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ABSTRACT

We present laboratory results from our compound semiconductor program designed to produce X- and gamma-ray detectors with both high spectral and spatial resolution and with high quantum efficiencies over the energy range 1 to 500 keV. A number of materials are presently under study, including GaAs, InP, CdZnTe, HgI₂ and TlBr. Extensive measurements on simple monolithic detectors and small format arrays have been carried out both in our laboratory and at the ESRF, HASYLAB and BESSY II synchrotron radiation facilities. The results have been used in conjunction with a material science program ultimately intended to produce near Fano limited, monolithic detectors and large area pixelated arrays for the next generation X-ray astrophysics and planetary space missions.

Keywords: Compound semiconductors, GaAs, InP, CdZnTe, HgI₂, TlBr, X-ray and gamma-ray detectors

1. INTRODUCTION

Over the past few decades, considerable effort has been expended in developing a range of compound semiconductors for use as photon and charged particle detectors. While astrophysics has pioneered the use of semiconductor detectors based on silicon at soft X-ray energies (below 10 keV or longward of 1 Å), the hard X-ray band (10 to 200 keV) has proved particularly difficult to develop and has remained relatively unexplored. This band is important in astrophysics because it bridges the transition between thermal and non-thermal emission processes predicted to occur throughout the galaxy. By coincidence, this band is also of crucial importance in medicine since it encompasses all the main energies used in clinical radiology. Similarly, in environmental redemption, a significant fraction of expected lines lie in this energy region. The key material requirements for these applications are; *a*) high effective atomic number to provide sufficient stopping power, *b*) a wide enough band-gap to ensure room temperature operation, *c*) a time response matched to the expected photon flux rate (potentially up to 10 million photons mm⁻²s⁻¹ for Diffraction Enhanced Imaging) and *d*) a uniformity in spatial response in excess of 99.99% (a precision dictated by the dynamic range required for low contrast imaging - such as mammography). Unfortunately, progress at these energies has been slow, primarily because traditional high resolution detectors either suffer from poor detection efficiencies above 10 keV, as in the case of Si based technology, or are very constrained by cryogenic and fabrication problems in the case of Ge based detectors. Wide-gap compound semiconductors offer the possibility of room temperature operation, whilst maintaining sub-keV spectral resolution at hard X-ray wavelengths. In addition, compounds drawn

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Figure 1. Left: the limiting achievable energy resolution as a function of band-gap energy at 5.9 keV. Curves are given for two values of the Fano factor, 0.1 and 0.2. Right: the $1/e$ absorption depth for a variety of compound and elemental semiconductors, clearly illustrating the absorption advantage of any of the compounds over Si.

Parameter	Si	InP	GaAs	Ge	$\text{Cd}_{0.9}\text{Zn}_{0.1}\text{Te}$	HgI_2	TlBr
Density (g cm^{-3})	2.33	4.78	5.32	5.33	5.78	6.4	7.56
Average atomic number	14	32	31.5	32	49.1	62	58
Band gap energy (eV)	1.12	1.35	1.43	0.67	1.572	2.15	2.68
Pair creation energy (eV)	3.62	4.2	4.2	2.96	4.64	4.2	6.5
Electron mobility ($\text{cm}^2 \text{V}^{-1} \text{s}$)	1400	4400	8000	3900	1000	100	30
Hole mobility ($\text{cm}^2 \text{V}^{-1} \text{s}$)	1900	150	400	1900	100	4	4
Electron lifetime (s)	$>10^{-3}$	1.5×10^{-6}	10^{-5}	$>10^{-3}$	3×10^{-6}	10^{-6}	2.5×10^{-6}
Hole lifetime (s)	10^{-3}	$<10^{-6}$	10^{-6}	2×10^{-3}	1×10^{-6}	10^{-5}	3.7×10^{-5}
Electron $\mu\tau$ product ($\text{cm}^2 \text{V}^{-1}$)	>1	5×10^{-3}	8×10^{-2}	>1	4×10^{-3}	10^{-4}	5×10^{-4}
Hole $\mu\tau$ product ($\text{cm}^2 \text{V}^{-1}$)	~ 1	$<1.5 \times 10^{-4}$	4×10^{-5}	>1	5×10^{-5}	4×10^{-5}	2×10^{-6}
Crystal structure	Cubic	Cubic (ZB)	Cubic (ZB)	Cubic	Cubic (ZB)	Tetragonal	Cubic (CsCl)
Knoop hardness (kg mm^{-2})	1150	460	750	692	?	<10	12
Melting point ($^\circ \text{C}$)	1412	1060	1238	958	1092-1295	259	460
Dielectric constant	11.7	12.4	12.8	16	10.9	8.8	29.8
Resistivity (Ω/cm)	$<10^4$	10^6	10^7	50	3×10^{10}	10^{13}	10^{12}
$1/e$ abs depth (mm) @ 10 keV	0.118	0.020	0.051	0.050	0.011	0.011	0.118
@ 100 keV	23.19	1.597	3.46	3.51	1.01	0.46	0.32
Typ. fwhm $\Delta E(\text{keV})$ @ 60 keV	0.42	12	0.7	0.3	1.5	3.5	7.9
Intrinsic fwhm $\Delta E(\text{keV})$ @ 60 keV (Fano noise)	0.415	0.443	0.439	0.250	0.393	0.409	0.550
Typical detector thickness (mm)	0.3	0.2	0.2	20	2	10	1

Table I. Compilation of the physical properties of materials considered in this study, grouped according to density. For comparison, the properties of the elemental semiconductors, Si and Ge are also listed. The Fano noise was calculated using the "best" reported values of the Fano factor.

from groups II-VI of the periodic table have high enough atomic numbers to ensure good photon detection efficiencies above 10 keV. Compounds in this range have band gap energies from ~ 1.35 to ~ 2.6 eV and average atomic numbers from ~ 30 to ~ 90 . In fig. 1 (left) we plot the intrinsic energy resolution achievable as a function of band-gap energy. Curves are given for two values of the Fano factor, 0.1 and $0.2^\dagger$. We have also illustrated the temperature ranges in which different compounds can be expected to operate. For the figure, we can see that room temperature operation can only be achieved for band-gaps above ~ 1.4 eV, while thermoelectric cooling can be used for Si down to Ge. Below Ge cryogenic cooling is required. In fig. 1 (right) we show the $1/e$ absorption depth for a variety of compound and elemental semiconductors. From the figure, we can see the inherent shortcoming of silicon, in that at 100 keV its $1/e$ absorption length is ~ 22 mm!, whereas for TlBr it is only 300 μm . A compilation of the physical properties of a range of compound semiconductors is given in Table I along with those of the elemental semiconductors, Si and Ge for comparison. The wide range of band-gaps and effective Z , (*i.e.*, stopping power) is particularly interesting, since it suggests that materials can be “engineered” to specific applications and wavelengths – for example, in space physics, using wide-gap semiconductors, such as CVD diamond to produce “solar blind” X-ray detectors or detectors to operate in the hot and harsh radiation environments of Jupiter or the inner planets.

Figure 2. Left: the standard detector housings used for monolithic detectors (a) and small arrays (b). Right: internal views of both housings showing two GaAs detector assemblies – a 1 mm planar detector and a 300 micron pitch 4×4 array, complete with a 16-channel hybrid preamplifier. All detectors are mounted on 2 stage Peltier coolers and read-out using low noise resistive feedback or transistor reset preamplifiers.

[†]although in general, $F=0.14$ for compound semiconductors.

Our detector research program has centered on compound semiconductors, including, GaAs, InP, CdZnTe, HgI₂ and TlBr. Results have been reported elsewhere [1-11]. Although a significant fraction of this program is spent on the production of arrays, in this paper we will concentrate on monolithic detectors, since their responses are more intimately related to basic material properties, rather than fabrication or operating techniques (for example, using near field effects to improve energy resolution in materials with poor transport properties of one carrier).

2. EXPERIMENTAL

Base material is processed into detectors and packaged in standard housings as shown in fig. 2. The detectors are mounted on ceramic holders, which in turn are coupled to two stage Peltier coolers capable of cooling the detectors to -30°C . The hot side of the Peltier can be water-cooled allowing the detectors to be cooled by an additional -10°C . From Table 1, we note that the mobility-lifetime product ($\mu\tau$) of electrons in compound semi-conductors is much greater than that for holes. Initial tests showed that biasing detectors to collect holes from the illuminated electrode gave significantly better spectral resolution than collecting electrons, indicating that hole drift lengths must be significantly less than those of the electrons. The preamplifier input FET and feedback components were mounted directly adjacent to the detector and are also maintained at the detector operating temperature. The rest of the analogue chain consists of a resistive feedback or transistor reset pre-amplifier (depending on the level of the leakage current) used in conjunction with an ORTEC[®] 671 spectroscopy amplifier. Gaussian shaping is used to enhance the signal to noise ratio by limiting the bandwidth. Both the signal amplitude and rise time are digitized by two Canberra 8071 12-bit ADC's and processed and stored by a PC.

2.1. Synchrotron radiation measurements

X-ray experiments have been carried out in our laboratory and at three synchrotron radiation beamlines located at the European Synchrotron Radiation Facility (ESRF) in Grenoble, France, in the radiometry laboratory of the Physikalisch-Technische Bundesanstalt (PTB) at BESSY II in Berlin, Germany and the Hamburger Synchrotronstrahlungslabor (HASYLAB) in Hamburg, Germany. Each of the beamlines covers a particular energy range. For example, the low energy response of devices is studied at the Four-Crystal Monochromator (FCM) beamline [12] at BESSY II over the energy range 1.75 keV to 11 keV, while high energy responses are studied from 11 keV to 100 keV using the X-1 beamline [13] at HASYLAB. The intermediate energy range (8 - 30 keV) is studied at the BM5 beamline at the ESRF [14]. These beamlines utilize four crystal or channel-cut crystal monochromators to produce highly monochromatic X-ray beams across a combined energy range 2.3 keV to 100 keV. To achieve such an extreme energy range, a combination of InSb[111], Si[111], Si[311] and Si[511] reflections are used, yielding intrinsic energy resolutions of ~ 1 eV at 10 keV rising to 20 eV at 100 keV. At low energies, detectors are directly coupled to the beamlines vacuum system, in order to ensure the efficient transmission of photons into the detector. At intermediate and high energies, the detectors were decoupled from the beamlines' vacuum system and the beam is incident on the detector through a small air gap between the end of the beampipe and the detectors Be window. This greatly simplifies the experimental operation. At the lowest energies it is also possible to insert helium bags into this gap to reduce beam scattering and increase the beam transmission into the detector. Monochromatized synchrotron radiation is essential for the characterization of our devices, since it can be produced in small, well defined beams that do not contain low energy contamination events commonly associated with fluorescent target sources (FTS). Such events cannot be easily distinguished from partial energy loss events within the detector. Additionally, the count rates at synchrotron facilities can be made sufficiently high to avoid the drift and stability problems also associated with FTS. For arrays, well-defined beams are essential to decouple the responses of the individual pixels. Another important point is that beams can be produced up to 100 keV which effectively allows us to probe a sizable, if not the entire, volume of a detector, thus effectively separating the responses of holes and electrons.

A typical experimental set-up is shown in fig. 3. Beam from the monochromator is collimated by an X-Y slit system and is normally incident on the detector, which, in turn, is mounted on an X-Y table capable of positioning the sensitive elements to an absolute precision of ± 1 μm in each axis. To prevent throughput problems, the monochromator is detuned to such a level that the count rate at the detector is typically a few hundred cts^{-1} . Detectors are scanned in both position and energy. The beam spot size used in most of the measurements was 50×50 μm^2 . Pencil-beam measurements

Figure 3. The experimental set-up at the BM5 beamline at the European Synchrotron Research Facility (ESRF) in Grenoble, France. Highly monochromatic radiation from the monochromator and focusing optics passes through a slit system before being incident on the detector, which can be manipulated with respect to beam using an X-Y stage. To prevent pile-up and throughput problems, the monochromator is de-tuned to such a level that the count rate at the detector is typically a few 100 cts s^{-1} .

were also complemented with additional full-area illumination measurements using a set of standard radioactive sources (^{55}Fe , ^{57}Co , ^{109}Cd , ^{241}Am) and six fluorescent target sources (Cu, Rb, Mo, Ag, Ba and Tb). In addition to detector characterisation, we have also carried out a series of basic metrology measurements to map X-ray Absorption Fine Structure (XAFS) around the edges of detector materials and derive near edge linear attenuation coefficients for detector modelling [15,16].

2.2 Gallium arsenide (GaAs)

Gallium arsenide is a particularly interesting material because its material properties are very close to Ge, while its Fano limited energy resolution is close to Si. Compared with other compounds, its spectral performance has steadily improved, primarily due to improvements in both bulk material properties and detector fabrication techniques. Our detectors were originally produced from both bulk Vertical Gradient Freeze (VGF) material and epitaxial material. The results for VGF material were disappointing, however good results were obtained with epitaxial material. Chemical Vapour Phase Epitaxy (CVPE) was chosen over other epitaxies because it can produce high quality thick ($>300\text{ }\mu\text{m}$) layers, up to 5 cm in diameter. However, although, CVPE GaAs is extremely pure (defect density $10^{12} - 10^{13}\text{ cm}^{-3}$), the resistivity of the material is relatively low ($<10^7\text{ }\Omega\text{cm}$). In order to suppress the leakage currents (to a level of $<0.1\text{ nA}$), a rectifying p-i-n contact structure was used. This is illustrated in fig. 4. The intrinsic layer of this diode can be depleted with a relatively low voltage ($<100\text{ V}$ for $100\text{ }\mu\text{m}$ thick material) due to its low defect and impurity density. The pin structure was achieved during the wafer manufacturing phase by depositing high purity intrinsic layer ($40 - 400\text{ }\mu\text{m}$) by CVPE onto an n+ bulk GaAs wafer and then depositing a p+ layer ($10\text{ }\mu\text{m}$) on top. However, the thick n+ and p+ layers also have some disadvantages, in that the thick n+ layer prohibits the bonding of any pixellated array read-out integrated

Figure 4. Left: schematic of GaAs detector construction. Right: Nomarski photo-micrographs of the two detectors described in the text, – a 1 mm diameter and 2 mm diameter detectors, both fabricated on 40 μm thick epitaxial material.

circuit onto the n+ side and the p+ layer reduces the efficiency of the detectors for soft X-rays below a few keV. A series of these detectors has been produced to access the material and electronic properties of the base material and fabrication techniques. Two such detectors, a 1 mm diameter device and a 2 mm diameter device, are shown in fig. 4 (right). Both were fabricated from the same 40 μm thick epitaxial wafer and have been extensively tested at HASYLAB over the energy range 12 keV to 98 keV. For the tests, they were operated at a bias of 150 V, a shaping time of 6 μs and a detector temperature of -40°C . Although there is nearly a factor of 4 difference in detection area, there is relatively little difference in spectral performance, which implies that the resolution is not capacitively limited.

Figure 5. Left: the measured spectral response of a 1 mm diameter, 40 μm thick GaAs detector. The distributions for the 2 mm diameter detector look similar. The smaller peaks which appear at an energy of ~ 11 keV below the photopeaks are due to the Ga and As escape peaks. Right: a comparison of the measured FWHM energy resolutions of the two detectors. For completeness, we also show the individual noise contributions to the resolution function of the 1 mm diameter detector.

In fig. 5 (left), we show a composite of energy-loss spectra recorded by the 1 mm detector at HASYLAB. The spectral distributions measured by the 2 mm diameter device are similar. The peak at ~ 10 keV is due to a combination of Ga and As fluorescent lines from the p+ layer. Likewise, the peaks located ~ 11 keV below the photopeaks are due to the Ga and As escape peaks. From the figure, we see that the level of the continuum is extremely low in both devices, being at worse $\sim 1\%$ of the photopeak amplitude. Both detectors are remarkably linear, with average rms non-linearities of 0.2% over the energy range 12–98 keV. This indicates that charge collection efficiencies must be $> 99\%$ – a figure confirmed by Monte-Carlo simulation. The energy resolutions measured by both devices are shown in fig. 5 (right), along with the best-fit resolution functions. At 12 keV the measured FWHM energy resolutions are 542 eV in the 1 mm diameter detector and 772 eV in the 2 mm diameter detector. At 98 keV, the corresponding resolutions are 1.0 and 1.2 keV. These should be compared to the calculated Fano resolutions of ~ 220 eV and 560 eV at the same energies. For completeness, we have also shown the individual components to the resolution function for the 1 mm diameter device. At the energies below 70 keV, the resolution is dominated by leakage current, whereas at high energies, both Fano noise and trapping noise become comparable, becoming appreciable fractions of the resolution function.

The spatial response of both detectors was measured by raster scanning a 12 keV pencil beam of size $20 \times 20 \mu\text{m}^2$, across the active area of the detector with an intrinsic spatial resolution of $25 \mu\text{m}$ in both dimensions. Spectra were then accumulated at each position for a fixed time interval and the total count rate above a 1 keV threshold, the peak centroid position (*i.e.*, gain map) and the FWHM energy resolution determined by best-fitting. The results are shown in fig. 6 for each of the devices, in which we plot the centroid of the fitted peak (*i.e.*, the gain) at each position. For both detectors, the uniformity in response within the active area is in excess of 99% and is independent of energy.

Figure 6. The spatial response of the two GaAs detectors to 12 keV X-rays measured with a $20 \times 20 \mu\text{m}^2$ photon beam, raster scanned across the surface of both detectors with a grid step size of $25 \mu\text{m}$.

It is clear from fig. 5 (right) that the spectral performance of these devices is dominated by electronic noise and not by material properties. Later detectors using low-noise front-end electronics show significantly better spectral performances at low energies. For example at 12 keV, the latest generation of 1 mm diameter devices show an energy resolution of ~ 450 eV at 12 keV. Additionally, whereas the energy resolutions of previous generation detectors would improve continuously with decreasing temperature [4], the resolution of the present generation is optimum at about $+5^\circ\text{C}$ and is only 740 eV at 12 keV, at room temperature. Following on from this work, we have explored new front-end electronics featuring resistor-less feed-back designs. Using these, and matching the detector capacitance to that of the gate of the input FET has resulted in resolutions of 219 eV being measured at 5.9 keV ($T=243$ K) and 266 eV at room temperature [6]. In this case, the devices were $40 \mu\text{m}$ thick, of pixel size $250 \times 250 \mu\text{m}^2$. Recently we have produced a series of small and intermediate format arrays on $40 \mu\text{m}$ and $325 \mu\text{m}$ thick epitaxial material. Preliminary results for a 32×32 array fabricated on $325 \mu\text{m}$ material have been presented elsewhere [17]. For this array, the pixel sizes were $250 \times 250 \mu\text{m}^2$ and the inter-pixel gap, $50 \mu\text{m}$. Detailed X-ray metrology carried out on four widely separated pixels showed the pixels to be very uniform both in their energy and spatial responses. At room temperature, the typical energy resolutions were 270 eV at 5.9 keV and 520 eV at 59.54 keV. At $+5^\circ\text{C}$, the corresponding resolutions

decreased by ~10% to 240 eV and 468 eV, respectively. For comparison, the Fano noise at these energies is 140 eV and 420 eV ($F=0.14$).

2.3 Indium phosphide (InP)

Indium phosphide is a group III-V direct band-gap material whose resistivity and mobilities are intermediate between Si and GaAs. It is particularly interesting for future space applications because structurally, it has a strong potential for creating integrated devices and micromachines. Whilst the rest of its properties are similar to GaAs, it is potentially a more attractive material because of its larger stopping power (2–3 times that of GaAs), and higher drift velocities (again, 2–3 times that of GaAs at hard X-ray wavelengths). Compared to other semiconductor materials, InP has one of the lowest cost per unit of stopping volume in the hard X-ray band, which is important for large scale applications, as in high energy physics experiments.

Figure 7. Left: the first prototype $3.14 \text{ mm}^2 \times 180 \mu\text{m}$ thick, InP detector. Right, top: the detectors response to a 40 keV, $20 \times 20 \mu\text{m}^2$ X-ray beam. Bottom: a composite of energy-loss spectra recorded at HASYLAB.

InP was synthesized from solution and purified by vacuum distillation. Semi-insulating material was produced by doping with Fe and a monocrystal grown by liquid encapsulated Czochralski. Wafers were sliced from the boule along the $\langle 100 \rangle$ direction and detector platelets diced from the wafer. These were lapped and polished by chemical and mechanical processing to a thickness of $180 \mu\text{m}$. A p+ layer was then deposited on one side of the plate by vapour phase epitaxy using Zn as a dopant. Circular Au/Ti contacts of diameter 2 mm were deposited on the top and the bottom of the plate. The completed detector is shown in fig. 7 (left). The response of the detector to monoenergetic X-rays is also shown in fig. 7 (right). The device is clearly spectroscopic and, in fact, these data represent the best spectroscopic performance yet reported for an InP detector. These data were taken at a temperature of -60°C . At cryogenic temperatures of -170°C , the spectral acuity is substantially improved, as can be seen in fig. 8 (right). While hole tailing still dominates the spectrum at high energies, at low energies the FWHM spectral resolution is improved by a factor of 3 at 5.9 keV, from 2.6 keV to 0.8 keV as the temperature is reduced.

The resolution results indicate that the present material is limited by its low charge collection efficiency, due to trapping caused by crystal imperfections and over compensation. De-trapping, if it occurs, must be a minor contributor to the signal. In particular, the tailing on higher energy lines in fig. 1 is indicative of poor hole transport. This limits maximum detector thicknesses to about 400 μm . At the lowest energies (< 10 keV) parallel noise, due to high leakage

Figure 8. The detectors response to ^{241}Am at -60°C (left) and -170°C (right) from which it can be seen that there is a clear improvement in spectra acuity. The insets show the response to ^{55}Fe .

currents, dominates the response. As we have previously found in materials, such as GaAs and TlBr, the future development of indium phosphide lies in *a)* improvements in material quality and homogeneity and *b)* the development of an effective blocking contact technology. In the short term, significant improvement could also be achieved by further cooling or by optimizing material compensation, perhaps by using an alternative dopant.

2.4 Cadmium Zinc Telluride ($\text{Cd}_{1-x}\text{Zn}_x\text{Te}$)

Cadmium zinc telluride (CdZnTe) is probably the most widely used compound semi-conductor. It has a cubic, zinc-blende type lattice with atomic numbers close to that of CdTe and a density ~ 3 times that of Si. CdTe was originally the focus of experimental study in the 1960's, until it was discovered that the addition of a few percent of zinc to the melt results in an increased band-gap as well as the energy of defect formation. This in turn, increases bulk resistivities and reduces the dislocation density, resulting in lower leakage currents and higher temperature operation. Specifically, resistivities of CdZnTe are typically between one and two orders of magnitude greater than that for CdTe and thus leakage currents are correspondingly lower. CdZnTe tends not to suffer from the polarization effects normally associated with CdTe. Typical energy resolutions at 59.54 keV are in the few keV range at room temperature and decrease with decreasing temperature. Additionally, CdZnTe detectors have also been demonstrated to operate at elevated temperatures [18] making them particularly attractive for remote sensing applications.

A series of CdZnTe crystals were obtained from eV Products, USA. They were produced by the high pressure Bridgman (HPB) technique with a stoichiometric composition of $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$, where $x \approx 0.1$. This results in a band-gap energy of 1.572 eV, a resistivity at room temperature of $5 \times 10^{10} \Omega \text{ cm}$ and a density of 5.9 g cm^{-3} . Spectroscopic grade crystals were selected from the bulk material by visual inspection and I-V screening. Further screening was carried out using infrared (IR) transmission imaging and electron backscatter diffraction (EBSD). IR microscopy is used to identify material defects in the bulk, such as inclusions, precipitates and voids. Precipitates (denoting excess Te) appear in the transmission images as distributed dark speckles, generally of the order of 10–20 μm and smaller in size. The first series of detectors were fabricated on crystals $5 \times 5 \times 1 \text{ mm}^3$. After cutting and polishing, sputtered platinum contacts were deposited. Irradiation is into the front contact of the detector, which is connected to negative bias voltage. The back contact is a circular pad of diameter 2 mm, surrounded by a concentric guard ring. The guard is not used as a controlling electrode, but is grounded to control surface leakage current. At a bias of -100V , the typical leakage currents were of

Figure 9 Left: composite pulse height spectra of monoenergetic lines measured by a $5 \times 5 \times 1 \text{ mm}^3$ CdZnTe detector at the ESRF at a detector temperature of -20°C . The beam size was $50 \times 50 \mu\text{m}^2$, incident at the center of the detector. Right: the spatial response measured at 10 keV.

the order of $\sim 10 \text{ nA}$ at room temperature. In fig. 9 (left) show a composite of the detector's response to monoenergetic X-rays ranging from 6 to 30 keV. The energy-loss spectra are plotted logarithmically to illustrate the high fraction of events that contribute to the photopeaks and the very low level of partial energy losses. In fact, the background level constitutes $< 0.1\%$ of the peak amplitude. The energy resolution was found to be dominated by electronic noise and was approximately constant ($\sim 1 \text{ keV FWHM}$) across the entire energy range. In fig. 9 right, we show the measured spatial response recorded by raster scanning a $50 \times 50 \mu\text{m}^2$, 10 keV beam across the detectors surface. From the figure it can be seen that the detector is very uniform, in fact to a level commensurate with statistics and illustrates the effectiveness of the material screening program. In order to suppress leakage currents and therefore reduce electronic noise, a second set of detectors were subjected to a proprietary surface treatment and annealing procedure. This helped to reduce leakage currents to $\sim < 1 \text{ nA}$. For the best crystal (a $4 \times 4 \times 2.5 \text{ mm}^3$ device), this resulted in a reduction in the FWHM energy resolution at 59.54 keV from 1.6 keV to 1.0 keV at -20°C , using a resistive feedback preamplifier. At room temperature, under full area illumination, the FWHM energy resolutions were 1.6 keV at 5.9 keV rising to 2.9 keV at 59.54 keV. In order to reduce electronic noise further, the detector was fitted with a new resistor-less feedback preamplifier. In this case, the measured FWHM energy resolutions recorded at BESSY II and HASYLAB were 380 eV at 6 keV and 820 eV at 60 keV. Lastly, based on the study of Toney *et al.* [19], we would expect the optimum performance of a detector with a zinc fraction of 0.1 to occur at a detector temperature of $\sim -25^\circ\text{C}$. This was found to be indeed the case at high energies (60 keV), but at low energies (6 keV), lower temperatures gave better performance – presumably due to the small additional reduction in noise incurred by the cooling of the front-end FET. The optimum overall performance was found at a detector temperature of -37°C at which, the measured FWHM energy resolutions were 311 eV at 5.9 keV and 824 keV at 59.54 keV.

2.5 Mercuric Iodide (HgI_2)

Mercuric Iodide (HgI_2) has been investigated as a room temperature X- and gamma-ray detector material since the early 1970's [20]. Its wide band-gap in conjunction with the high atomic number of its constituent atoms makes it an attractive material for room temperature operable X- and particularly gamma-ray spectrometers. In fact, very little improvement is achieved in spectral resolution by cooling the detectors. Also, the fabrication of a pn-junction is usually not necessary, as dark currents are generally very low. HgI_2 is highly reactive with many metals, hence only a few materials can be used as electrical contacts, usually colloidal carbon (aquadag) or Pd. We have investigated a number of HgI_2 detectors produced by Eurorad and Constellation Technology Inc., including a 7 mm^2 , $500 \mu\text{m}$ thick detector, a $10.3 \times 10.3 \times 1.76 \text{ mm}^3$ detector and a $12 \times 12 \times 3 \text{ mm}^3$ detector. All detectors were contacted with sputtered Palladium contacts and coated with a thin (few microns) polymer coating (Parylene) for surface passivation and protection from evaporative degradation. Fig. 10 shows a composite of energy spectra measured with the 7 mm^2 detector at BESSY-II

(left) and the 106 mm² detector at the ESRF (right). The noise threshold (defined to be the lowest energy for which the low energy noise attains an amplitude of 0.5 of the photopeak) is 2.6 keV. As can be seen, for incident energies < ~20 keV, the individual photopeak responses are symmetric about the centroid. Above this energy the photopeaks become increasingly tailed due to hole trapping. For the 7 mm² device, the resolutions range from 500 eV at 2.3 keV to 5.7 keV at 100 keV. In the 106 mm² device, they range from 1.3 keV at 8 keV to 1.6 keV at 27 keV. In terms of spatial uniformity, both devices are reasonable uniform, however gross non-uniformities are apparent near bond wires and particularly in some regions around the contact perimeter. The 144 mm² device has not been tested with synchrotron radiation, but gave a FWHM energy resolution of 2.7 keV at 59.54 keV.

Figure 10. Left: a composite of pulse height spectra measured at BESSY-II with a 7 mm², 500 µm thick HgI₂ detector. The beam size was 50 × 50 µm², incident at the center of the detector. Right: composite of pulse height spectra measured at the ESRF with a 106 mm², 1.76 mm thick HgI₂ detector.

By accumulating a series of ²⁴¹Am spectra, 1 hour, 2 hours, 12 hours and days after the application of bias, the effects of polarization have been investigated. Polarisation is usually defined as any time dependent change, which occurs in the performance of a detector and is generally a bias related effect. In HgI₂, polarisation effects are believed to stem from trapping in the bulk of the crystal and from non-optimal detector fabrication [21,22]. It was found that polarization effects manifest themselves primarily as an increase in the level of the low energy continuum, which gradually decays with time after the application of bias. This can be more than a factor of 3 at 10 keV over 12 hours. In fact, it was found that reproducible results could be obtained by applying bias at least 12 hours before measurement.

Figure 11. TlBr Detector fabrication. The boule shown above (a) is cut into wafers using a wire saw. Contacting was initially achieved using aquadag and a Be bronze spring (b). More recent detectors (c) were produced using evaporated gold *via* a mask and lift-off process. Contacting was achieved by gluing bond wires to the anode and cathode.

2.6 Thallium Bromide (TlBr)

Thallium bromide (TlBr) has been identified as a promising material candidate for gamma-ray spectroscopy, in view of its large density. In fact, its density is the same as bismuth germanate ($\rho=7.6 \text{ g cm}^{-3}$). It has a CsCl-type cubic lattice structure with physical properties amenable to easy and rapid purification using standard growth techniques. It melts with a single-phase transition, allowing good quality crystals to be grown directly from melt. However, the processing of thallium halogen crystals requires special attention since they are extremely toxic and anomalously soft and relatively low stresses can induce severe structural damage. Prototype detectors have been fabricated from a thermally grown mono-crystal, produced by the Bridgman-Stockbarger technique (fig. 11a). The boule was sawn into 1 and 2 mm thick wafers using a wire saw and lapped using diamond paste, followed by mechanical and chemical polishing to an optically smooth and transparent finish. A number of detectors of dimensions were $2.8 \times 2.8 \times 0.8 \text{ mm}^3$ were diced from the wafers.

From the I-V characteristics, resistivities were found to be in the range $(6 - 10) \times 10^{10} \Omega \text{ cm}$. At nominal biases of a few hundred volts, the average recorded leakage currents were $\sim 10 \text{ nA}$ at room temperature and 1 nA at -2°C . The measured electron and hole mobility-lifetime products were found to be $3 \times 10^{-4} \text{ cm}^2\text{V}^{-1}$ and $1 \times 10^{-5} \text{ cm}^2\text{V}^{-1}$, respectively, which are about an order of magnitude higher than previously reported values. Initially, contacting was achieved using aquadag and pressure contacting metal springs (fig. 11b). However, while the spectroscopic performance of these devices were as good as the best reported (*e.g.*, [23]), the spatial response was highly variable and non-uniform (see fig. 12 – left). In addition, detectors displayed polarization and aging effects on time scales ranging from hours to days. Based on these results, a 2nd generation of devices were produced in which the detector fabrication procedures were completely overhauled and the contacting was changed to an evaporative gold deposition process following lift-off lithography (fig. 11c). These changes resulted in a substantial improvement in detector performance

Figure 12. Left: the spatial response of a first generation detector measured with a $25 \times 25 \mu\text{m}^2$, 25 keV raster scanned across the detector with $40 \mu\text{m}$ spatial resolution. Right: the corresponding spatial resolution of a second generation detector of the same size. In this case the beam size was $50 \times 50 \mu\text{m}^2$ and the beam energy 12 keV. The spatial resolution step size was $40 \mu\text{m}$.

over first generation devices. For example, the measured energy resolution at -24°C was 2.1 keV for the 5.9 keV line from ^{55}Fe and 2.6 keV FWHM for the ^{241}Am γ -ray line at 59.5 keV (the electronic equivalent noise was 1.8 keV). Although these detectors did not suffer from the instability or non-uniformity problems normally associated with TlBr detectors (see fig. 12–right), they did display polarization effects (*i.e.*, changes in gain and spectral broadening) above $\sim 40 \text{ keV}$, which showed a correlation with energy deposition per unit time. The source of this instability is unclear at this time but it is presumably also related to hole trapping. It suggests that the hole de-trapping times are significantly longer than the electronics integration time resulting in modification and partial collapse of the internal electric field. Interestingly, although the detectors showed no spectral degradation when exposed to a fluence of 10^{11} cm^{-2} , 10 MeV protons, polarization effects worsened considerably, becoming apparent at photon energies as low as $\sim 10 \text{ keV}$.

Figure 13. A composite of pulse height spectra of monoenergetic lines measured at BESSY-II, the ESRF and HASYLAB by a prototype $2.8 \times 2.8 \times 0.8 \text{ mm}^3$ TlBr detector. The beam size was $20 \times 20 \mu\text{m}^2$, incident at the center. Note the separation of hole and electron distributions at the higher energies.

X-ray characterizations were carried out from 2.3 keV to 100 keV. From figure 13 (left), we can see that the energy resolution is excellent, being almost an order of magnitude better than that previously reported for similar sized detectors. Surprisingly, for energies less than 30 keV, the energy resolution is constant ($\sim 830 \text{ eV}$) and is entirely dominated by electronic noise. At higher energies (fig. 13-right), we can see for the first time, the onset of hole trapping is clearly seen with a clear separation of hole and electron distributions at the higher energies. However, even at 100 keV, a photopeak is apparent, which has not been observed before. Based on these results, we have produced a prototype 3×3 array (fig. 14-left). In fig. 14 (right), we present preliminary data from the array showing its spatial response to a 15 keV, $20 \times 20 \mu\text{m}^2$ pencil beam, raster scanned across the surface with $40 \mu\text{m}$ spatial resolution. From the figure we see that the response is reasonably uniform and demonstrates the potential for producing large mega pixel X-ray imagers. Spectrally, the performance of the array is encouraging and clearly demonstrates the small-pixel effect, yielding typical energy resolutions of 2 keV at 60 keV. Detailed results from this array are presented elsewhere at this conference [24].

Figure 14. Left: the 3×3 , 1 mm thick TlBr array (see text). The array has a pixel size of $350 \times 350 \mu\text{m}^2$ with an inter-pixel gap of $100 \mu\text{m}$. Right: spatial response of the array to a 15 keV, $20 \times 20 \mu\text{m}^2$ X-ray pencil beam.

3. DISCUSSION AND CONCLUSIONS

While the performances of most compound semiconductors are not yet close to the Fano limit, experimentally they are close to satisfying the requirements of many of the anticipated applications in medicine, environmental redemption and space physics. For the future development of compound semiconductors, problems of hole trapping and material uniformity must be addressed. These limit the useful thicknesses of detectors (and ultimately their high energy performance) to about 0.2 – 1.0 mm. Additionally, the compounds with the poorest hole transport, also exhibit instability and time dependent effects which in turn, can present throughput problems. Until the particular defect(s) can be identified, single carrier pulse processing techniques offer the only means of obviating the problem - albeit at the expense of detection efficiency. The fact that the performance of most compounds can be significantly improved with only modest cooling has important consequences for medical and space applications where power, mass and volume are at a premium. Such cooling can be readily achieved with Peltier systems or passive radiator panels alleviating the need for complex and expensive cryogenic systems – as in the case of Ge detectors. It should be noted, that while HgI₂ and TlBr are primarily being developed for hard X- and gamma-ray applications, they also make surprisingly good soft X-ray detectors with usable responses down to ~ 1 keV [*c.f.*, 8,11]. Indeed, a 5mm², 200 µm HgI₂ detector, operated at room temperature, has displayed near Fano performance at 5.9 keV [25]. Finally, to summarize, Table 2 lists some of the best resolutions obtained with our detectors. For completeness, we also list the resolutions at room temperature where possible, since there are many applications in which resolving power is not a primary requirement. For comparison purposes, the resolutions are given at both the 5.9 keV ⁵⁵Fe line and the 59.54 keV ²⁴¹Am line, since most results are quoted at these energies.

Table II. The best energy resolutions achieved with prototype detectors. The measurements were carried out under uniform illumination using ⁵⁵Fe and ²⁴¹Am sources. For the iron line measurements, the equivalent FWHM pulser resolutions were 220 eV (Si), 400 (GaAs1), (GaAs2), 163 eV, 760 eV (InP), 290 eV (CdZnTe), 343 eV (HgI₂), and 574 eV (TlBr). For completeness, we also list the resolutions at room temperature (RT) were possible, since there are many applications in which resolving power is not a primary requirement. The detector temperatures at 59.5 keV are the same as those listed for 5.9 keV.

Material	Detector size Area × thickness	ΔE @ 5.9 keV (eV)	ΔE @ 59.5keV (eV)
Si	0.8 mm ² , 500 µm	245 @ -15°C	524
		750 @ +15°C	800
GaAs1	0.8 mm ² , 40 µm	450 @ -22°C	670
		572 @ RT	780
GaAs2	250 × 250 × 40 µm ³	219 @ -30°C	468
		266 @ RT	487
InP	3.142 mm ² , 200 µm	911 @ -170°C	3050
		2480 @ -60°C	9200
CdZnTe	3.142 mm ² , 2.5 mm	311 @ -37°C	824
		1508 @ RT	2900
HgI ₂	7 mm ² , 500 µm	438 @ -19°C	1540
		600 @ RT	2400
TlBr	3.142 mm ² , 800 µm	800 @ -30°C	2300
		1800 @ RT	3300

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