} cm√Hz/W
  - Spectral measurements indicate cutoffs as great as 19 μm
- 30K results
  - Blackbody D* ≈ 3×10^{10} cm√Hz/W
  - Peak D* ≈ 6×10^{10} cm√Hz/W (BLIP D* ≈ 1.2×10^{11} cm√Hz/W)
- Initial results show cutoffs are longer than desired

80K Noise Increases as Expected at High Bias

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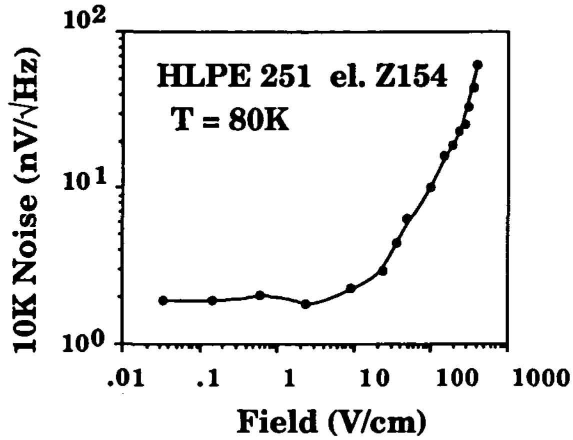

D* at 80K Limited by Noise from Long Cutoff

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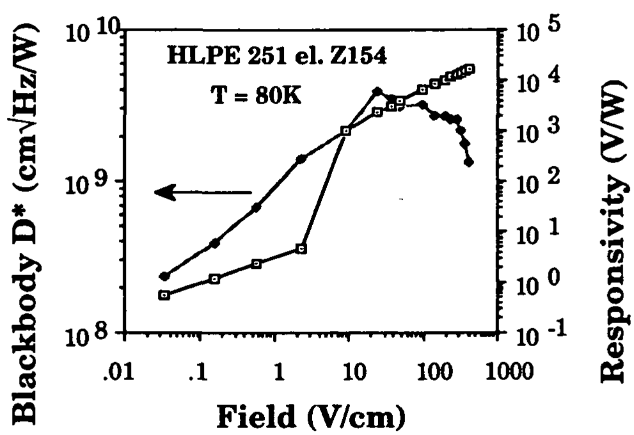

- **80K Blackbody D* ≈ 5 x 10^9 cm√Hz/W**

Spectral Cutoffs of 19 μm at 80K Measured for HgZnTe PCs

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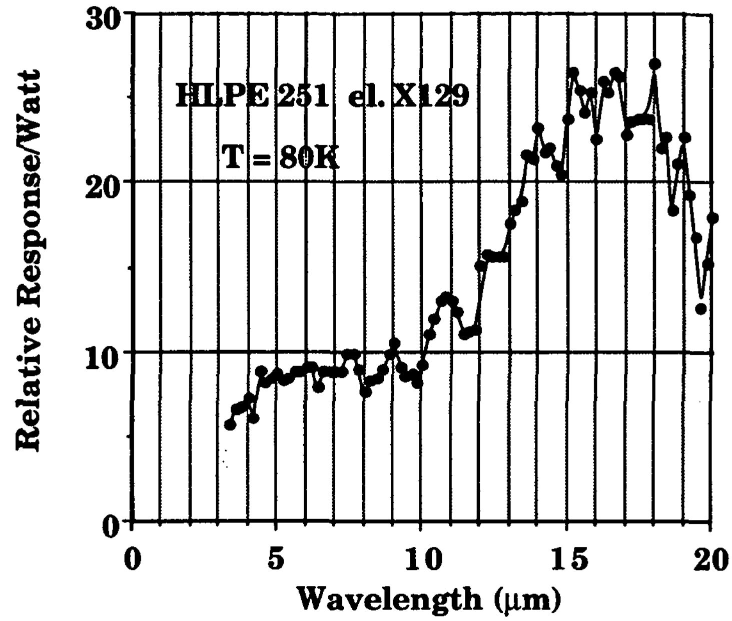

- Initial HgZnTe Devices Longer Than Desired
- Performance Should Improve With Decreased Wavelength

Excellent Blackbody Responsivity for HgZnTe Lot 1 at 30K

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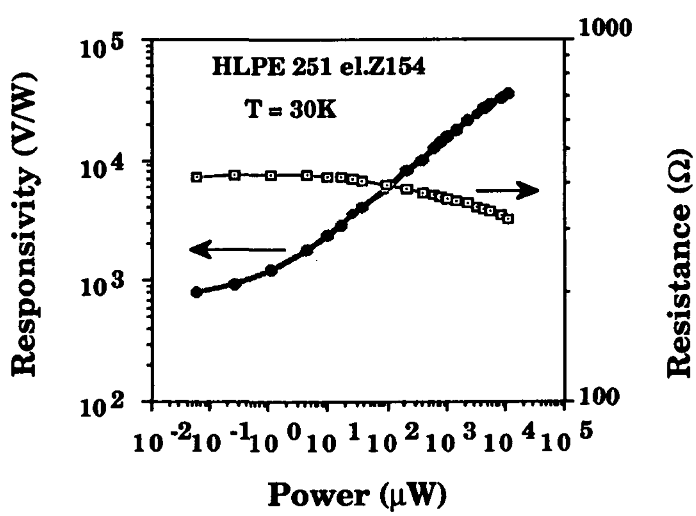

- **Blackbody Responsivities up to 3×10^4 V/W at 30K**
  - **Comparable with conventional HgCdTe PC**
- **Responsivity still not saturating at highest bias**

Noise Reduced at 30K for HgZnTe PC Lot 1

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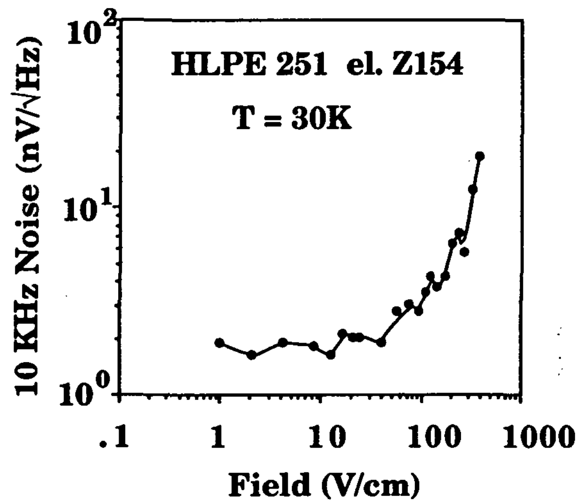

Peak D* at 30K Close to BLIP

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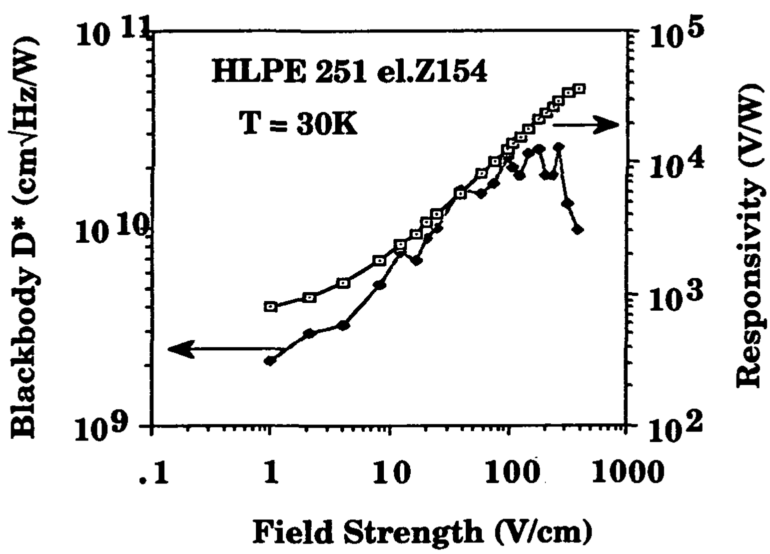

- Peak D* of 6×10^{10} cm√Hz/W

Summary and Future Plans

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- Excellent VLWIR performance demonstrated with initial HgZnTe PCs
- Results show that HgCdTe processing largely compatible with HgZnTe
  - Trapping mode PCs should perform as well in HgZnTe as in HgCdTe
- Sources for improving next HgZnTe device lot defined
  - Shorter cutoff
  - Thinner layers
- Ultimate test of HgZnTe's promise will be accelerated life testing