Purification and Preparation of TlBr Crystals for Room Temperature Radiation Detector Applications

Icimone B. Oliveira, Fábio E. Costa, José F. D. Chubaci, and Margarida M. Hamada

***Abstract*—Thallium bromide (TlBr) is a semiconductor compound with a high atomic number and a wide bandgap, being a very promising material to be used as room temperature radiation detectors. In this work, commercial TlBr powder was used for growing crystals for detector applications. To reduce impurities, this material was purified by the zone refining technique. Trace impurities at ppb/ppm level were analyzed using inductively coupled plasma mass spectroscopy (ICP-MS). The efficiency of the purification was evaluated through studies of the decrease impurities concentrations in the TlBr powder and in the purified materials. The crystal quality was verified by X-ray diffraction (XRD). To evaluate the crystal as a semiconductor detector, systematic measurements of the transmittance, resistivity, and the radiation response (^{241}Am, ^{57}Co, ^{125}I, and ^{133}Ba) gamma rays were carried out.**

***Index Terms*—Thallium bromide (TlBr), zone refining, crystal growth, radiation detector.**

I. Introduction

THERE HAVE been attempts to develop room-temperature X- and gamma ray detectors for various applications [1]. Over the past decade, compound semiconductors have attracted considerable attention as possible alternatives to Si and Ge for charge particle and photon detection [2]. The application of these detectors has been somewhat restricted since Ge detectors provide high-resolution capabilities only at cryogenic temperatures (77 K), because of their low resistivity at room temperature, and Si detectors exhibit sufficient detection efficiency for only low energy rays (less than 20 keV), because of their low photon stopping power at higher energies. Thus, there has been a strong interest in developing semiconductors that have high photon stopping power and can operate at room temperature, without sacrificing the advantages of Ge and Si detectors. The main physical semiconductor properties required for fabrication of room temperature semiconductor detectors are: 1) high atomic number and density for high stopping power; 2) a bandgap large enough to keep leakage currents low at room temperature; and 3) large electron and hole mobility-lifetime products for efficient charge collection [3]. High-Z compound semiconductors such as CdTe, $Cd_{1-x}Zn_x$ Te (CZT), HgI_2, PbI_2, and TlBr have been investigated as materials for nuclear radiation detectors that can operate at room temperature. CdTe and CZT are routinely used, although both materials suffer from poor hole transport properties, which limit the maximum thickness and therefore the high-energy response of detectors. For high energies and specifically γ-ray applications, TlBr has emerged as a particularly interesting material in view of its wide bandgap (2.68 eV) and its large density (7.5 g/cm^3) [4]–[6]. TlBr crystals are composed of high atomic number elements ($Z_{Tl} = 81$ and $Z_{Br} = 35$) and with high resistivity ($>10^{10}$ Ωcm) [4]–[8]. These are important factors in applications where compact and small thickness detectors are necessary for X-ray and gamma ray measurements.

Due to its physical, chemical and electronic properties, TlBr can be used as a radiation detector or photodetector coupled to scintillator crystals. Several studies about the preparation of TlBr detectors have been carried out and progress has been made by the improvement of the purification methods, growth and characterization of the crystal. There is agreement in the literature that the TlBr crystal purity is a crucial factor for its optimal performance as a radiation detector. However, as far as we know, no results on reduction of the TlBr impurities have been found in the literature. In this work, TlBr crystals grown by the Bridgman method from materials purified by zone refining technique have been characterized to be used as room temperature radiation detectors.

II. Device Fabrication

Commercially available TlBr (Merck—99.0%) powder was purified by the conventional zone refining method (ZR) [9]. In this method, the expected result is a charge much purer at the ingot middle section than at the end sections.

The ampoule containing the starting material was evacuated to 10^{-5} Torr and sealed off. It was mounted in the zone refining furnace and the heater moved at a speed of 2 cm/hr along the length of the ingot. The length of the molten zone was about 3 cm in this experiment. The furnace temperature was set to approximately 480 °C and this process was repeated 1, 20, and 30 multiple times. The number of zone refining passes is important to the effectiveness of purification. The purification efficiency was evaluated by inductively coupled plasma mass spectroscopy (ICP-MS) technique. Samples from 40-cm zone refined ingots cut in eight sections of 5 cm each were analyzed for the determination of the impurities concentration.

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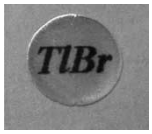

Fig. 1. Surface TlBr wafer (11-mm diameter and 0.5-mm thick).

The purest section of the TlBr ingot was employed for the crystal growth by Bridgman method. The crystals were grown with a rate of 1–2 mm/hr at 480°C in a vertical furnace. The crystals obtained were denominated M01 (01 ZR pass), M20 (20 ZR passes), and M30 (30 ZR passes). After the crystal growth, annealing was performed to improve the cristallinity of the TlBr crystals, at 150 °C for 24 h. The crystalline quality was analyzed by X-ray diffraction.

Crystals were then sawed into several thick wafers with a diamond saw, followed by mechanical polishing. In order to remove damage from the crystal cleavage, wafers surfaces were then etched using a 10% bromine in methanol solution and rinsed with a methanol solution. The resulting wafers were clear, with a good quality surface. A typical TlBr wafer is shown in Fig. 1.

Optical transmission measurements were made on the crystals. These measurements were performed at room temperature using a Shimadzu spectrophotometer with a wavelength varying in the range between 300 to 600 nm.

Finally, radiation detectors were fabricated by vacuum deposition of gold on both sides of the wafers. Electric wires were connected to the electrodes using graphite paint.

Thallium bromide detectors were tested using conventional nuclear instruments. An Ortec 142 charge sensitive preamplifier, an Ortec linear amplifier and an Adcam 918A multichannel analyzer were used for the radiation response measurements. ^{241}Am, ^{57}Co, ^{125}I, and ^{133}Ba gamma radiation sources were employed.

III. Results and Discussions

To assess the effectiveness of zone refining as a means of purification of TlBr, the ICP-MS technique was employed to investigate the presence and concentrations of some impurities in the zone refined TlBr and in the commercial TlBr powder. The following impurities were identified: Li, Na, K, Se, Mg, Ca, Cr, Fe, Cu, Zn, Ba, Ag, In, Sn, Cs, Au, Hg, Pb, La, U, and I. We point out that the reduction of the impurities present in the TlBr after zone refining is being reported for the first time in this work.

Table I and Fig. 2 show some impurities present in the TlBr powder and in the purest section of the TlBr ingot after 1 (ZR1), 20 (ZR20), and 30 (ZR30) zone refining passes.

As it can be observed, there was a strong reduction of the impurities after the first pass of ZR. In the following passes, the impurity concentrations decrease more slowly. For ZR20 and ZR30, the ingot bottom section showed the darkest color, followed by bright yellow color in the remaining sections. On the other hand, the ZR1 ingot showed a uniform color along the whole length.

TABLE I
Some Impurity Concentrations (PPM) in the TlBr Powder and in the Purest Section of the TlBr Ingot by ICP-MS

	Powder	ZR1	ZR20	ZR30
Li	23.36	0.37	0.04	0.03
Ca	3.76	0.26	0.19	0
Cr	2.72	0.11	0.08	0.07
Fe	13600.0	204.0	153.0	107.0
Cu	1476.4	26.82	11.15	5.04
Ba	324.72	1.62	1.22	0.57

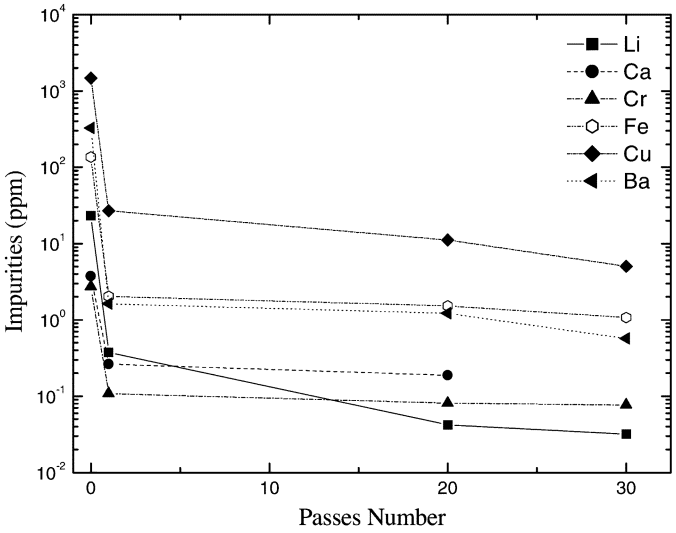

Fig. 2. Impurity concentration decrease as a function of the purification passes number. The Fe value was divided by 100 for better visualization.

Studies for the improvement of the TlBr purification methodology evaluation have been carried out, aiming to establish the number of passes to achieve the maximum reduction of the impurities concentration to obtain high quality radiation detectors.

The crystals grown by Bridgman method were transparent and bright yellow. Fig. 3(a) shows the X-ray diffraction pattern of TlBr power exhibiting a complete set of reflections. In Fig. 3(b), the result shows that the M30 crystal has a similar structure to the cubic crystalline pattern of TlBr. The diffractogram indicates that the crystal is preferentially oriented in the (110) direction. It is worthwhile observing that there was no other crystalline phase in the grown samples since all detected peaks correspond to the TlBr sample peaks oriented in the (110) direction. Similar diffractogram was obtained for M20 crystal. This result is in agreement with the literature [10].

Fig. 4 presents the optical transmission measurement for M30 crystal. Similar result was obtained for M20 crystal. The TlBr optical transmission decreases to zero for wavelengths below 435 nm. The bandgap $(\mathrm{E_g})$ value may be obtained from the position of the absorption edge of an optical transmission measurement. The $\mathrm{E_g}$ obtained in our measurements was $2.8\ \mathrm{eV} \pm 0.3$, close to the values reported in the literature (2.6–2.7 eV) [11], [12].

Fig. 5 shows the results of the leakage current as a function of the applied bias voltage for M20 and M30 crystals. For the 550 μm thick M20 crystal, the maximum tension that could be applied was 600 V, while for the 360-μm thick M30 crystal, a bias voltage up to 1000 V can be applied. Above

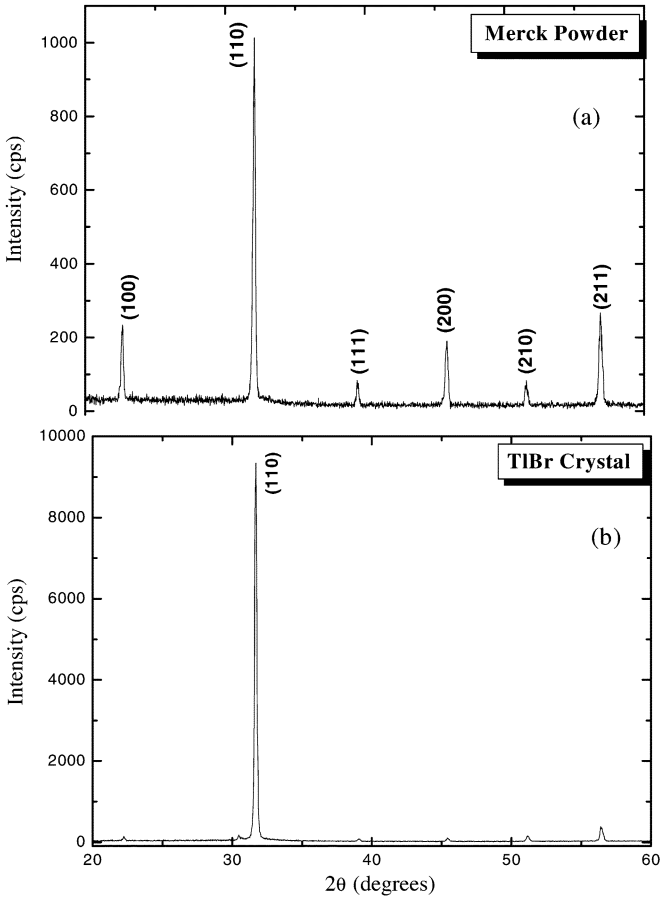

Fig. 3. X-ray diffraction of (a) TlBr powder and (b) TlBr crystal.

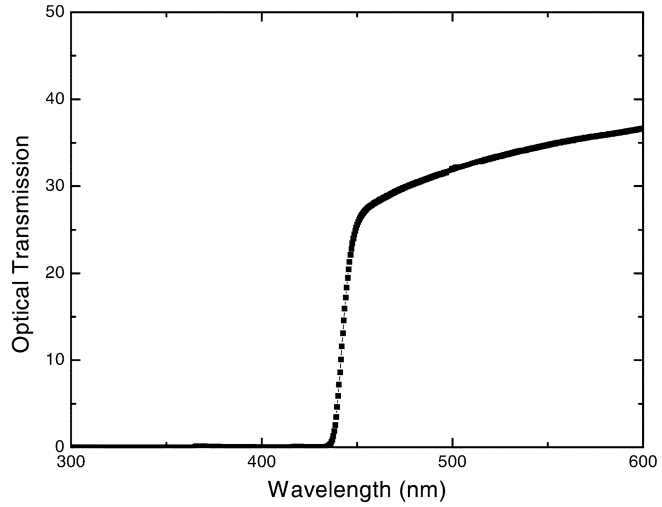

Fig. 4. Optical transmission of TlBr crystal.

these tension values, it was observed many spikes, making the measurements impossible. The resistivity value was estimated to be 2.4×10^{11} Ωcm for both detectors.

For M01 crystal, no radiation response was observed. Above 10 V of bias, the occurrence of the spikes was so large, that obscured the signal current. This result suggests that the purity and the cristallinity quality of the crystal are important parameters, which should be evaluated in the crystal to be used as a radiation detector.

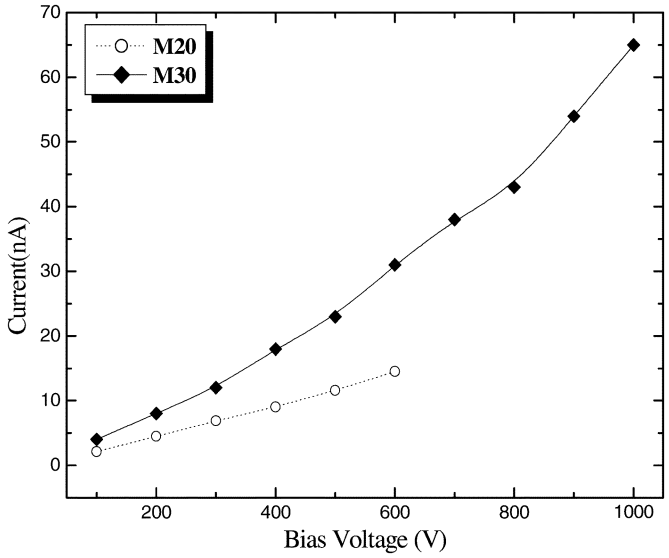

Fig. 5. Current-Voltage curves for (a) M20 detector and (b) M30 detector.

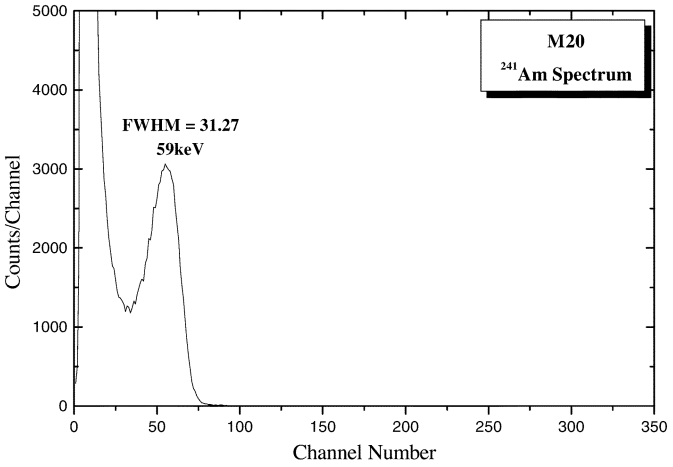

Fig. 6. ^{241}Am spectrum from M20 TlBr detector.

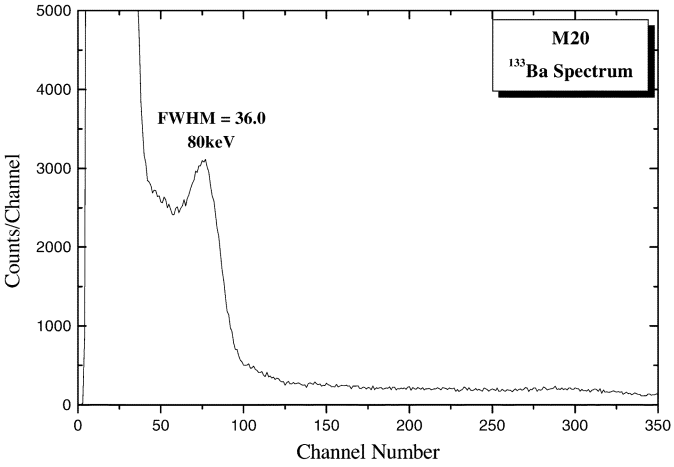

Fig. 7. ^{133}Ba spectrum from M20 TlBr detector.

Figs. 6–8 present the pulse height spectra of the M20 detector under gamma ray excitation. The detector was 2.8 mm^2 in electrode area and 550-μm thick. The FWHM of the 59 keV peak

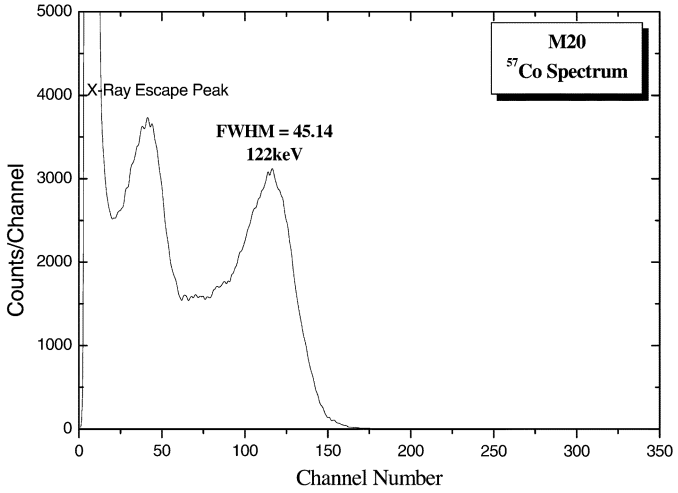

Fig. 8. ^{57}Co spectrum from M20 TlBr detector.

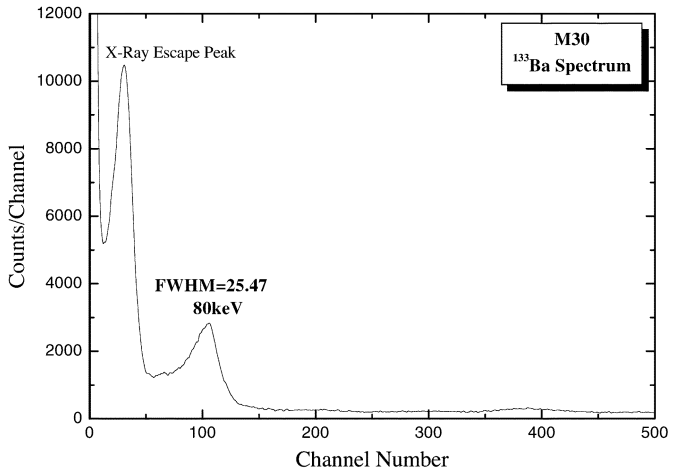

Fig. 9. ^{133}Ba spectrum obtained from a M30 TlBr detector of 510-μm thick.

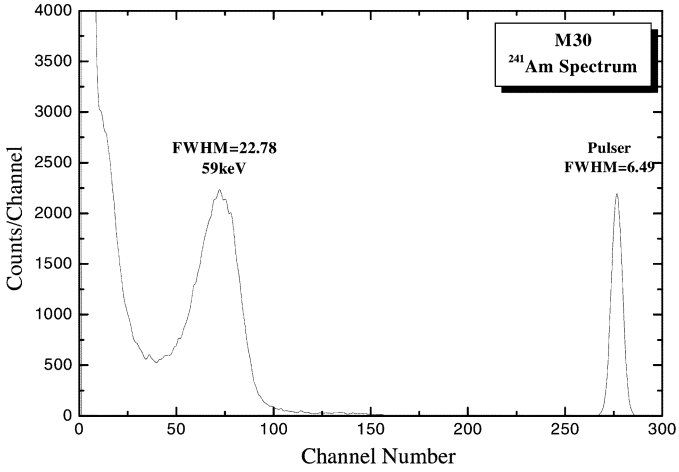

Fig. 10. ^{241}Am spectrum obtained from a 360-μm thick M30 TlBr detector.

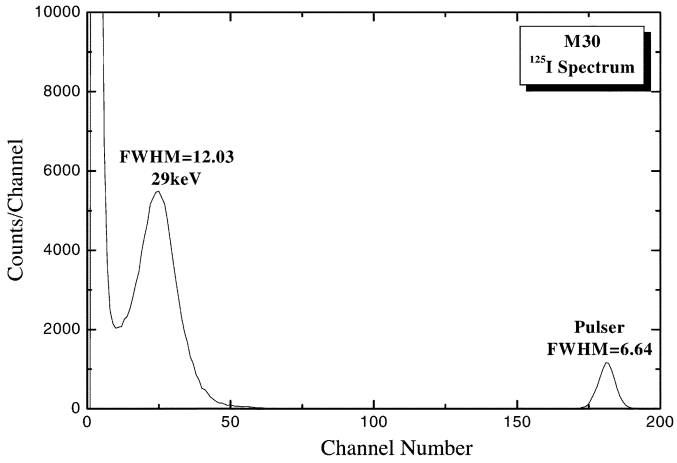

Fig. 11. ^{125}I spectrum acquired from 360-μm thick M30 TlBr detector.

was about 31.27 keV (53%), 80 keV peak was 36 keV (45%) and 122 keV peak was 45.14 keV (37%).

Figs. 9 to 11 present the pulse height spectra of the M30 detector under gamma ray excitation. The detectors were 3.5 mm^2 in electrode area and 360–510 μm thick.

Fig. 9 shows the γ-ray spectrum of ^{133}Ba obtained from the TlBr detector at room temperature. As shown in this figure, the spectrum shows an 80 keV peak as well as the X-ray scape peak. The FWHM of the 80 keV peak was about 25.47 keV (25%), while for M20 was 36 keV (45%), showing a significant improvement for the detector prepared with purer crystals.

Fig. 10 shows the γ-ray spectrum of ^{241}Am obtained from the TlBr detector at room temperature. The FWHM of the 59 keV peak was about 22.78 keV (32%). The energy resolution was deteriorated in the tail on the lower energy side of the peak, probably due to the incomplete charge carrier collection. However, the FWHM of 22.78 keV (32%) for the M30 in the 59 keV peak was also better, when compared to that of 31.27 keV (53%) for M20.

A ^{125}I spectrum acquired with the TlBr detector is shown in Fig. 11. The detector exhibited an energy resolution of 41% (FWHM = 12.03).

These results demonstrate the importance of the TlBr crystal purity for its application as a radiation detector, as described in the literature [1], [4]–[8]. According to the literature [13], the mobility-lifetime products ($\mu\tau$) could be limited by charge carrier trapping in the TlBr crystal due to the chemical impurities. This suggests that the additional purification is effective in improving $\mu\tau$. Other limitations could be caused by imperfections in the cristallinity, imparted during crystal growth or later during the ohmic contact preparation in the crystal to be used as radiation detectors [13].

Moreover, a gradual degradation in the detector resolution occurred over a period of several hours after applying bias voltage. This no-stability in the energy resolution may be due to the polarization phenomena. Polarization is the result of the build-up of trapped or fixed charges in a semiconductor. This effect reduces the electrical field in many regions of the device, resulting in lower charge collection efficiency. On the other hand, the reduction of the detector leakage current can also occur due to polarization [14]. This reduction was observed in our leakage current measurement as time passed, so it was expected a improvement in the energy resolution. However, this was not observed in our measurement, suggesting that the polarization also occurred in our detectors.

In order to obtain TlBr detectors with better gamma-ray spectroscopy, detailed studies are necessary for understanding the polarization phenomena [15]. Further research efforts will be directed on the study of the polarization effect in our detectors. In addition, electronic systems and pulse-processing techniques should be investigated to improve the energy resolution and the detector efficiency.

IV. Conclusion

Material processing, especially purification, was found to have influence on the detector response suggesting that improvement in performance of TlBr devices could be possible with more purification. The zone refining was effective to reduce the concentration of TlBr impurities. The ICP-MS analysis showed to be a special technique to identify and quantify the impurities in the TlBr crystal and to evaluate the reduction of the impurities, after the purification.

The energy resolution of the detectors has been currently limited by incomplete charge collection. Further improvement of the detector performance will be achieved by investigation of structural and surface properties, by optimizing the measurement conditions and by reducing electronic noise in our system.

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