DEFECTS AND IMPURITIES IN MERCURIC IOIDE PROCESSING

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ABSTRACT

In the fabrication of mercuric iodide (HgI₂) room temperature radiation detectors, as in any semiconductor process, the quality of the final device is very sensitive to the impurities and defects present. Each process step can change the effects of existing defects, reduce the number of defects, or introduce new defects. In HgI₂ detectors these defects act as trapping and recombination centers, thereby degrading immediate performance and leading to unstable devices. In this work we characterized some of the defects believed to strongly affect detector operation. Specifically, we studied impurities that are known to be present in typical HgI₂ materials. Leakage current measurements were used to study the introduction and characteristics of these impurities, as such experiments reveal the mobile nature of these defects. In particular, we found that copper, which acts as a hole trap, introduces a positively charged center that diffuses and drifts readily in typical device environments. These measurements suggest that Cu, and related impurities like silver, may be one of the leading causes of HgI₂ detector failures.

INTRODUCTION

Red mercuric iodide (α-HgI₂) has been researched for almost three decades for use as a room-temperature radiation detector material. It has several properties which make it an extremely attractive material for this purpose. The high average atomic number of the constituent atoms (Z_Hg=80, Z_I=53, or Z_avg=62) results in a high efficiency for stopping photons into the low MeV range. The electron-hole pair creation energy of 4.2eV at room temperature leads to a sufficiently large signal response per photon. And finally, the room temperature bandgap of 2.13eV results in a resistivity on the order of 10^{14} Ω·cm and a dark current on the order of picoamps for typical device structures. These properties combine to give a material that has been used to produce some of the highest resolution room-temperature x-ray and gamma-ray detectors [1-4]. In addition, the capability for room temperature operation results in the possibility of compact spectrometer field instruments for applications such as environmental monitoring or special nuclear materials (SNM) monitoring.

However, these positive properties are balanced by several negative properties. Some of the basic properties of HgI₂ cause many of the problems. The fact that it is a compound semiconductor immediately leads to stoichiometry issues. The material has a relatively high vapor pressure at room temperature, and in addition, the iodine is generally preferentially sublimed at a faster rate, yielding mercury rich surfaces. The red tetragonal α-HgI₂ phase undergoes a phase transition around 125°C to the yellow orthorhombic β-HgI₂ phase which destroys the crystallinity of the material upon return to room temperature. Finally, the material is mechanically very soft and also delaminates easily at the iodine layers.

The extrinsic factors that degrade mercuric iodides’ usefulness are related to carrier trapping centers that are introduced into the material. These can arise from structural damage to the crystal or stoichiometric changes during the crystal growth and device fabrication processes. Of interest here, however, are the impurities that are introduced into the material, either from the original starting materials (generally mercuric chloride and potassium iodide), or further along in the fabrication. Several impurities are believed to play a role in mercuric iodide detectors, ranging from hydrocarbons to metallic elements. The impurities of interest here are copper and related metals.
These factors all lead to problems in the initial yield of high quality detectors, and the long term reliability of the detectors. These two problems combine to limit the applications of these sensors, particularly in the commercial arena. Given that the basic intrinsic material properties cannot be changed, one of the primary ways to improve the material is to identify the impurities that are deleterious to the detector performance, and work to reduce their presence. In this work we studied how copper and related impurities can be a prime source of problems in mercuric iodide detectors.

EXPERIMENTS AND RESULTS

Mercuric Iodide Detector Response

Mercuric iodide and other high resistivity room temperature semiconductor radiation detector materials allow for a very simple device structure. A bulk slab of material has simple ohmic contacts applied to opposite faces and a bias applied. The incoming x-ray or gamma-ray photon interacts with the semiconductor material yielding a number of electron hole pairs proportional to the photon energy. These carriers then drift in the applied field. This motion of carriers, or current pulse, is converted to a voltage pulse via a charge-sensitive preamplifier. This voltage pulse is then pulse-height-analyzed (PHA) and a count placed into the memory channel corresponding to the pulse magnitude. Therefore, the spectrum of event counts versus channel number, or pulse height, is directly proportional to the energy spectrum of the radiation seen by the detector, and the system can be thusly calibrated.

For this work a standard x-ray/gamma-ray detector characterization setup was used to measure the spectral response of a HgI₂ detector. A high voltage power supply was used to provide a negative bias to the entrance electrode. A custom-built box housed the detector under test and connected to a Tennelec TC170 charge sensitive preamplifier, modified for DC coupling, by way of a BNC connector. A Tennelec TC241 spectroscopy amplifier was used to shape the pulses from the preamplifier, and a The Nucleus MCA card and software were installed in a PC to collect the spectra. For the detector itself, a 1cm² by 2mm thick slab of mercuric iodide had 200Å thick 6.35mm diameter palladium contacts sputtered on each side and Pd wire leads aquadagged on. This is representative of the actual devices used in spectrometer systems. The detector was biased at -1000V and irradiated with a 1μCi Americium-241 source placed about 2cm above the entrance electrode. Each spectrum was collected over a 1000s livetime. ²⁴¹Am has a gamma photon at 59.54keV and several x-ray escape peaks in the 14 to 21keV range. The gamma photopeak energy lies roughly in the center of the range of energies of interest for HgI₂ detector applications.

The previously given description of detector operation is an idealized model, in which the photopeak would be a one channel wide delta function at the appropriate pulse height for the number of carriers created by an incident photon (for example, the 14,176 electron-hole pairs for a 59.54keV gamma-ray). However, even in a "perfect" detector, i.e. one with complete charge collection, the peak would still be broadened to a gaussian shape because of carrier statistics. The more critical problem, however, is that many other processes degrade the spectral response more seriously. Anything that leads to a change in the voltage pulse height at the PHA greater than the digitization step size will lead to an error in the spectrum. The simplest possibility is that there is a constant amount of charge that is not collected, because it is trapped. This means that all of the pulses are reduced in magnitude, and the spectrum is thus shifted to lower channels. A constant change like this, although resulting in a reduction of the signal to noise in the system, can be "corrected" by simply recalibrating the energy scale. The more serious problem lies in the variable effects of real trapping processes. The trapping process is stochastic, such that the amount and timing of charge trapping is statistically broadened. Thus, events will have pulse heights reduced by different amounts. Therefore the photopeak is broadened on the low channel side. This is generally called "hole-tailing" as holes are usually the carriers trapped which lead to diminished pulses. Figure 1 shows the detector response of the mercuric iodide device above, which exhibits this hole-tailing problem. If the carriers that were trapped are released after the original pulse's collection time, the pulse heights of subsequent events can actually be larger than expected, though this rarely is visible in spectra, as the probability for the timing to be correct is low!
Finally, the problem of particular interest here, if the trapping process itself is changing, the effects on spectral response will be changing. Mercureic iodide detectors all exhibit this effect to some degree, particularly in the initial biasing characteristics. When a detector has been completely fabricated and is biased for the first time, the spectral response is very poor and changes significantly over time. It generally requires hours of bias for a device to stabilize to its high performance level. Figure 2 shows the evolution of the energy spectrum for the above detector, which actually required almost 200 hours to stabilize, as it was fabricated from material of lower than usual quality.

![Figure 1. 241Am spectrum from mercureic iodide detector exhibiting hole tailing.](image1)

![Figure 2. 241Am spectrum versus time after initial biasing for mercureic iodide detector.](image2)

Figure 1. 241Am spectrum from mercureic iodide detector exhibiting hole tailing.

Figure 2. 241Am spectrum versus time after initial biasing for mercureic iodide detector.

From Figure 2 one can study the detailed spectral evolution. After three days of biasing, the spectrum is just increasing in total counts and decreasing in peak widths. However, in the initial period, the first day in particular, the spectrum undergoes more substantial changes. There appear to be at least two separate peaks arising in the region of the expected gamma photopeak. One of these becomes the photopeak, while the peak at higher pulse height eventually disappears. As mentioned above, this higher than expected pulse height peak could be related to detrapping coincident with later events. However, the processes underlying this initial biasing behaviour require further study.
Impurities in Mercuric Iodide

Given that mercuric iodide is a somewhat primitive technology in semiconductor terms, impurities still tend to be present at significant levels. One set of methods for quantifying the elemental impurities are the Inductively Coupled Plasma Optical Emission and Mass Spectroscopy (ICP-OES and ICP-MS, respectively), which vaporize and ionize a sample solution with a plasma and measure the presence of a range of elements. The ICP-OES technique can generally measure down to the high ppb range, while the ICP-MS method can reach the high ppt region. Both of these techniques have been used on many HgI$_2$ samples, from initial material to purified material ready for crystal growth to completed crystals, as readily detectable levels of impurities are common. For example, copper is seen in the 100ppb to 1ppm level over a wide variety of samples, and therefore, it is fairly well accepted that copper is indeed present in most material [5]. Many of these impurities, such as copper, are electrically active, and thus are believed to be a prime cause of hole trapping. The presence of such an electrically active impurity would lead to a smaller signal and the distortion of the energy spectrum as seen in Figure 1 above.

Other experiments have shown that the impurities, as expected, can be equally well introduced during subsequent processing of the crystal for detector fabrication. Another good method for locating and identifying impurities present in a sample is low temperature photoluminescence (PL). PL has been used extensively on HgI$_2$, and the material has a rich PL spectrum. In general, impurities can be detected down to the ppt level, but can rarely be quantified. One common step used throughout the fabrication process is the wet chemical etch in a dilute solution of potassium iodide (KI). The KI etch is used to remove mechanical damage from cutting, etc., and to remove the “aging” from the surface that results from the high vapor pressures of the Hg and I. Previous experiments have shown, however, that impurities in the KI solution are readily incorporated into the HgI$_2$, and that these impurities readily diffuse throughout the sample in a matter of days. In addition sheet resistance measurements of thin film metal layers of copper have been conducted which showed that a large fraction of the Cu "disappears" into the HgI$_2$. Therefore, copper can be introduced into the bulk material during the detector fabrication process as it readily diffuses throughout the sample, and it has been shown to degrade detector performance [6-10].

Leakage Currents Characterization

The existence of these mobile impurities complicates the carrier collection situation further. First, there is a current associated with the movement of any charged impurity itself, which leads to a heightened noise level. Secondly, the trapping effects of the impurity center varies unpredictably as the impurity moves in the bulk material. The previous work cited above demonstrated the high diffusivity of copper in HgI$_2$. The experiment here demonstrates the mobility of the copper impurity in an electric field in mercuric iodide. In this experiment we intentionally doped a sample with a charge of copper. We then monitored the leakage current, or dark current, versus time to determine the movement of the copper-related centers.

The measurement system consisted of several instruments controlled and monitored by a personal computer via a GPIB (IEEE-488) interface. The sample was biased using a high voltage power supply capable of supplying up to 10mA at 500V. The sample bias voltage was monitored with a standard digital multimeter and stable within +/-1V. The leakage current was measured with a Keithley Instruments 485 picoammeter, with resolution down to 0.1pA. Finally, a switching assembly was fabricated that allowed for computer controlled reversal of bias direction, and removal of bias for other measurements. With this setup the copper doped/contacted devices were biased and monitored over a period of days to capture the "transients" in the leakage currents.

The first set of samples used in this experiment were two similar 1cm$^2$ by 0.1mm thick HgI$_2$ crystals. A 6.35mm diameter, 2500Å thin film of high purity copper was sputter deposited onto one face of the sample, and a palladium lead was attached with aquadag. This translates to a doping level of about 2800ppm if the copper is distributed uniformly throughout the bulk of the HgI$_2$. On the reverse side, an aquadag contact of similar area was made. The samples were then placed in a dark desiccator cabinet and connected to the measurement circuit. One sample had a positive 350V bias applied to the front, doping contact, while the other had the positive bias applied to the back contact, effectively giving a negative bias to the doping contact. In both cases
this translates to an electric field on the order of 3.5V/μm, which is higher than the normal detector fields of 1V/μm. This higher field accelerates the mobile processes. Figure 3 shows the results obtained for these two samples.

The leakage current for the positively biased sample exhibited a peak that sharply rose from the initial leakage current of 0.1pA to 0.7μA. The peak decayed more slowly to a background leakage current of 5pA. This higher leakage level possibly indicates that the material had been damaged by the presence and movement of the high level of impurities, as the very initial leakage current was closer to the typical value for detectors.

Integrating the current gives the total charge moved, which should be representative of the impurities moved, as the intrinsic electron conductivity in the mercuric iodide is very low. The majority of the impurities, over 99%, appear to move in the first six hours. The total charge moved was 8.5x10^{-5}C, or 5.3x10^{10} single charges. This represents about 8% of the total number of atoms present in the deposited Cu film, assuming a singly charged impurity.

The negatively biased sample exhibited only a very small and brief current transient. Here 2.5x10^{-5}C or 1.5x10^{10} single charges were moved. This is consistent with the view that the Cu forms a positively charged center, which is held at the negative contact. The transient that does occur is the movement of the few impurities that had diffused into the substrate back into the contact area.

These results show that the copper impurity, which may be a copper iodide (CuI) or something related, exhibits a single positive charge. The impurity drifts in the field as a positively charge carrier with an ionic mobility. For the second set of leakage current measurements one, different sample had the applied field periodically reversed. This experiment was done to confirm the above conclusions, and more importantly, to see if the copper impurities remain mobile after traversing the bulk of the mercuric iodide.

This sample was a 1cm² by 1mm thick HgI₂ crystal, with a 6.35mm diameter, 250Å thin film sputtered onto one face. This translates to a doping level of about 28ppm, which is two orders of magnitude lower than the first two samples. This sample also had a 350V bias which now translates to an electric field on the order of 0.35V/μm, which is one order of magnitude lower than before. Figure 4 shows the results obtained for this sample.

The leakage current for this sample exhibited a peak that sharply rose from the initial leakage current of 0.1pA to about 2nA. The peak decayed more slowly to a background leakage current of 0.2pA. The leakage current this time had returned more-or-less to its initial level, indicating that the material had not been damaged in this case because of the much lower level of impurities flowing through the sample. The majority of the impurities, over 97%, appear to move in the first four hours. The total charge moved was 4.3x10^{-6}C, or 2.7x10^{13} single charges. This represents about 0.04% of the total number of atoms present in the deposited Cu film. This amount is significantly lower than that of the first samples, most likely because of the lower field.
When the bias is reversed after one day a similar transient develops. Here $2.8 \times 10^{-6} \text{C}$ or $1.7 \times 10^{13}$ single charges were moved, with 98% in the first two hours. This means that only 64% of the impurities moved back across. The remainder were either pinned somewhere in the bulk, or removed or stabilized at the back contact.

![Graph](Image)

**Figure 4.** Leakage currents versus time for reversing field on copper doped HgI$_2$.

**CONCLUSIONS**

Detector characterizations were used to highlight the degradation in performance frequently seen in mercuric iodide room temperature radiation detectors. This work sought to understand some of the causes of these failures by studying the copper impurities that are present in mercuric iodide and that are introduced during processing. Previous measurements revealed the high diffusivity of copper in mercuric iodide at room temperature. The leakage current measurements on doped samples shown here were used to demonstrate that the copper impurity is charged and mobile, and can easily be swept back and forth through the bulk crystal by an applied electric field. These measurements show how copper can affect the operation of detectors. In particular, the copper presents two means of detector failure. First, the presence of the copper introduces a defect center that traps carriers associated with the incoming photons, and leads to decreased and statistically broadened pulse heights. Secondly, the copper is seen to be mobile, which leads to changes in detector performance, particularly as the bias is changed. The movement of copper and similar impurities, such as silver, may actually be the cause of the needed conditioning time. When a detector is first biased, a fraction of the impurities are swept through the sample and remain at the back contact until the bias is removed when diffusion becomes the dominant mechanism. These results suggest that copper must be removed from and kept away from the mercuric iodide crystal and detector. Purifications are required to remove it from starting material, and the subsequent processing must be "clean".

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**REFERENCES**

5. E. Soria, (private communication).

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