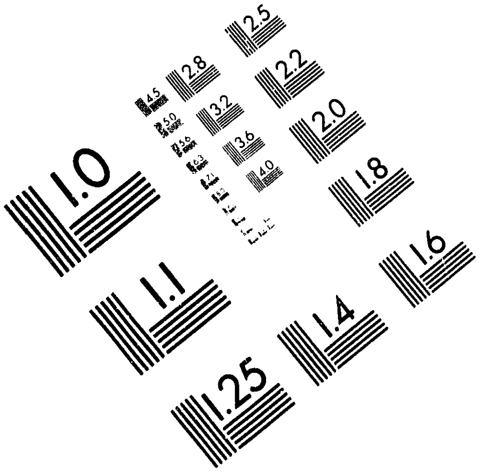

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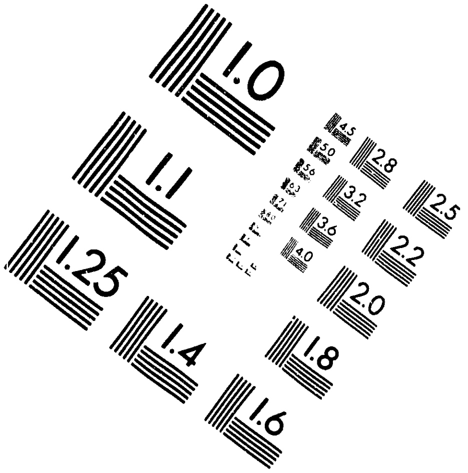

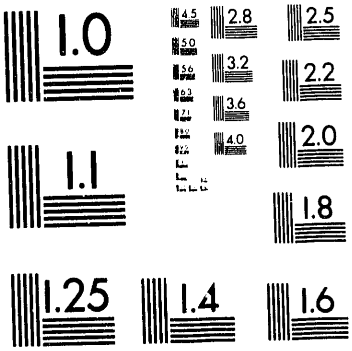

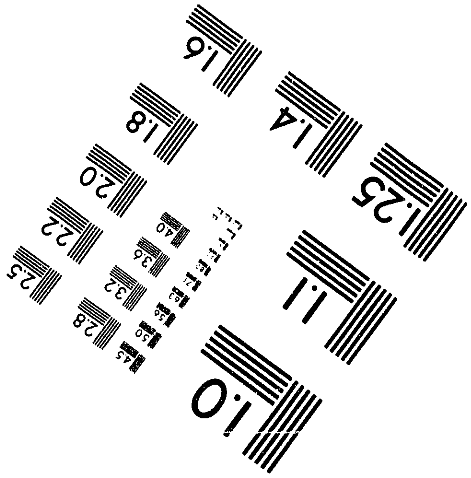

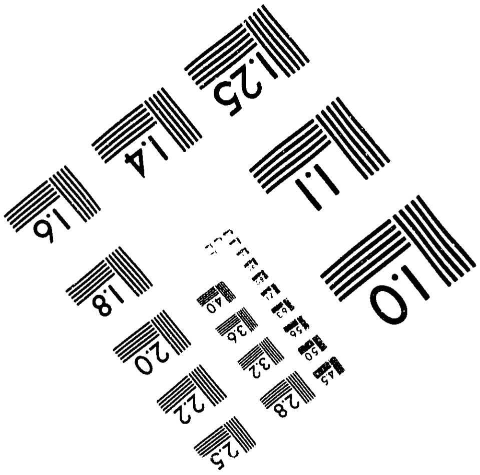

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ELECTRONIC CHARACTERIZATION OF MERCURIC IODIDE GAMMA RAY SPECTROMETERS*

EGG 10617-2182
UC-706

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ABSTRACT

During the past four years the yield of high resolution mercuric iodide (HgI_2) gamma ray spectrometers produced at EG&G/EM has increased dramatically. Data is presented which demonstrates a strong correlation between starting material and spectrometer performance. Improved spectrometer yields are attributed to the method of HgI_2 synthesis and to material purification procedures. Data is presented which shows that spectrometer performance is correlated with hole mobility-lifetime products. In addition, the measurement of Schottky barrier heights on HgI_2 spectrometers has been performed using I-V curves and the photoelectric method. Barrier heights near 1.1 eV have been obtained using various contacts and contact deposition methods. These data suggest the pinning of the Fermi level at midgap at the HgI_2 surface, probably due to surface states formed prior to contact deposition.

INTRODUCTION

In recent years important advances have been made in the production of high resolution HgI_2 spectrometers as a result of progress in the areas of material purification, crystal growth, and device fabrication. Methods have been developed for synthesizing high-purity mercuric iodide[1] which have led to increased yields of large volume, spectrometer grade detectors[2]. Control of the crystal growth angle allows the production of crystals whose shape can be optimized for particular detector requirements. For example, crystals grown with a large C-face can be used for large area imaging arrays[3]. In the area of detector fabrication, the long-term stability of HgI_2 detectors has been greatly improved due to advances in encapsulation methods[4]. Also, there has been progress in developing suitable transparent electrical contacts for HgI_2 photodetectors. (HgI_2 photodetectors can be used as a replacement for photo-multiplier tubes in scintillation spectrometers[5].)

Electronic characterization techniques have played a central role in the development of methods for improving the performance of HgI_2 spectrometers. These techniques have also provided a better understanding of the physical mechanisms which effect detector response. For example, the correlation of starting materials and purification methods with detector performance and charge transport parameter measurements suggests that impurities greatly effect the electronic properties of HgI_2. Spectral response and hole lifetime measurements have allowed a better understanding of the mechanisms associated with polarization effects in HgI_2 gamma ray spectrometers and also indicated methods for minimizing these effects[6]. Finally, measurement of Schottky barriers of electrical contacts on HgI_2 has provided information about electrode properties and associated charge injection mechanisms[7].

BULK ELECTRONIC MEASUREMENTS

Spectrometer Performance vs. Material Purification

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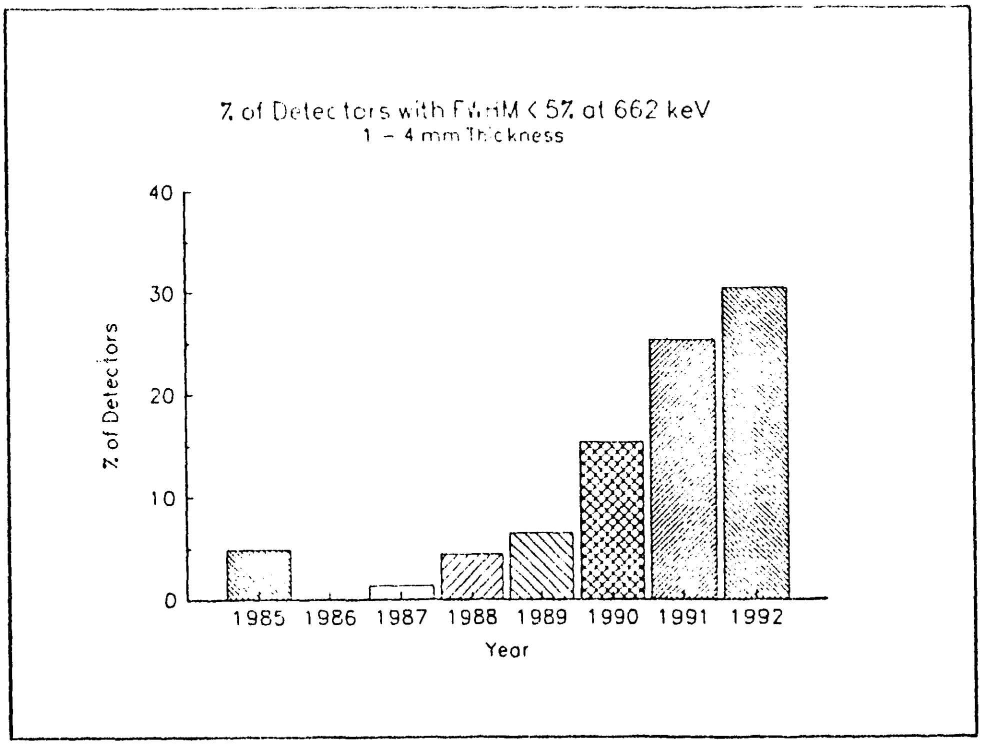

Figure 1. Percent of HgI_2 detectors of 1 - 4 mm thickness with < 5% FWHM resolution at 662 keV vs. year.

Since 1985 HgI_2 detectors have been fabricated at EG&G Energy Measurements and tested for their gamma-ray response at the rate of about eight per month. The detectors are 1 - 4 mm thick, 3 - 6 cm^2 area and have either evaporated palladium (Pd), or colloidal carbon contacts. Figure 1 shows the percent of these detectors which exhibit better than 5% FWHM energy resolution for the 662 keV peak of ^{137}Cs for each year. (About 90 detectors/year were tested.) Prior to 1987 all HgI_2 crystals were grown from HgI_2 supplied by various commercial vendors. Prior to crystal growth these starting materials undergo a series of melt and sublimation steps to improve purity. The drop in yield from 1985 to 1986 is attributed to differences in the purity among different lots of material. Due to the low yields of spectrometer-grade detectors and the unreliable quality of the vendor-supplied material it was apparent that better purification methods were needed.

In 1986 synthesis of HgI_2 by precipitation from an aqueous solution of $HgCl_2$ and KI was attempted in order to obtain a more reliable starting material[1,2]. During the period from 1987 to 1990 the synthesis process was gradually adopted as the primary method for obtaining raw HgI_2 material for crystal growth due to encouraging results obtained from the testing of gamma ray spectrometers. This is shown in Figure 1 by the dramatic increase in yield of high resolution spectrometers (<5% FWHM at 662 keV) during this period. Recently, efforts have been directed toward improving the purity of the starting materials used in the synthesis process ($HgCl_2$ and KI). Figure 1 shows a further increase in yields from 1991 to 1992 which has been attributed to further refinements in the synthesis process, primarily the purification of the $HgCl_2$ by open-tube sublimation. This is further demonstrated in Figure 2 which shows the average quality factor of gamma ray spectrometers produced from HgI_2 which was synthesized using $HgCl_2$ that had undergone 0, 1, or 2 open-tube sublimations. The quality factor is defined to be,

$$\textit{quality factor} = \sqrt{\frac{\textit{peak/valley ratio}}{\textit{\%FWHM}}}$$

where the %FWHM and the peak/valley ratio are for the 662 keV gamma ray peak of ^{137}Cs. This quantity may be considered a good indicator of spectrometer performance.

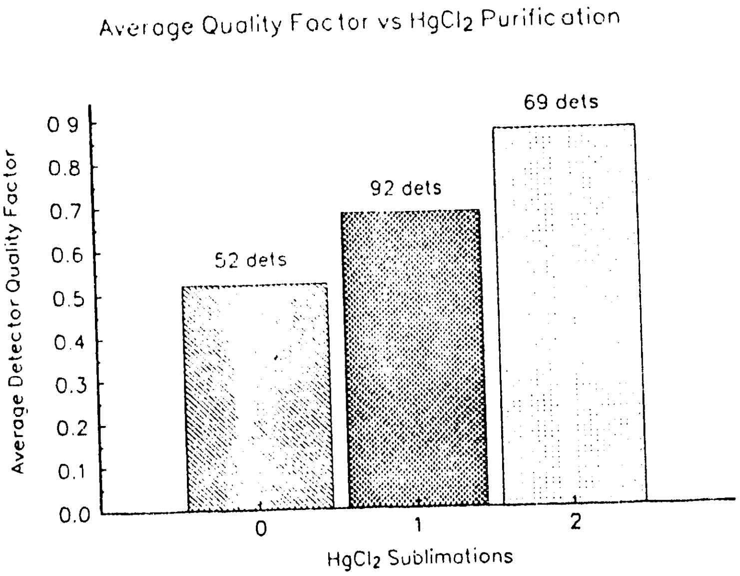

Figure 2. Average quality factor (based on 662 keV response) of HgI_2 detectors vs. number of $HgCl_2$ sublimations.

(In Figure 2 the number above each of the bars in the graph indicates the number of detectors that were tested to obtain the average quality factor for each group.) Figure 3 shows an example of a ^{137}Cs spectrum acquired with a 1.7 mm X 3.24 cm^2 spectrometer. It appears that further increases in yield and performance for large volume spectrometers can be acheived by purification of the starting materials used in the synthesis process. Presently, methods for obtaining high purity KI are being investigated along with alternative methods for purifying $HgCl_2$. Analysis of trace impurities using inductively coupled plasma/mass spectroscopy, anion chromatograpy and total carbon analysis is also being pursued.

In order to determine the effect of non-stoichiometry on detector performance, crystals have been grown from synthesized HgI_2 which has been doped with either Hg or I. The excess Hg or I was either added to the growth ampoule, or added prior to the melt stage of purification. Seven detectors fabricated from a crystal with Hg added to the growth ampoule all failed to produce a resolvable 662 keV peak under ^{137}Cs irradiation. In contrast, fifteen detectors fabricated from 9 crystals which were grown from the same (un-doped) synthesis material produced good results - 13 of the 15 detectors produced resolvable 662 keV photopeaks. The detectors from the Hg-doped material also showed poor hole lifetimes - an average of 0.9 μsecs as compared to 8.1 μsecs for the undoped detectors. These results are consistent with those of a previous study[7]. Doping with I during the melt stage has also been implemented and appears to have no significant effect. Nineteen detectors from 12 I-doped crystals were compared to 30 detectors from 18 undoped crystals of the same batch of synthesis material. No significant difference was observed in detector performance, spectrometer yield, or charge transport parameter values.

Charge Transport Parameter Measurements

In order to make routine measurements of electron and hole transport parameters, software has been developed which allows gamma ray pulses from a HgI_2 detector (coupled to a charge sensitive preamp) to be recorded and analyzed[2]. Pulses are digitized with a Lecroy 9450 digital oscilloscope and stored on a personal computer. Each pulse

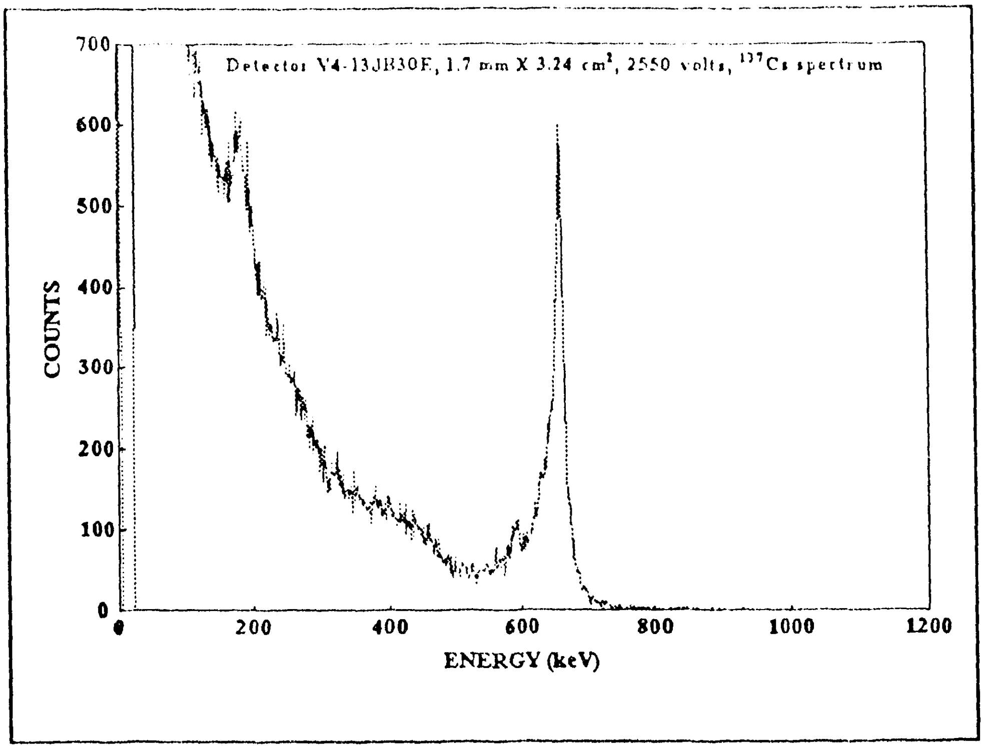

Figure 3. ^{137}Cs spectrum from a 1.7 mm × 3.24 cm^2 HgI_2 detector at 2550 volts bias. The 662 keV peak exhibits a 2.4% FWHM and 12:1 peak-to-valley ratio.

is fit to the Hecht relation to obtain electron and hole mobilities and hole lifetimes. At typical spectrometer bias voltages of 1 - 3 kilovolts, negligible electron trapping is observed so that electron lifetimes cannot usually be obtained by this method. However, low hole mobilities and hole trapping often limit the performance of thick spectrometers due to incomplete charge collection. The hole mobility-lifetime product is therefore an important indicator of detector quality. The correlation between detector performance and hole mobility-lifetime products is demonstrated in Figure 4 with data acquired from 21 recently fabricated spectrometers of 2 - 3 mm thickness and 6 cm^2 area.

Polarization

Most HgI_2 gamma ray spectrometers exhibit some degree of polarization, or change in spectral response, after application of a bias voltage. This polarization is observed as a gradual improvement in energy resolution over a period of a few days, or weeks, accompanied by a shift of counts from energies well above the photopeak region to the photopeak. An example is shown in Figure 5. This behavior has been examined under various experimental conditions and described in detail in a previous paper[6]. The main experimental results can be summarized:

1) Evidence of polarization has been observed in dozens of HgI_2 gamma ray spectrometers. The occurrence of counts at energies above the peak region appears to be a gain phenomenon with the maximum gain always less than 2. This has been verified by absolute efficiency measurements using a calibrated electronic system. The "high energy tailing" of the gamma ray peaks decreases with time when the detector is left under bias.

2) Gain decreases with increasing bias voltage. Counts in the high energy tail above the peak shift closer to the photopeak channel as the bias is raised.

3) Gain is associated with increased hole trapping. It has been observed that hole lifetimes increase over time as the detector is left under bias while the spectral response improves. Data from four detectors in which increasing hole lifetimes were measured over a three to four week period is shown in Figure 6. During this time the detectors exhibited polarization similar to the that shown in Figure 5.

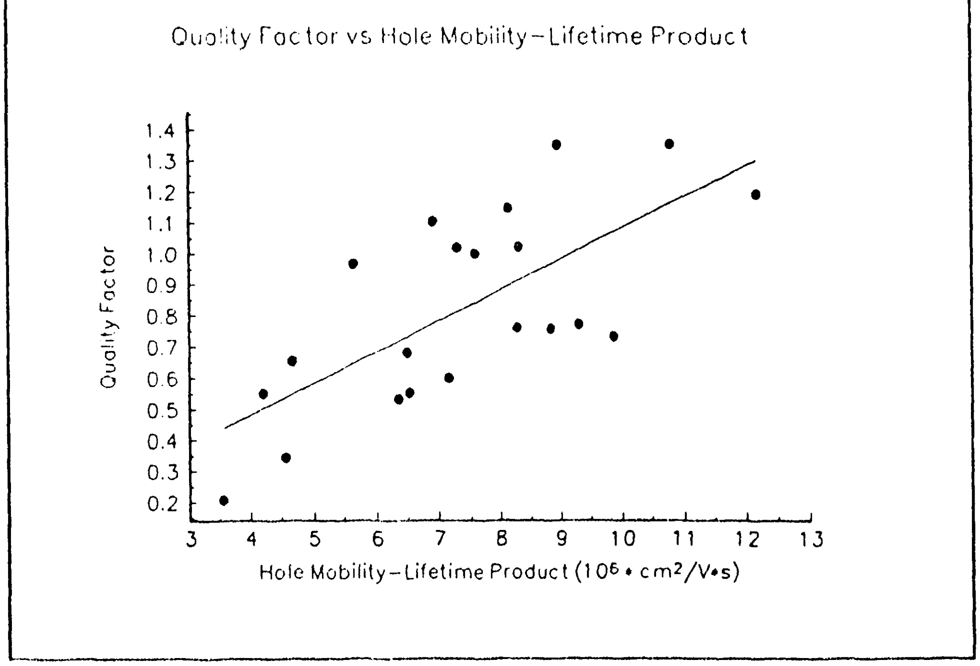

Figure 4. Quality factor plotted as a function of the hole mobility-lifetime product for 21 HgI_2 detectors. (The solid line is a least-squares fit of the experimental data.)

4) Gain is observed primarily at gamma ray energies which penetrate significantly into the detector bulk (>50 kev). Gain is also observed in detectors fabricated with different contact materials and deposition methods. This suggests that this type of polarization is a bulk phenomenon and not related to contacts or surface effects.

5) Gain is reduced by irradiating the detector (under bias) with a strong gamma source, or by illumination with strong white light. Furthermore, illumination of the positive (semi-transparent) electrode with strongly absorbed (above bandgap energy) light will reduce or eliminate gain, while illumination of the negative electrode restores gain.

The experimental evidence suggests that this type of polarization is due to an Auger recombination mechanism[6,9,10]. In this Auger recombination process a charged center containing two or more trapped electrons may act as a recombination site for a hole. The energy released by recombination is tranferred to a remaining trapped electron which is then ejected into the conduction band. This process gives rise to charge multiplication and, as is shown in reference 6, the gain is ≤ 2. This agrees with the experimental results.

It has been observed that light exposure can have a strong effect on the high energy tail observed in the spectra of detectors which exhibit polarization. By illuminating either the positive, or negative (semi-transparent) electrode with strong, highly absorbed (short wavelength) light, either holes or electrons can be injected into the detector bulk. It is observed that brief (5 minutes) illumination of the positive electrode can substantially reduce or eliminate the high energy tail in the gamma ray spectral response while similar illumination of the negative electrode increases the high energy tail. This has been interpreted as due to the filling or emptying of the Auger recombination centers by the injected charge[6].

At present, the origin of the Auger recombination centers is unknown. In spite of the increase in spectrometer yields due to improved material processing, the degree of polarization (high energy tailing) does not appear to have decreased. Furthermore, the amount of polarization does not appear to depend on the stoichiometry. Crystals which have been doped with excess I produce detectors which do not exhibit any more, or less, polarization. Also, the intensity of the I color observed in the growth ampoule - another measure of I excess - does not appear to correlate with polarization. (Hg-doped

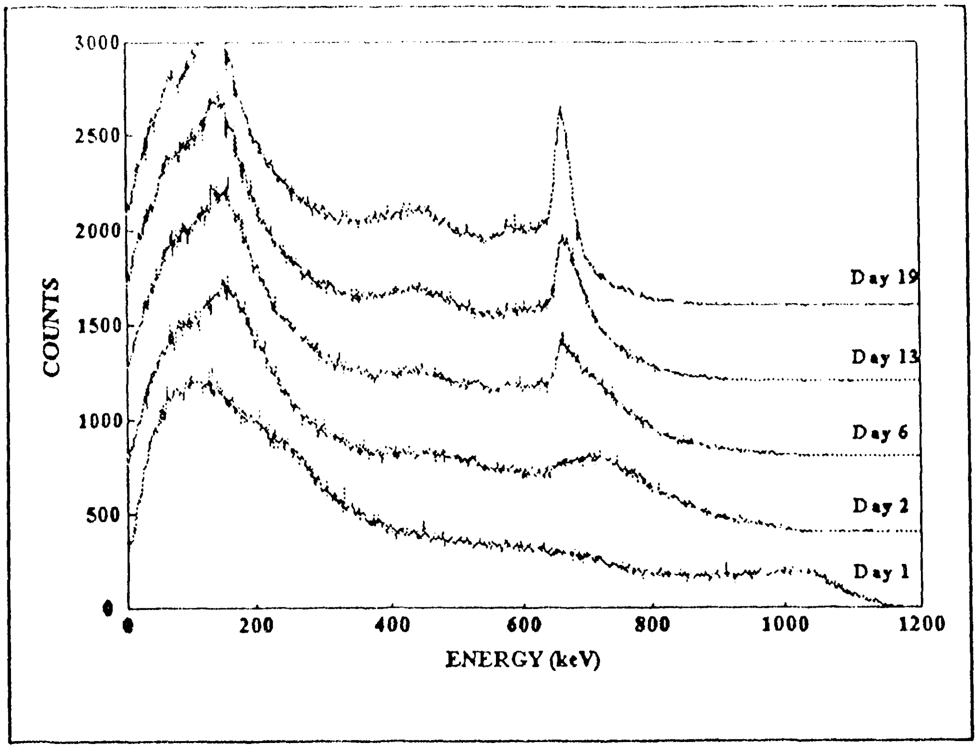

Figure 5. Stacked plot of ^{137}Cs spectra acquired over a 19-day period with a 2.1 mm × 6.2 cm^2 detector at 2000 volts bias.

detectors do not exhibit significant spectral features so polarization is difficult to define.) This suggests that polarization is not due to stoichiometry variations. On the other hand, variations in bulk hole trapping have been associated with crystallinity variations in HgI$_2$ crystal samples[12]. As mentioned before, polarization and gain is associated with increased hole trapping so there is the possibility that crystalline defects may act as centers for Auger recombination. However, impurities may also play a role.

Contact Material	Barrier Height (eV)	Contact Material	Barrier Height (eV)
Evaporated Palladium	1.10	Sputtered Tungsten	1.12
Colloidal Carbon*	1.10	Sputtered Platinum	1.10
Conducting Polymer**	1.10	Sputtered Tantalum	1.11

* "Aquadag", painted on.
** "Hydrogel", adhesion.

Table 1. Schottky barrier heights for various contacts on HgI$_2$ determined by I-V measurements.

CONTACT MEASUREMENTS

I-V Measurements

Blocking (rectifying) contacts are required to minimize the leakage (emission) current and associated noise. Typical contacts on HgI$_2$ detectors form reverse-biased Schottky barriers which limit the leakage current to approximately 10^{-11} - 10^{-10} amps at

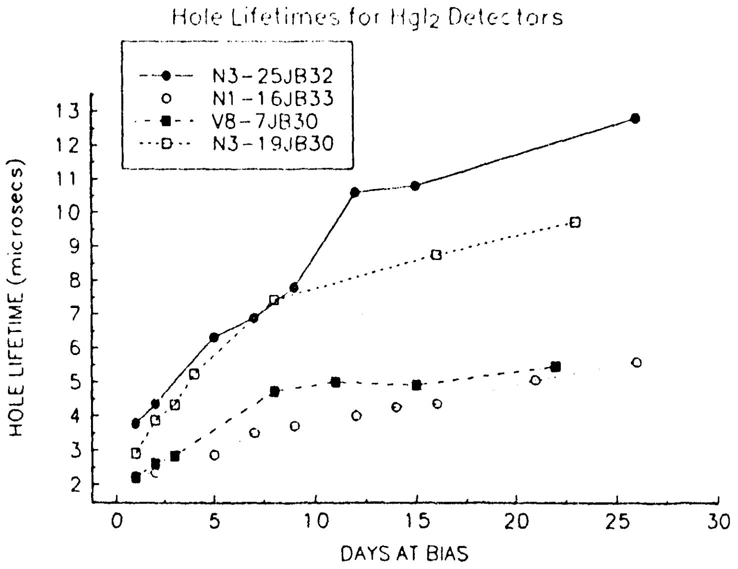

Figure 6. Hole lifetimes of four HgI_2 detectors measured periodically over three to four weeks after applying bias voltage.

a typical operating bias of a few hundred to a few thousand volts. In order to investigate charge injection mechanisms and to evaluate different contact materials, current-voltage (I-V) curves have been measured for various contacts on HgI_2 detectors. Data was acquired with a Keithley 237 high voltage source measure unit and stored on a personal computer. Following the method of reference 7, the leakage current was allowed to stabilize after each voltage step before recording the current value. Under these experimental conditions it was found that Richardson's thermionic emmission equation[11,12] gives a good fit to the data:

$$J = A^* T^2 e^{-\frac{q\phi_B}{kT}},$$

where,

J = current density (Amps/cm^2)
A* = effective Richardson constant (approximately 120 Amps/cm^2/°K^2)
q = electron charge (Coulombs)
ϕ_B = Schottky barrier height (Volts)
k = Boltzmann constant (Joules/°K)
T = Temperature (°K).

The barrier height depends on the electric field at the cathode as

$$\phi_B = \phi_{BO} - \sqrt{\frac{qE_c}{4\pi\epsilon}},$$

where,

ϕ_{B0} = Schottky barrier height at zero bias (Volts)
E_c = Electric field at the cathode (Volts/cm)
ϵ = high frequency dielctric constant (Coulomb^2/Joule/cm).

E_c is assumed to be proportional to the bulk electric field which is just the applied bias voltage divided by the detector thickness, V/L. Therefore, a plot of log(I) as a function of $V^{1/2}$ should give a straight line whose intersection with the voltage axis will give the barrier height. Figure 7 shows a typical I-V curve from a 1.2 mm × 64 mm^2 HgI_2 detector with Pd contacts. A least-squares fit of the data gives a barrier height of 1.08

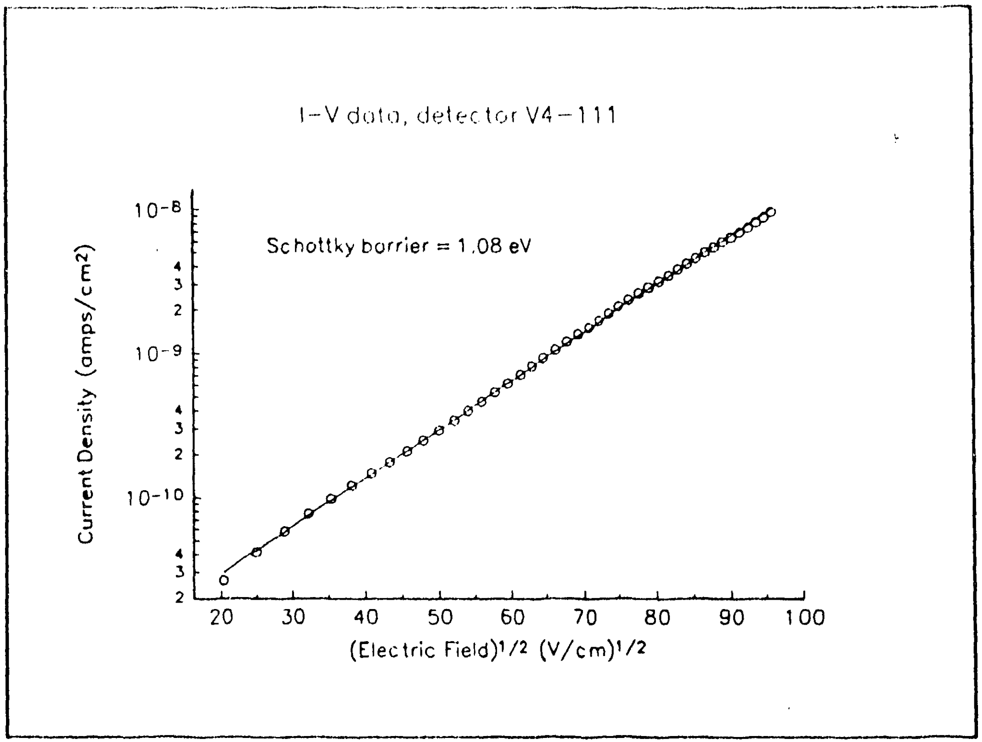

Figure 7. I-V data (circles) from a 1.2 mm × 64 mm^2 HgI_2 detector along with a least-squares fit (solid). The calculated Schottky barrier height is 1.08 eV.

eV.

Schottky barrier heights have been measured for six different contact materials on 20 HgI_2 detectors and the results are shown in Table 2. (Each value represents an average of measurements on 2 or more detectors.) These contacts represent both different materials and deposition methods but in all cases the barrier height was near 1.10 eV. This suggests that the barrier height is "pinned" at the HgI_2 surface prior to contact deposition.

Photoelectric Measurements

Schottky barrier heights have also been measured using the photoelectric method[11]. In this method photons having an energy greater than the barrier height energy, but less than the bandgap energy, are incident on a semi-transparent contact. Under these conditions the photocurrent depends on the photon energy approximately as,

$$I_{ph} = C(h\nu - \phi_B)^2,$$

where,

C is independent of the photon energy and,

I_{ph} = photocurrent (Amps)

$h\nu$ = photon energy (eV).

A plot of $I_{ph}^{1/2}$ as a function of the photon energy should give a straight line whose intercept with the energy axis determines the barrier height. Figure 8 shows data acquired with a semi-transparent Pd cathode contact on a 2.3 mm × 6.2 cm^2 HgI_2 detector. In these experiments an Instruments SA model H-20 monochrometer and PRISM scanning system were used for data acquisition. The value for the barrier height of 1.11 eV is in good agreement with results from I-V curve measurements for this detector. Barrier heights were measured for evaporated Pd contacts on eight HgI_2 detectors and an average value of 1.085 ± 0.046 eV was obtained.

SUMMARY AND DISCUSSION

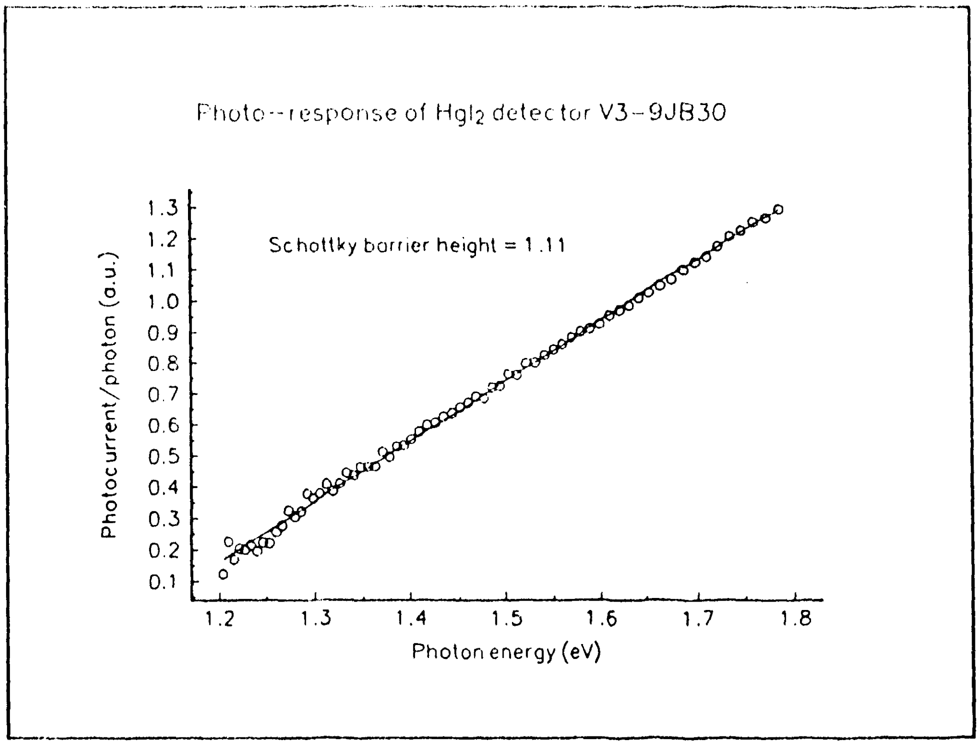

Figure 8. Square root of photoresponse (sub-bandgap energy photons) of 2.3 mm × 6.2 cm^2 detector as a function of photon energy. Least-squares fit gives a Schottky barrier height of 1.11 eV.

Data accumulated over an eight-year period indicates that correlations exist between HgI_2 gamma ray spectrometer performance, hole trapping, and material processing. The conclusion has been drawn that bulk defects associated with trace impurities have a major effect on detector response. Also, polarization has been associated with Auger recombination centers in the detector bulk, however, the particular defects responsible have not been positively identified. Schottky barrier heights have been measured on evaporated Pd contacts using both I-V curves and photoelectric measurements and both techniques indicate barrier heights near 1.1 eV. I-V curve characterization of Schottky barrier heights reveal no measurable difference between the most common electrode materials on HgI_2. Apparently, the surface Fermi level is pinned, prior to contact deposition, at about 1.1 eV which is approximately one half the bandap energy of 2.1 eV.

Considerable progress has been made in advancing practical methods for improving HgI_2 spectrometer performance and yields. However, it seems likely that further advances are possible once the specific defects responsible for hole trapping and polarization are determined. Further research in the areas of trace impurity analysis and mapping of crystallinity variations is currently under way. Alternative purification methods are also being investigated.

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