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A strong emphasis has been laid recently on the characterization of HgCdTe epilayers by double X-ray rocking curve. A careful examination of what has been up to now reported is far from being conclusive. In fact what is claimed as world record is only one particular point on a crystal. Above all, nobody has presently established a clear relationship between the FWHM of X-ray Rocking Curve peak and the electrical characteristics of this HgCdTe layer. We have just received our X-ray equipment during the Summer 87 and have started our own investigations. What we have in mind is (1) to understand the relationship between FWHM of the substrate - FWHM of the epilayer, (2) to establish a relationship between FWHM mobility and carrier lifetime for a given HgCdTe MBE layer grown under very well established growth conditions. We have already characterized numerous substrates and HgCdTe epilayers grown in the (111) orientation on CdTe and CdZnTe substrates. Mercury Cadmium Telluride

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AFOSR-TR- 87 - 1626

MBE GROWTH, CHARACTERIZATION AND ELECTRONIC DEVICE PROCESSING
OF HgCdTe, HgZnTe, RELATED HETEROJUNCTIONS
AND HgCdTe-CdTe SUPERLATTICES

DARPA - AFOSR - F49620-87-C-0021
November 13, 1986 - November 12, 1989

Quarterly Report
September 15, 1987

Jean-Pierre Faurie
University of Illinois at Chicago



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I. Growth and Characterization of high quality HgCdTe epilayers

A strong emphasis has been laid recently on the characterization of HgCdTe epilayers by double X-ray rocking curve. A careful examination of what has been up to now reported is far from being conclusive.

In fact what is claimed as world record is only one particular point on a crystal. Above all, nobody has presently established a clear relationship between the FWHM of X-ray Rocking Curve peak and the electrical characteristics of this HgCdTe layer.

We have just received our X-ray equipment during the Summer 87 and have started our own investigations. What we have in mind is (1) to understand the relationship between FWHM of the substrate - FWHM of the epilayer, (2) to establish a relationship between FWHM mobility and carrier lifetime for a given HgCdTe MBE layer grown under very well established growth conditions.

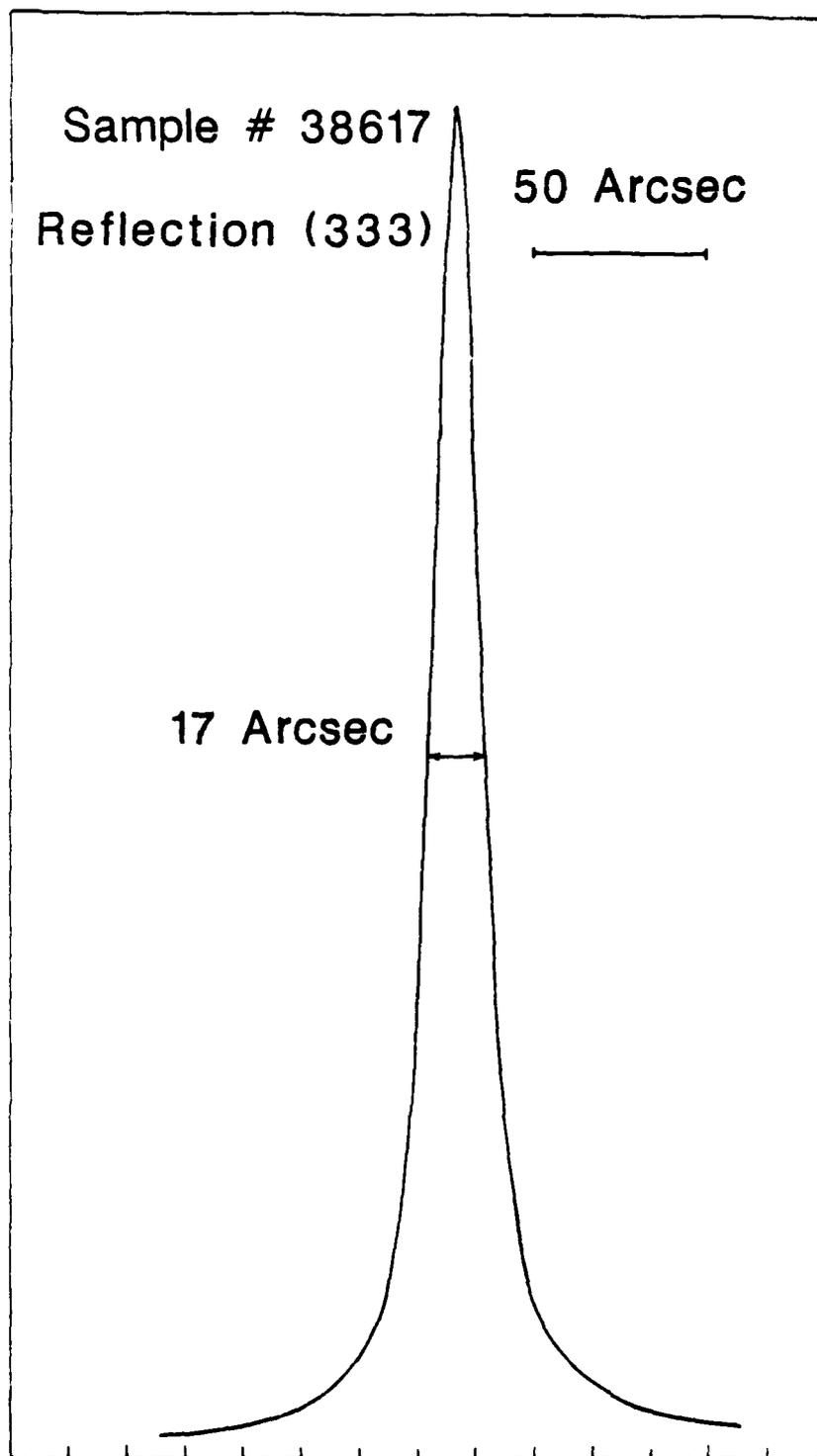
We have already characterized numerous substrates and HgCdTe epilayers grown in the (111) orientation on CdTe and CdZnTe substrates. Our preliminary conclusions are the following:

- 1 - if we want to do marketing with a FWHM of 17 arc see (Fig. 1) for a HgCdTe layer we can claim to have presently the world record.
- 2 - if we want to do material science we have to conclude that these values are not representative of what is currently obtained. In addition to that FWHM values are highly non uniform over the same epilayer. This problem, in our case, is without any doubt due to the non uniformity of CdTe and CdZnTe substrates (Fig. 1 to 7).

When the substrate is uniform enough, we have found that the FWHM of the epilayer is about 1.5 times larger than the half width of the substrate if it is CdZnTe and about 2 times if the substrate is CdTe (Fig. 8 to 10).

- 3 - Due to this lack of uniformity in the substrate quality it is not surprising that no correlation has been yet established between epilayer physical properties and FWHM. We are currently working on this problem.

Intensity (Arbitrary Units)



Intensity (Arbitrary Units)

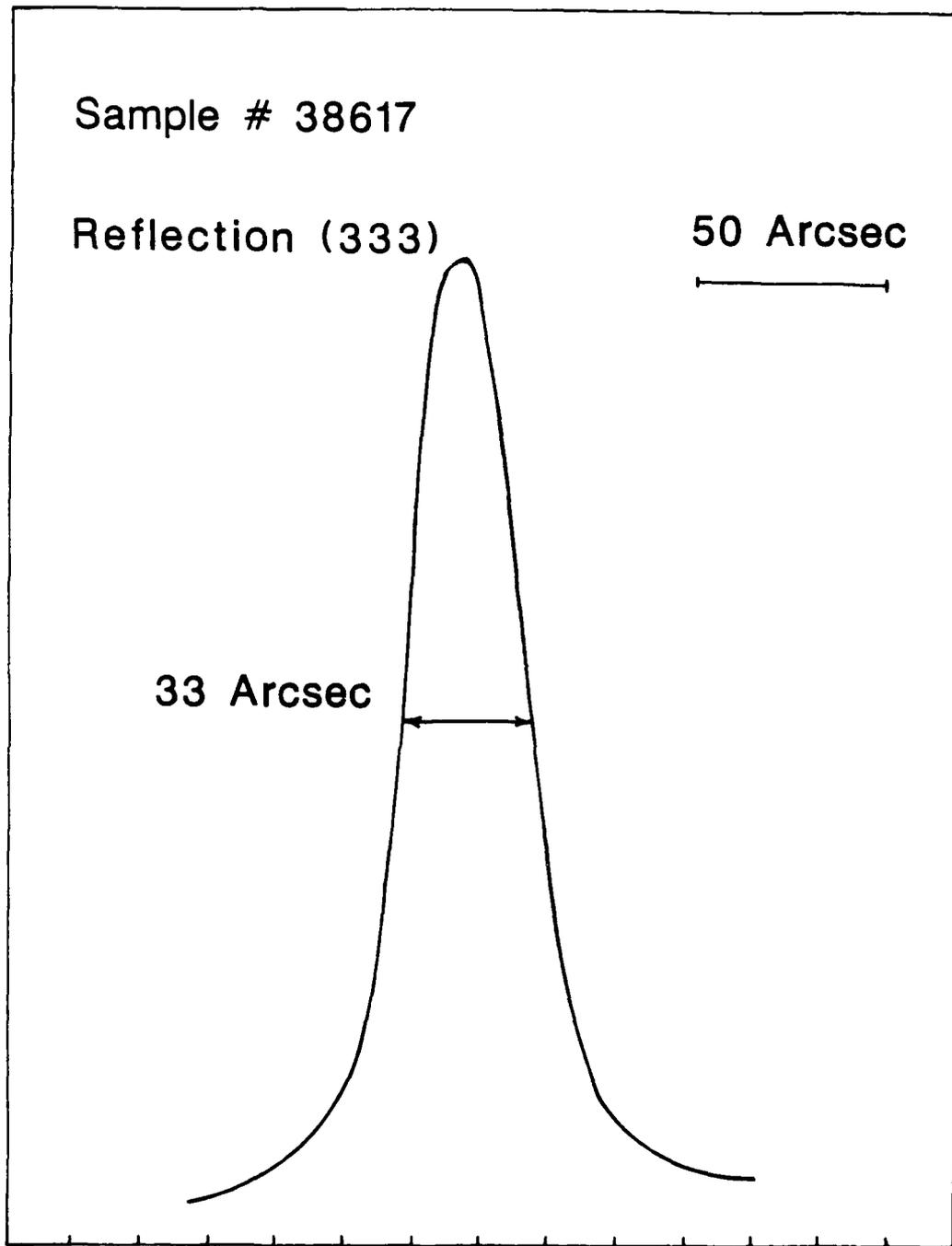
Sample # 38617

Reflection (333)

50 Arcsec

33 Arcsec

θ (Decreasing \rightarrow)



Intensity (Arbitrary Units)

Sample # 38617

Reflection (333)

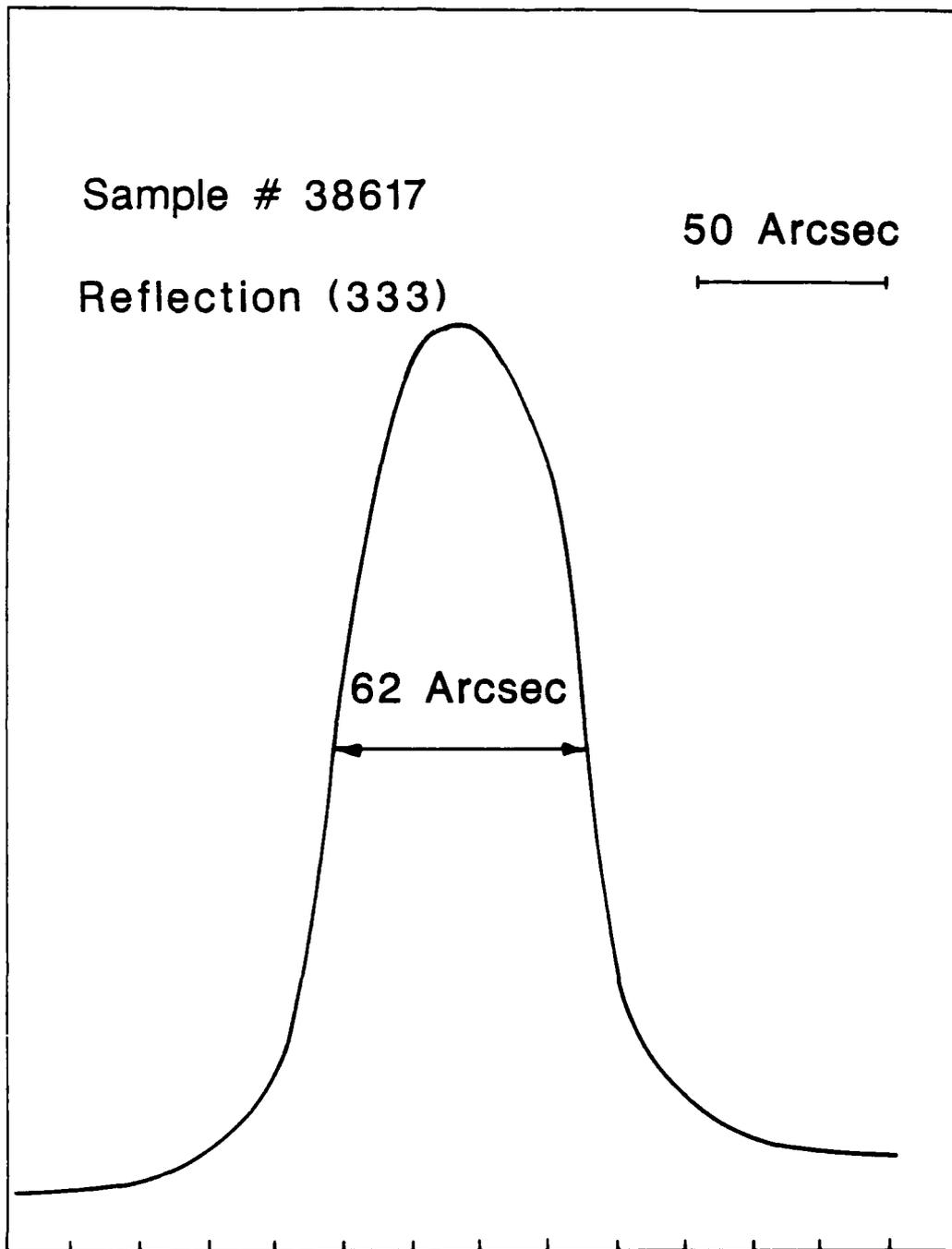
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62 Arcsec



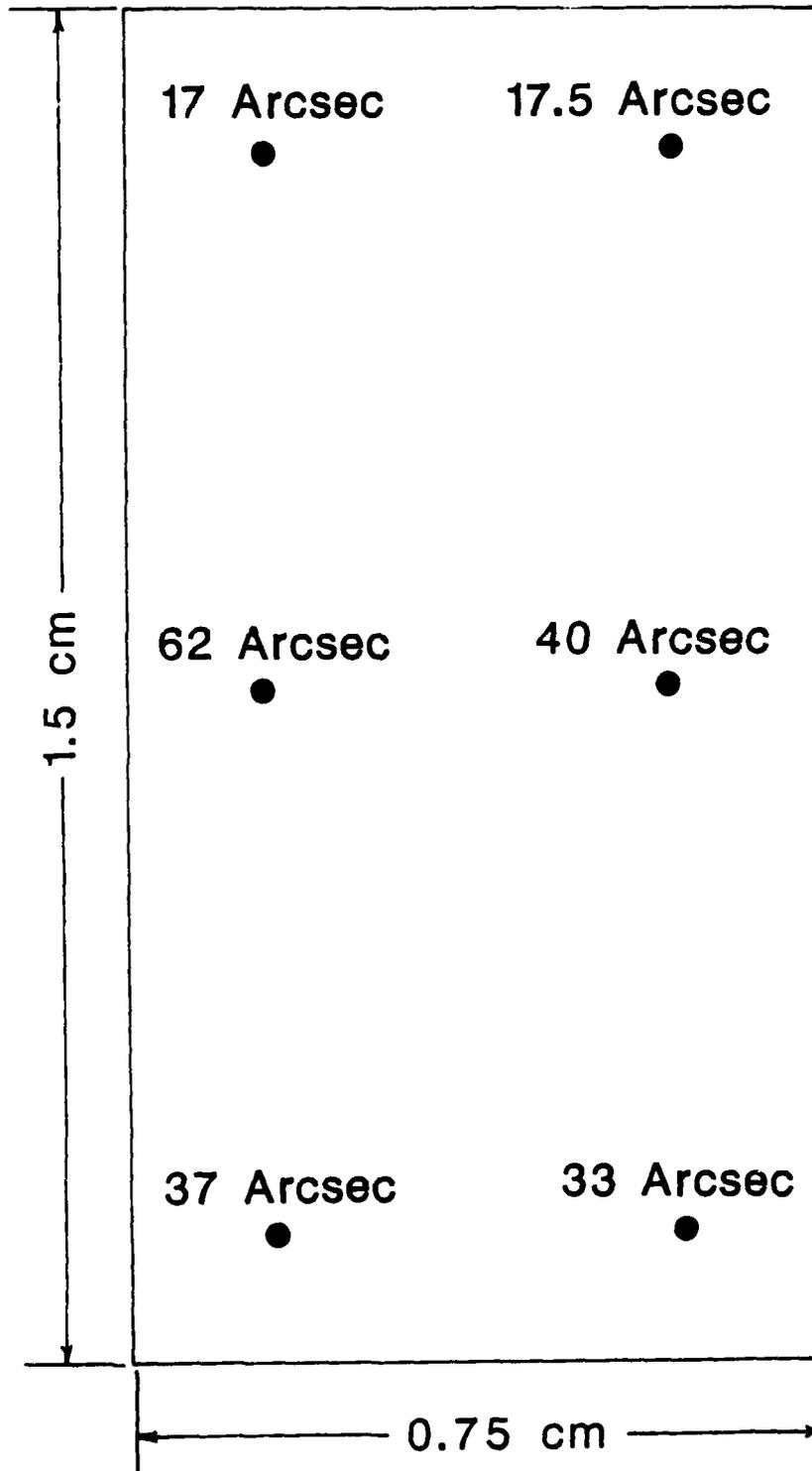
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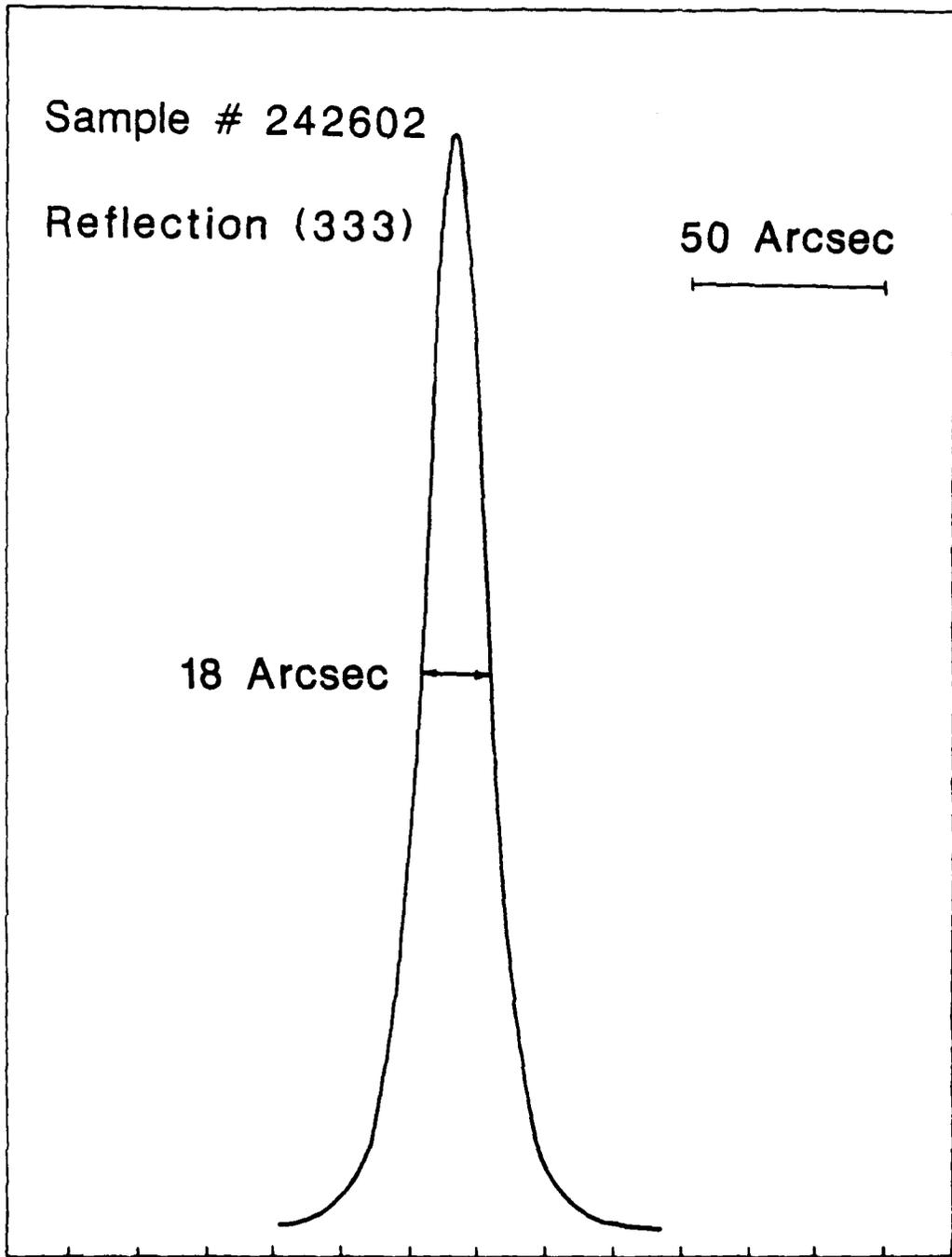
Sample # 38617

Substrate: CdZnTe

Layer Thickness: 5 μm



Intensity (Arbitrary Units)



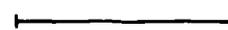
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Intensity (Arbitrary Units)

Sample # 242602

Reflection (333)

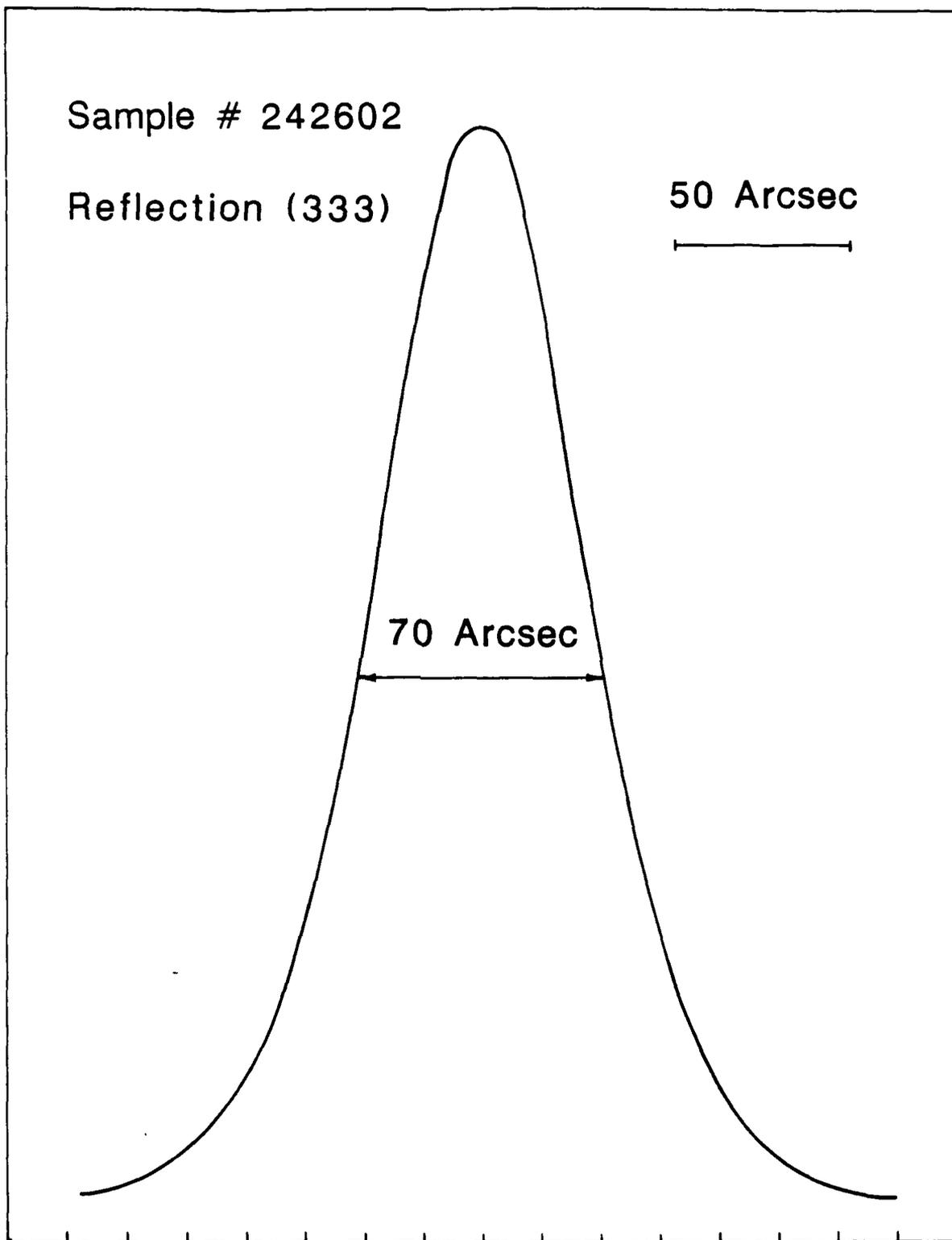
50 Arcsec



70 Arcsec



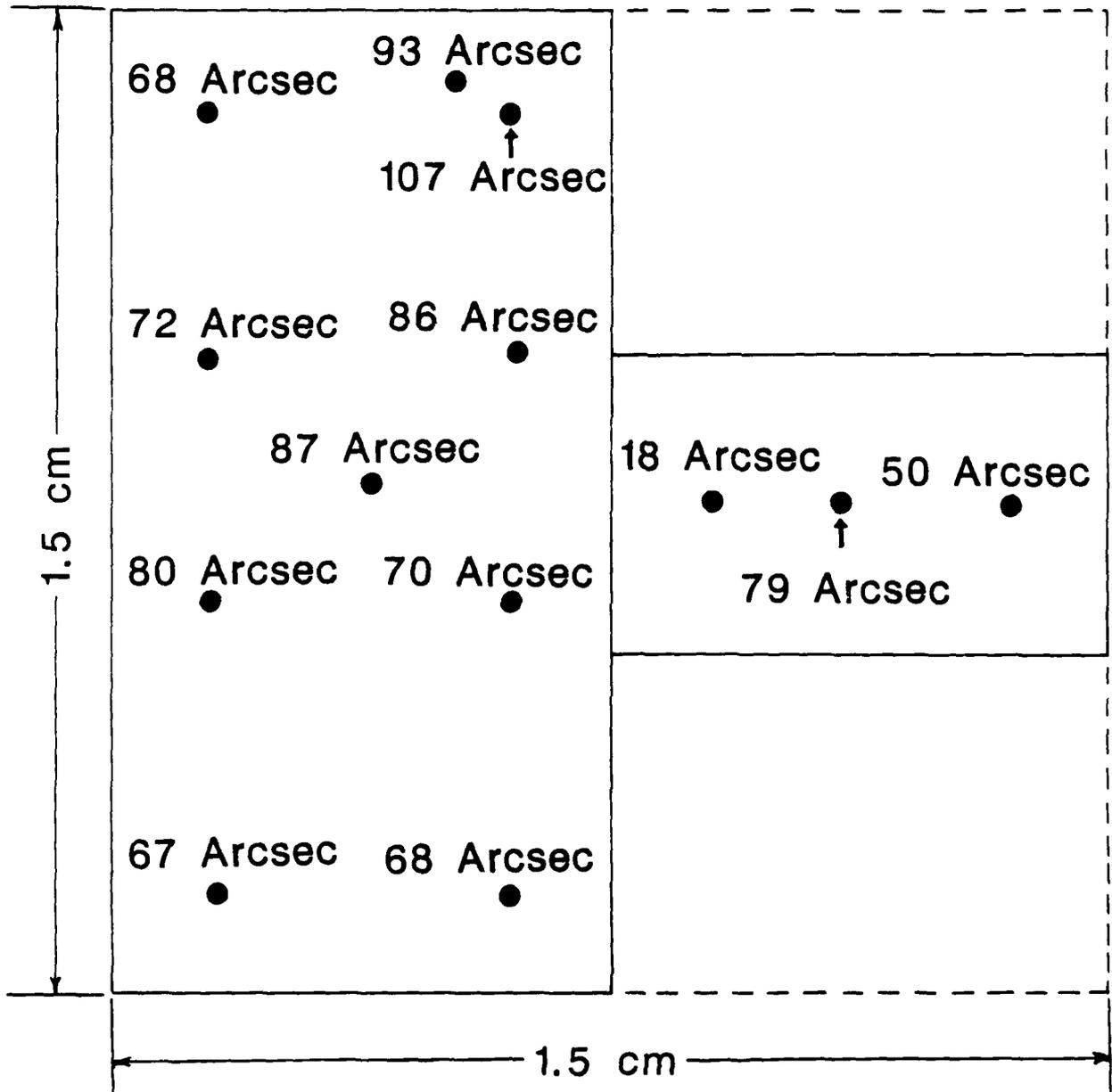
θ (Decreasing \rightarrow)



Sample # 242602

Substrate: CdTe

Layer Thickness: 12.1 μm



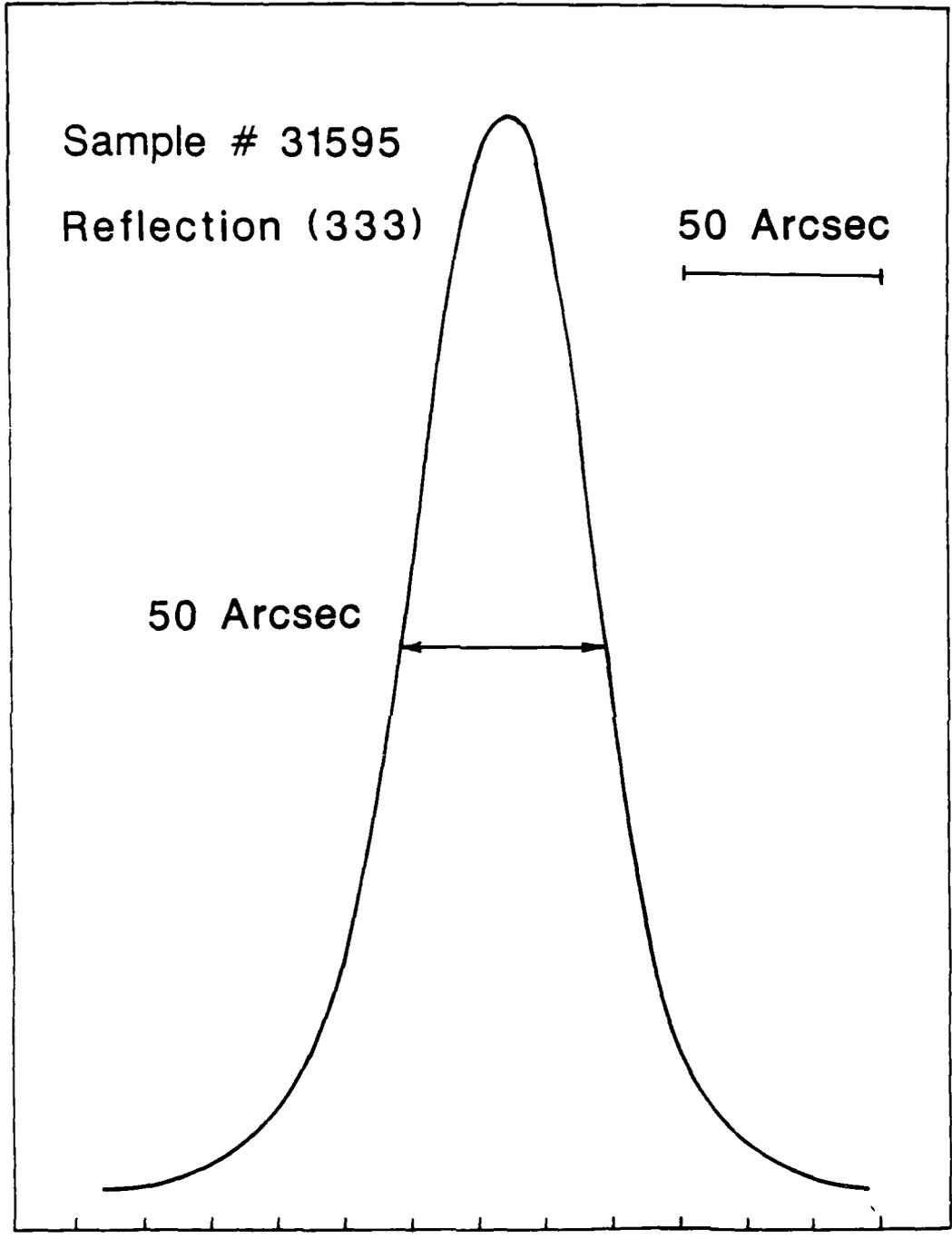
Intensity (Arbitrary Units)

Sample # 31595
Reflection (333)

50 Arcsec

50 Arcsec

θ (Decreasing \rightarrow)



Sample # 31595

Reflection (333)

50 Arcsec

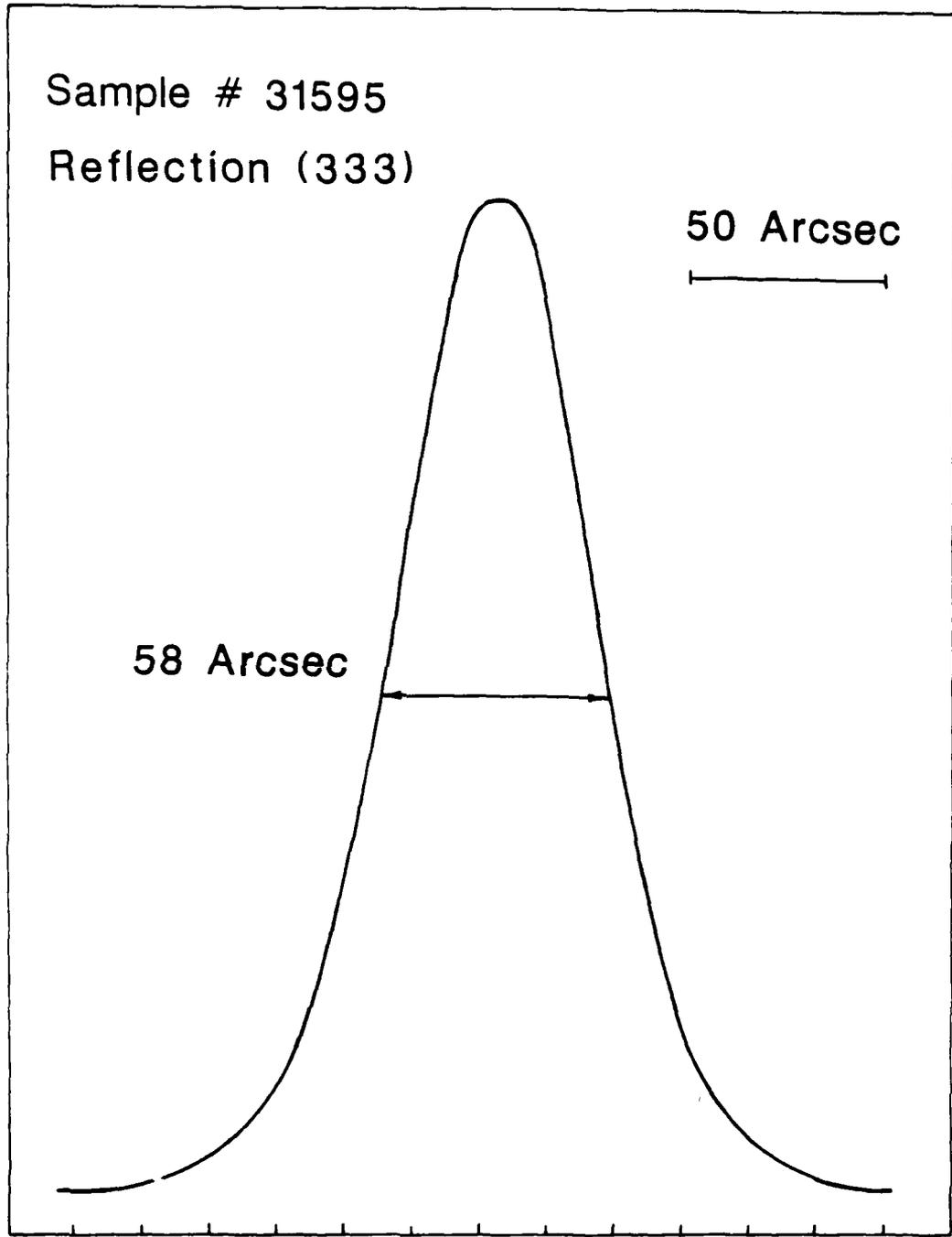


58 Arcsec



Intensity (Arbitrary Units)

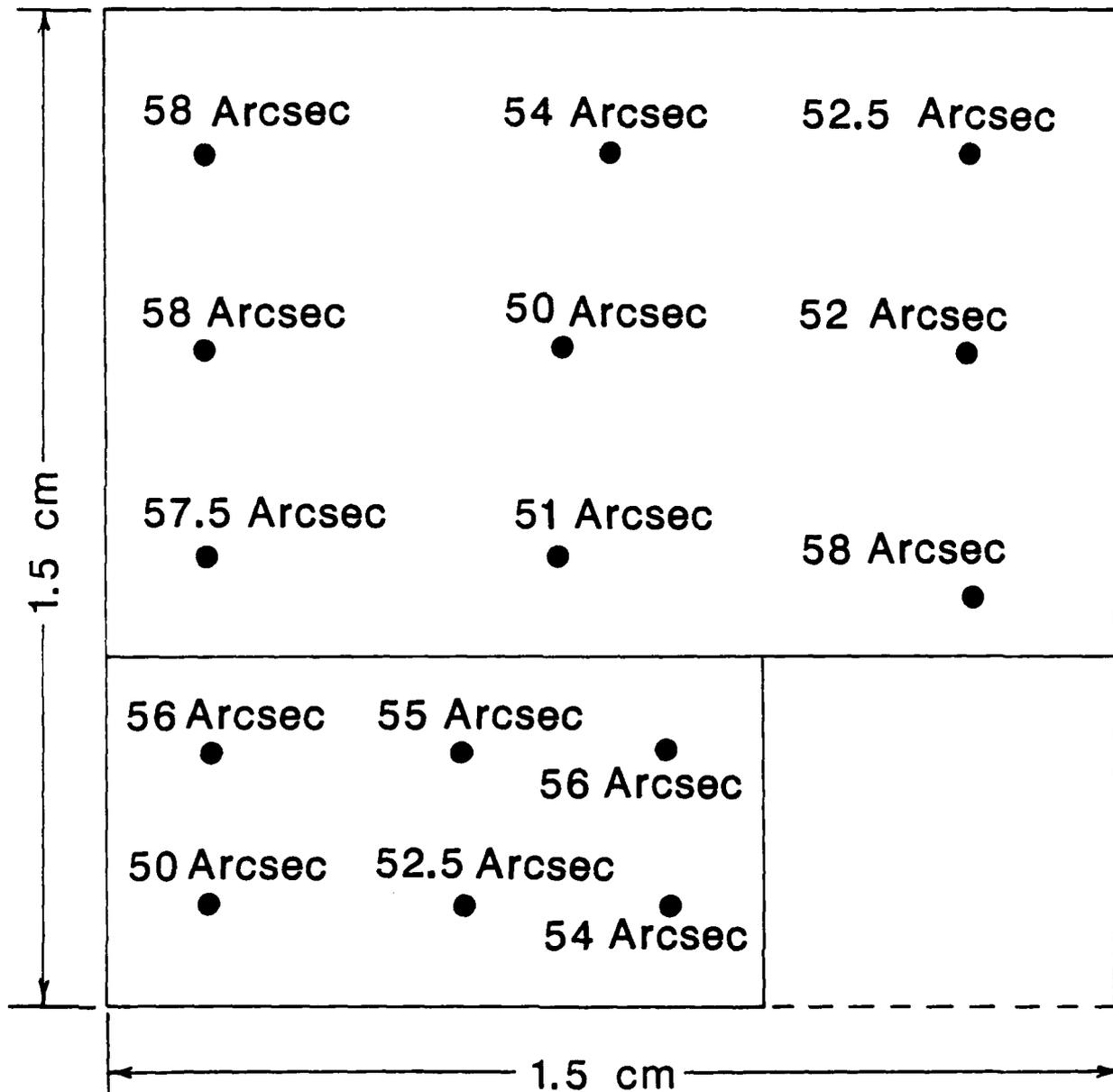
θ (Decreasing \rightarrow)



Sample # 31595

Substrate: CdZnTe (37 Arcsec)

Layer Thickness: 9.6 μm



II. MBE growth and characterization of two-inch diameter p- and n-type $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$ films on GaAs(100) substrate

The growth of a p-type layers on a two-inch GaAs(100) substrate has been previously reported (June 15, 1987 report). Since then we have grown several p- and n-type HgCdTe layers on 2 inch GaAs substrates.

Their surfaces were shiny and mirror-like from center to edge. Their thicknesses were uniform within 0.6%. Their Cd concentrations (x) were very uniform, exhibiting standard deviations $\Delta x/x$ as low as 0.7%. These films were completely uniform in their conduction types, that is, the n-type films were entirely n-type, and likewise for the p-type films. The Hall mobilities of these films show them to be of high quality, with values as high as $6.7 \times 10^2 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ for p-type ($x=0.22$), and $1.8 \times 10^5 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ for the n-type films ($x=0.21$). These results represent an important achievement towards the future of infrared detector technology.

For more detail see the attached paper submitted for publication in Applied Physics Letters entitled "Molecular Beam Epitaxial Growth and Characterization of Two-Inch Diameter $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$ Films on GaAs(100) Substrates."

III. Recent achievements in the growth by MBE of $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$

In the attached paper submitted for publication in the Journal of Vacuum Science and Technology experimental data on the influence of the substrate temperature on the Cd composition and on the growth rate when this temperature is above T_{max} (see the quarterly report of June 15, 1987 for the definition of T_{min} and T_{max}) are presented.

In this paper updated data on the best electrical performances of p-type and n-type HgCdTe epilayers grown by MBE are also included.

This paper is entitled "New Achievements on $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$ Grown by Molecular Beam Epitaxy."

IV. X-ray photoemission study of Hg clusters on $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$ surfaces

The (111)B surface of MBE-grown $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$ samples has been studied in detail using x-ray photoemission spectroscopy (XPS). The composition of the samples was in the range $x = 0.15$ to 0.97 . The smaller x values were obtained with three MBE

sources (CdTe, Te and Hg) as usual, whereas only two sources (CdTe and Hg) were used to obtain the larger values. A monochromatized and focussed Al K_{α} excitation line was used for the XPS measurements.

Two types of Hg have consistently been found for all the samples. These two types of Hg will be labeled Hg[1] and Hg[2] hereafter. From the binding energy with respect to the valence-band maximum, Hg[1] is clearly identified as Hg in HgCdTe. The second component is found at higher binding energy and is attributed to the presence of small Hg clusters on the HgCdTe surface. The radius of these clusters is deduced from the Hg[2]4f_{7/2} intensity measured with XPS. Values between 15Å and 40Å are obtained. The Hg[2]4f_{7/2} binding energy increases with decreasing cluster size. This is explained by the Coulomb energy $\sim e^2/r$ due to the unit charge appearing on the cluster during the photoemission process⁽¹⁾. This charge is not neutralized within the time scale relevant for photoemission, due to the semiconducting nature of the substrate. A good agreement between the experimentally observed binding energy shift and the calculated e^2/r behavior is observed. For large cluster sizes, a binding energy of 100.2 ± 0.2 eV is deduced. This is close to the value for bulk Hg (99.9 eV)⁽²⁾.

The apparent spin-orbit splitting of the Hg[2]5d levels decreases with decreasing cluster size. A total variation of 0.5 eV is measured. Our results are smaller than the value for free Hg atoms, except for the largest cluster sizes. This is attributed to the repulsion between the Cd4d and Hg5d levels, as initially discussed by Moruzzi et al.⁽³⁾.

From the influence of the sample preparation conditions on the amount of Hg in the clusters, we conclude that Hg outdiffusion is probably the major reason for the formation of these clusters.

Ref.: (1) G. K. Wertheim et al., Phys. Rev. Lett. 51, 2310 (1983), (2) S. Svensson et al., J. Elec. Spectros. 9, 51 (1976), (3) V. L. Moruzzi et al., Phys. Rev B10, 4856 (1974).

For more detail see the attached paper submitted for publication in Physical Review B, entitled "X-ray Photoemission from Small Mercury Clusters on II-VI Semiconductor Surfaces".

V. Direct measurement of the valence band discontinuity at the HgTe-CdTe heterojunction

The valence band discontinuity (ΔE_v) of the HgTe-CdTe heterojunction has recently attracted much attention. However, our knowledge of this value is far from being complete. There is much controversy, both theoretical and experimental, concerning its value. The magneto-optical and resonant Raman scattering¹ measurements performed at low temperature yield a value of less than 120meV for ΔE_v of the HgTe-CdTe(111)B heterojunction. This result agrees with the prediction of the common anion rule². The core level X-ray photoelectron spectroscopy (XPS) measured 0.36eV^{3,4} at room temperature in agreement with other theoretical predictions^{5,6}. The method of determination using only the cation core level difference is questionable because there is no proof that the difference between the core level and the valence band maximum in the two semiconductors does not change when the heterojunction is formed. This change, which could be due to band bending and/or interface chemical effect, would make such an indirect determination inappropriate. Therefore, we have investigated the valence band structure (VBS) of the heterojunction and present here the first direct measurement of the valence band discontinuity of the HgTe-CdTe heterojunction.

The HgTe-CdTe(111)B interface was grown in the MBE chamber and transferred under UHV conditions into the analysis chamber. The thickness of the thin overlayer, as determined from the core level XPS peak area, was chosen between 15Å and 30Å. The X-ray source used here is the Al $K_{\alpha_{12}}$ line which has the energy of 1486.6eV.

Since the escape depth of the valence electrons of the interface, here, is comparable with the thickness of the overlayer, the interface XPS spectrum covers the VBSs of the overlayer, substrate, and interface region. We have reported that the intensities of the substrate and overlayer core level peaks vary with thickness in a manner consistent with an exponential attenuation, indicating that the interface is abrupt in the monolayer range¹. In other words, the interface region is so narrow that the contribution of it in the interface XPS spectrum of the VBS can be neglected.

The principle of the direct measurement of the ΔE_v of HgTe-CdTe interface is to deconvolute the VBS of the interface spectrum using the normalized HgTe and CdTe valence band distribution. This normalization considers two parameters. One is the attenuated intensities of the clean substrate due to the overlayer. The other one is energy shifts due to the interface band-bending effect. After least-square fitting process, the value of ΔE_v can be obtained. We report here that the best fit gives an average value of 0.40eV for the valence band discontinuity of HgTe-CdTe(111)B interface

with different thicknesses and growth sequences. This result agrees with the result measured from the core level XPS method^{3,4}. We have also extended this method to the measurement on the ΔE_V of the HgTe-CdTe heterojunction in the (100) orientation and found that ΔE_V is equal to 0.290 eV.

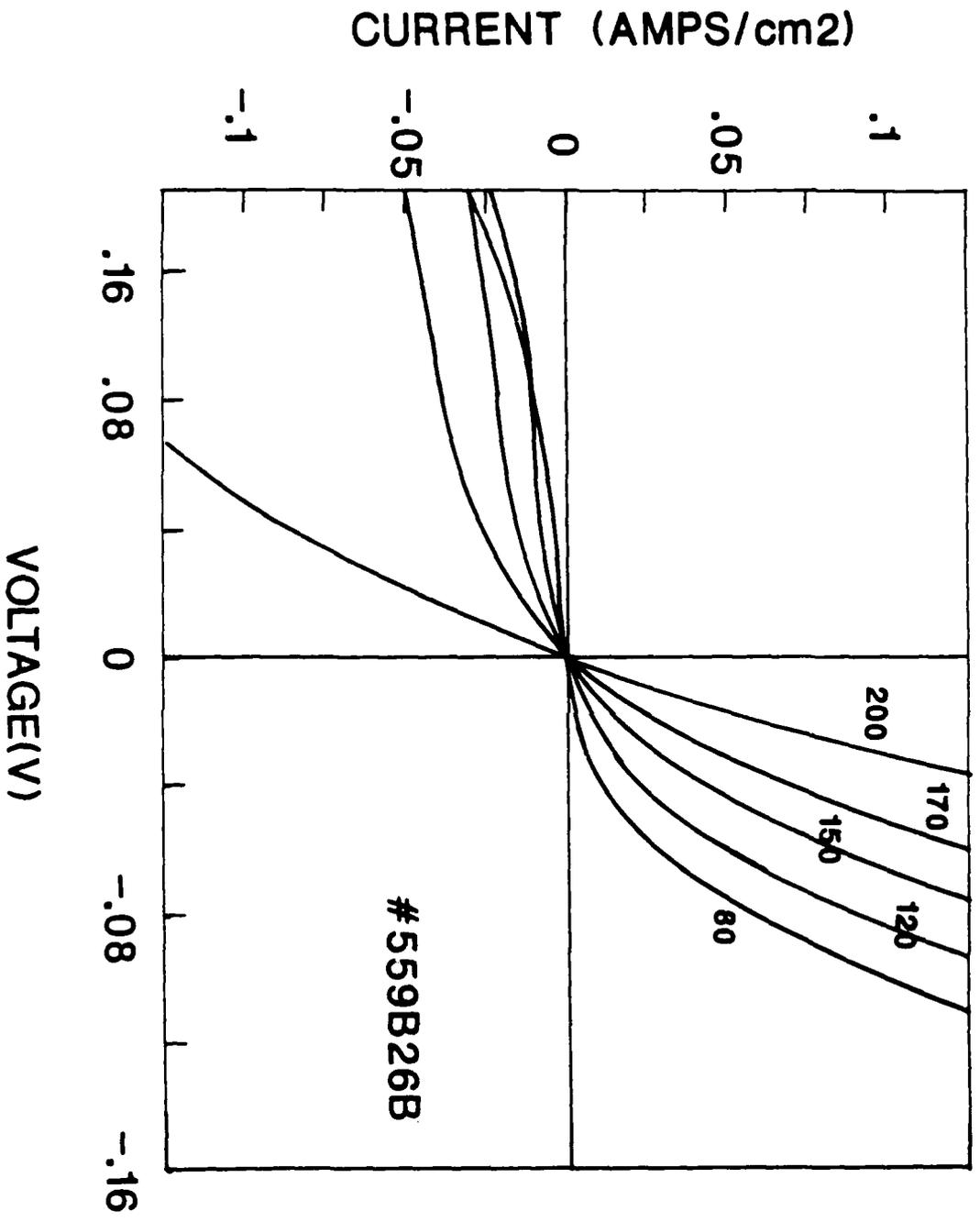
1. J.P. Faurie, C. Hsu, and Tran Minh Duc, J. Vac. Sci. Technol. A5, 3074 (1987) and references therein.
2. J. O. McCaldin, T. C. McGill and C. A. Mead, Phys. Rev. Lett. 36, 56 (1976).
3. S. P. Kowalczyk, J. T. Cheung, E. A. Kraut, and R. W. Grant, Phys. Rev. Lett. 56, 1605 (1986).
4. Tran Minh Duc, C. Hsu, and J.P. Faurie, Phys. Rev. Lett. 58, 1127 (1987).
5. J. Tersoff, Phys. Rev. Lett. 56, 2755 (1986).
6. S. H. Wei and A. Zunger, Phys. Rev. Lett. 59, 144 (1987).

VI. Si-doped $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$ homojunctions grown in situ by MBE

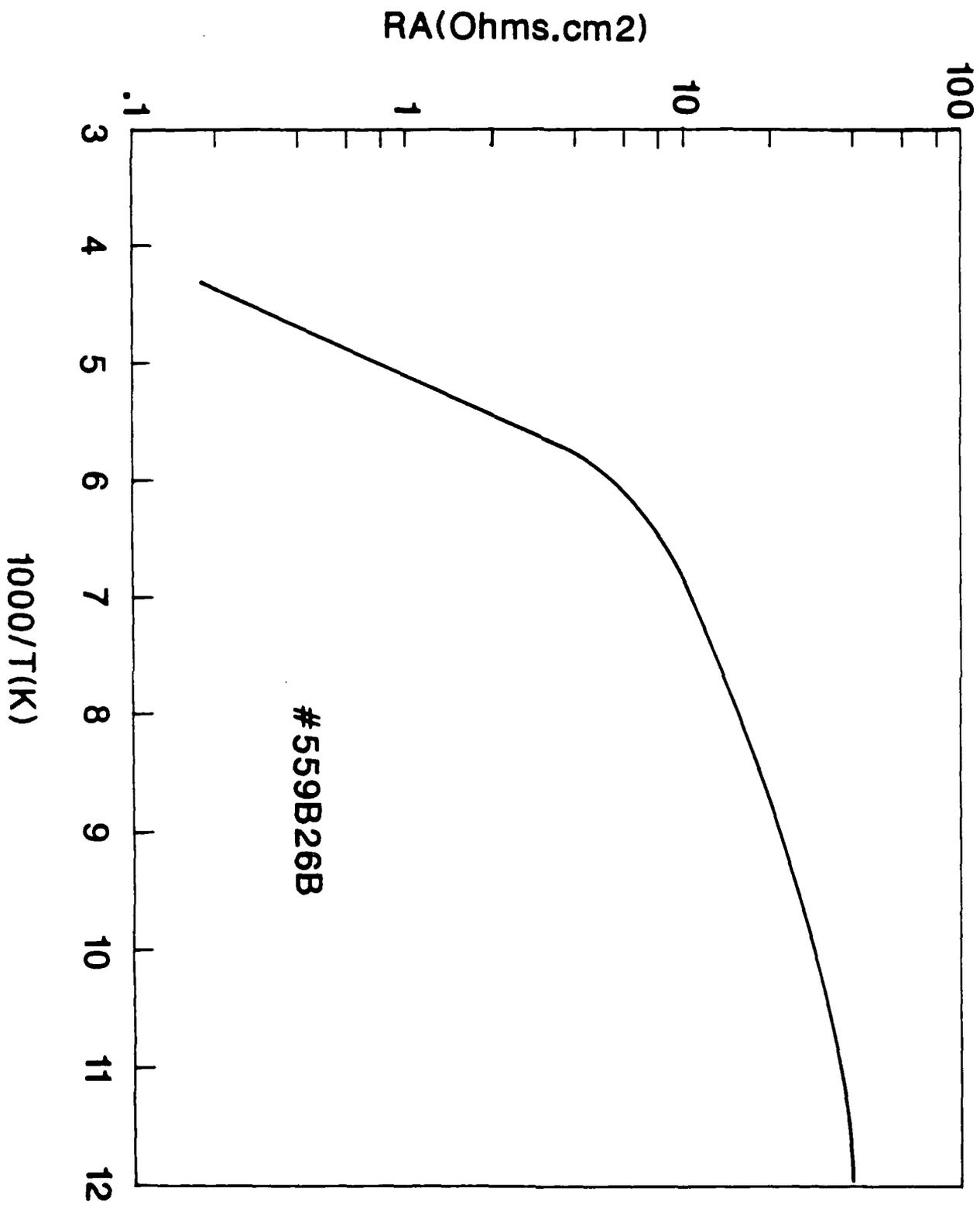
The first homojunctions with $x = .27$ were also measured recently. The bottom layer with a thickness of $4.2\mu\text{m}$ was doped to $2 \times 10^{16}\text{cm}^{-3}$ p-type by stoichiometry deviation, whereas the top layer with a thickness of $1\mu\text{m}$ was doped to $4 \times 10^{16}\text{cm}^{-3}$ n-type by silicon incorporation during the growth. A strong rectification is seen (fig. 5) when the top material is biased negatively as expected. The quality factor varies from 2.2 at 110K to 3.0 at 80K. The R_0A shows a two sloped variation versus $1/T$ as commonly seen in this case (fig. 12). The values reached at 80K vary from 15 to $40\ \Omega\text{cm}^2$ from device to device. Even though the photoresponse has not been measured yet, we saw that the devices are sensitive to the infrared, the photocurrent generated having the proper polarity at zero bias (reverse current). The capacitance measured at zero volt is consistent with the expected doping levels, the depletion width being shared between the two sides of the junction. It decreases with reverse bias, but I/C^2 does not follow a straight line versus voltage (fig. 13) indicating that the doping level is not uniform. We think that even though the junction was intentionally grown abruptly, the silicon has diffused in the p side.

We showed that $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$ junctions are possible in situ by MBE, but the control during the growth of the composition and the doping are very critical. In the near future heterojunctions will be attempted for gate control of FET channels. The R_0A values of the first homojunctions are still low compared to what is currently achieved on photodiodes. But we think that these results are very encouraging since the $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$ material was not annealed and reflects the as-grown conditions very difficult to achieve, especially on the p-side.

HOMOJUNCTION



HOMOJUNCTION



$1/C2 \text{ (cm}^4/\text{F}^2) \times 1\text{E}14$

