Influence of Crystalline Surface Quality on TlBr Radiation Detector Performance

Icimone B. Oliveira, Fabio E. Costa, Pedro K. Kiyohara, and Margarida M. Hamada

***Abstract*—In this study, TlBr detectors were fabricated from crystals purified by the multipass zone refining and grown by the Bridgman method. Detectors were prepared using TlBr 0.3-mm-thick wafers, with surface submitted to different mechanical and chemical treatments. Optical microscopy and scanning electron microscopy evaluated the TlBr wafers surface quality. To analyze the surface quality influence in the detector response, systematic measurements of the pulse height spectra and energy resolution were carried out for each prepared radiation detector. The radiation response for these detectors was performed under ^{241}Am gamma radiation excitation at room temperature. The influence of the surface quality of the TlBr wafer on its performance as a radiation detector was observed.**

***Index Terms*—Optical microscopy, radiation detector, scanning electron microscopy, surface quality, thallium bromide.**

I. Introduction

THALLIUM Bromide crystals are semiconductors composed of high atomic number elements ($Z_{Tl} = 81$ and $Z_{Br} = 35$) and with high resistivity ($> 10^{10}$ Ωcm). They have been the subject of many investigations due to specific technological features. Besides their good response to X- and γ-rays at room temperature, they are also suitable for applications as photodetectors and small dimension devices, with high radiation efficiency, as intra-operable surgical probes [1], [2].

The performance of radiation detectors is controlled by both intrinsic and extrinsic factors. Carrier lifetime, mobility and the atomic number of the material used for radiation detectors represent intrinsic parameters, while extrinsic factors such as crystallographic perfection and impurity levels can also play a major role in the performance of radiation detectors [3].

The TlBr detector has a wide bandgap (2.68 eV) and a high density (7.5 g/cm^3). Its large bandgap offers the possibility of low noise performance at room temperature [4], [5]. Nevertheless, the crystals have low electron and hole mobility plus significant hole trapping [6]. Because of these crystalline characteristics, efficient detectors can only be obtained with thin samples less than 1 mm thick. Although it is harder than other semiconductors (PbI_2 and HgI_2), TlBr is not sufficiently hard (Knoop hardness of 12) to prevent damage during its fabrication process [7]. TlBr is also highly toxic and must be handled with care [8].

The crystal cutting, surface polishing and subsequent etching are important processes during the manufacturing of the room temperature semiconductor radiation detectors, such as CZT, HgI_2 and TlBr. Both mechanical polishing and chemical etching can affect the surface leakage. The centers resulting from mechanical polishing may both enhance the carrier recombination on the surface by increasing surface trapping sites and affect the surface leakage current by providing more conductive pathways and altered electrical-field distributions. In some circumstances, the polarity effects can be introduced by surface processing and effectively removed by appropriate polishing and chemical etching [9].

The routine procedure to prepare a TlBr detector involves mechanical polishing of the crystal followed by chemical etching with a bromine methanol solution [2]. The polishing is used to delete the defects on the surface arising at the cutting and the etching solution is used to remove the damages caused after the mechanical procedure. Cui *et al.* [9] and Wright *et al.* [10] have reported that different etchants change the surface morphology of the CZT surfaces. Their studies established a correlation between the roughness of the surfaces and the resulting values of the detector leakage currents, with the smoothest surface producing the lowest noise in detectors. This information is important to optimize the surface processing and obtain a radiation detector with better performance. Therefore, it may be considered that treatments in the crystalline surface can affect the detector final performance.

Several works in the literature on the TlBr crystal surface treatment, describing the procedure of the mechanical polishing and chemical etching with bromine methanol solution, have been found [1], [5], [11]–[14]. However, as far as we know, studies on the effect of TlBr surface quality concerning its performance as a radiation detector have not been previously reported. In this work, the surface quality of the TlBr wafers prepared with different mechanical and chemical treatments was evaluated. The performance of each treated TlBr wafer as a radiation detector was also evaluated. The energy resolution and pulse height spectra of the TlBr detectors were performed under ^{241}Am gamma radiation excitation at room temperature.

II. Experimental

To produce pure TlBr crystals, commercial TlBr material (99.0%) was purified by zone refining process. Twenty zone refining passes were carried out in a furnace at the speed of 2 cm/hr. A small section of TlBr purified material was used for Bridgman crystal growth. Details of the purification and crystal growth were described in our previous paper [11]. TlBr crystals of 1 cm diameter and 3 cm long, transparent, uniform and without visual defects, were obtained for this work. The

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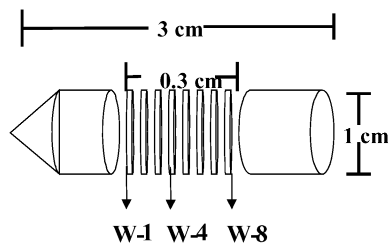

Fig. 1. TlBr crystal cut scheme.

crystals purity was evaluated by the ICP-MS technique. The impurities concentrations found were <10 ppm.

As shown in Fig. 1, a purer section of 0.3 cm was found in the crystal middle. From this section, 8 slices were cut transversally to direction [110], obtaining 8 TlBr wafers. In order to have less damage and smaller depths in the resulting layers, crystals were cut slowly, using a diamond saw, lubricated with glycerin during the process.

After cutting, some wafers were polished using abrasives of 12–3 μm, to obtain wafers with a final thickness of around 0.3 mm. The etching was carried out using 10% bromine in methanol solution at room temperature and rinsed with methanol. The thermal annealing was performed for some wafers, heating them to 100 °C under 10^{-3}mmHg vacuum for five days, in order to improve the crystallinity of these wafers.

The following treatment procedures were carried out for each wafer surface.

Wafer 1: no polishing or etching, named W-1;
Wafer 2: polishing and no etching, (W-2);
Wafer 3: no polishing and etching for 10 sec, (W-3);
Wafer 4: polishing and etching for 10 sec, (W-4);
Wafer 5: polishing and etching for 30 sec, (W-5);
Wafer 6: polishing and etching for 10 sec after five days of Br-methanol solution preparation, (W-6).
Wafer 7: polishing, etching for 10 cec and thermal annealing for five days at 100 °C prior to gold deposition, (W-7); and
Wafer 8: no polishing, etching for 10 sec and thermal annealing for five days at 100 °C prior to gold deposition, (W-8).

Previously, the surface of all eight wafers were examined by optical microscopy (OM) technique, before (no polishing or etching) and after each respective treatment described above. Subsequently, an Au thin layer was deposited on the surface of each wafer in order to make it conductive and able to perform the scanning electron microscopy (SEM) for surface quality analysis. The evaluation of the same surface before and after treatment was not possible to be carried by SEM because the surface could be affected in the Au removal.

To prepare the TlBr wafers as radiation detectors, 0.12-mm diameter Pd wires were attached to Au electrodes using a colloidal graphite suspension. The detector was assembled inside an aluminum box coupled to the Amptek A250 charge sensitive preamplifier. The conventional electronic setup, including the Ortec 556 voltage power supply, Ortec 450 amplifier and an oscilloscope, was used to evaluate the radiation response of each detector. The pulse height spectra were analyzed using an EG&G Ortec model 918A multichannel analyzer and ^{241}Am (59.5 keV) gamma radiation source. The source was placed outside the Al box, about 1 cm from the detector. The measurements were performed using the same set up and conditions for all prepared TlBr detectors, namely, bias of 100 V, shaping time of 3 μs, amplifier gain of 500 and collecting electrons. The linearity of the detector response in function of the source energy was evaluated using ^{241}Am (59.5 keV), ^{133}Ba (80 keV) and ^{57}Co (122 keV) gamma sources.

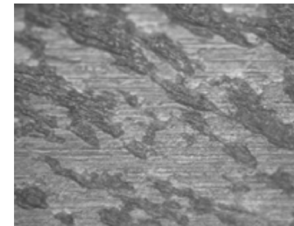

Fig. 2. OM micrograph of TlBr crystal (X20) no polishing or etching :W-1.

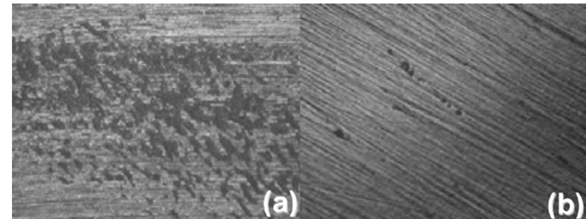

Fig. 3. OM micrograph of TlBr crystal (X20) (a) no polishing or etching and (b) after polishing: W-2.

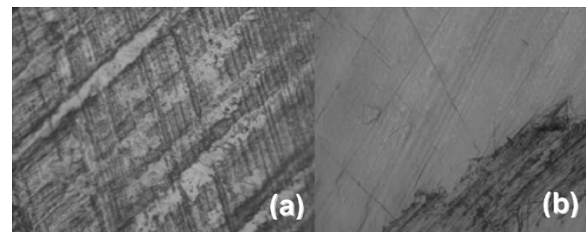

Fig. 4. OM micrograph of TlBr crystal (X20) (a) no polishing or etching and (b) after etching for 10 s: W-3.

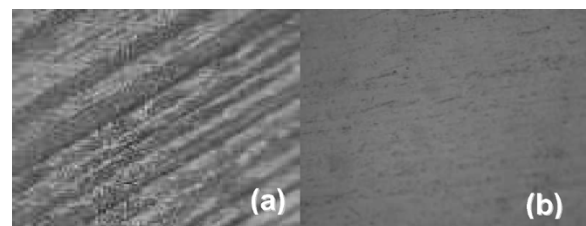

Fig. 5. OM micrograph of TlBr crystal (X20) (a) no polishing or etching and (b) after polishing and etching for 10 s: W-4.

III. Results and Discussion

Figs. 2 –9 show the TlBr wafer surfaces before and after each treatment by optical microscopy technique. All 8 wafers presented similar surfaces before treatment. Although the image resolution is low, a smoother and more uniform surface can be observed after the treatments.

Figs. 10 –13 show the SEM micrographs of each TlBr wafer surface in their final treatments. Each wafer was thoroughly examined and its uniformity was verified. As it can be seen from

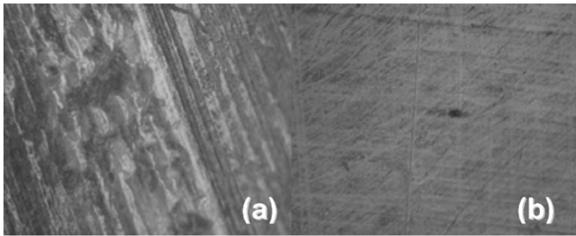

Fig. 6. OM micrograph of TlBr crystal (X20) (a) no polishing or etching and (b) after polishing and etching for 30 s: W-5.

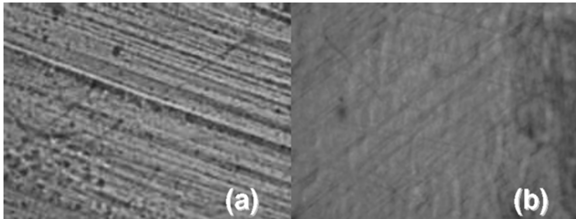

Fig. 7. OM micrograph of TlBr crystal (X20) (a) no polishing or etching and (b) after polishing, etching for 10 sec after five days of Br-methanol solution preparation: W-6.

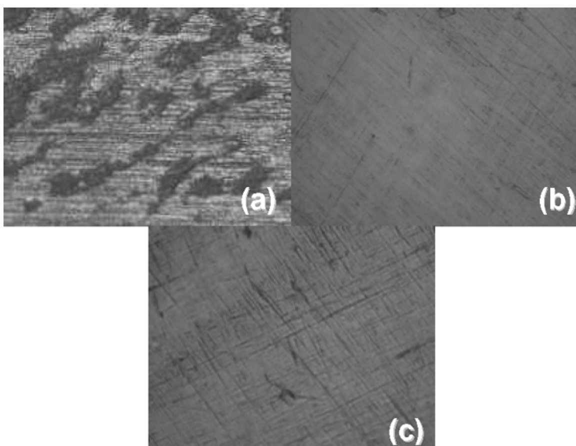

Fig. 8. OM micrograph of TlBr crystal (X20) (a) no polishing or etching, (b) after polishing, etching for 10 s, and (c) after polishing, etching for 10 sec and annealing for five days: W-7.

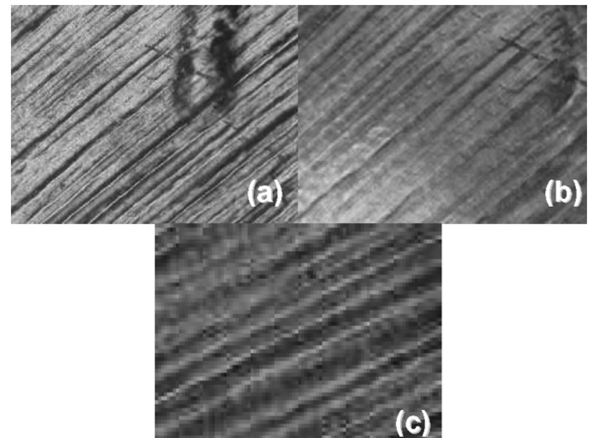

Fig. 9. OM micrograph of TlBr crystal (X20) (a) no polishing or etching, (b) after etching for 10 s, and (c) after etching and annealing for five days: W-8.

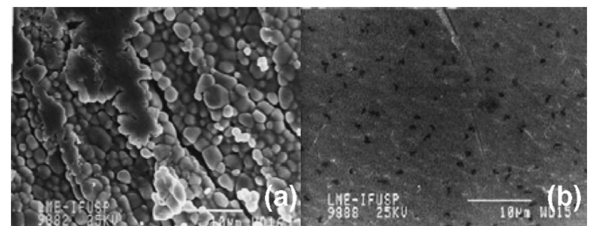

Fig. 10. SEM micrograph of TlBr crystal (X3500) (a) no polishing or etching: W-1, and (b) polishing and etching for 10 s: W-4.

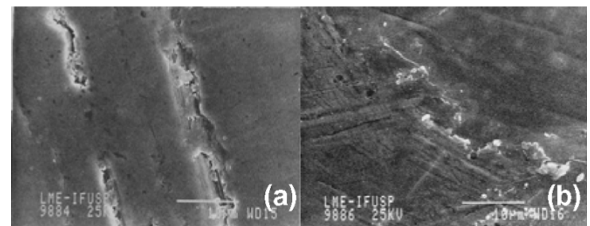

Fig. 11. SEM micrograph of TlBr crystal (X3500) (a) polishing and no etching: W-2 and (b) no polishing and etching for 10 s: W-3.

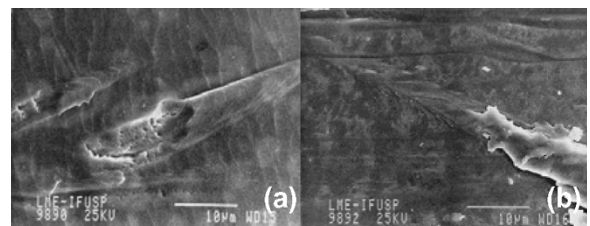

Fig. 12. SEM micrograph of TlBr crystal (X3500) (a) polishing and etching for 30 s.: W-5 and (b) polishing and etching for 10 s after five days of Br-methanol solution preparation: W-6.

these figures, the images obtained in the SEM micrograph evaluation present a better resolution compared to that of the optical microscopy. However, as this technique requires the Au deposition on the surface, it is impossible to evaluate the same surface before and after each treatment.

The TlBr morphology and defects caused by diamond saw on the crystal surface W-1 during the cutting can be observed in Fig. 10(a). This surface was not polished or etched.

As the Knoop hardness of TlBr is of 12 units, the plastic deformation can occur during the cutting and polishing of the small thickness crystalline wafers. The manual polishing was carried slowly, aiming to reduce the risks of a deep scratch or chips, as well as other major defects caused by mechanical processing. The chemical etching was performed to remove strains and defects in the slices. As it can be observed in Figs. 10(b)–(13b), there are significant differences in the resulting surfaces.

In some surfaces, the remainder scratches of the polishing process were kept visible. In the case of the wafer W-6, a Br-methanol solution prepared five days before was used for etching. Apparently, the etching action for wafer W-6 was weaker compared to that of W-4, as seen in Figs. 12(b) and 10(b), respectively. To verify if it was caused by the Br degradation, a chemical study was carried out after 0, 5, 10, 15, 20 and 30 days of the Br-methanol solution preparation. The results showed a gradual loss of about 1.1% of Br after five days and

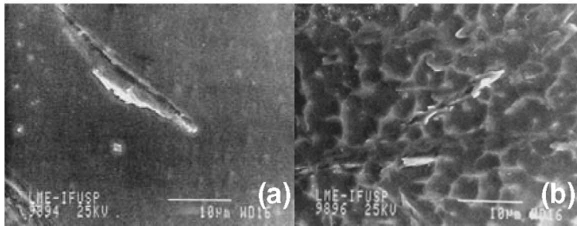

Fig. 13. SEM micrograph of TlBr crystal (X3500) (a) polishing, etching for 10 s and annealed for five days: W-7 and (b) no polishing, etching for 10 s and annealed for five days: W-8.

14% after 30 days. Thus, the remainder scratches in the W-6 were not due to a Br weaker action only, but probably caused by the cracks, resulting from stress during the growth and slicing.

Besides, the information of the Br degradation in the solution used is important, since the preparation of this solution is a hard and dangerous task, due to the Br toxicity. This study demonstrated that the Br-methanol solution is not necessary to be prepared at each chemical treatment, being possible to use it for a longer time.

Other wafer surfaces showed little fractures; probably caused during the cutting, which was evidenced after the treatment, as we can observe in Figs. 11(a)–13(a). In the W-4 [Fig. 10(b)], small holes or hollows were observed, but very shallow, which not affected abruptly the detector performance.

The difference in the resulting surface after thermal annealing can be seen in Fig. 13(a) and (b) compared to surfaces without the annealing. The W-7 [Fig. 13(a)] showed better uniformity in the surface, while in the W-8 [Fig. 13(b)] it was observed a surface similar to W-1 [Fig. 10(a)], with an increase of the grains. Both W-7 and W-8 were submitted to the same annealing time, but no polishing was made in the Wafer 8. This suggests that the polishing process influence considerably in the surface quality.

The performance of each wafer was evaluated by detector response. Fig. 14 presents the pulse height spectra of the wafers under ^{241}Am (59.5 keV) gamma radiation excitations, while Table I summarizes the pulse height and resolution values for each wafer. The pulse height values were determined from the inference of the peak position in the spectrum. As it can be observed in Fig. 14, the 59.5 keV peak positions were different for each detector. This may be attributed to the influence of the TlBr wafer surface quality in the charge carrier collection of the detector. The more the charge carrier is collected, the peak position is displaced to a higher channel number in the spectrum. The higher the peak position, the higher the pulse height. Consequently, this detector has a better radiation detection efficiency.

For a bias of 100 V, the detector produced from the wafer polished, etched and annealed (W-7) presented the best results of pulse height and resolution, as it can be seen in Fig. 14 and Table I. Comparable resolution values were obtained for detectors polished and etched at 10 and 30 s (W-4 and W-5), however improvement in the pulse height results are obtained by annealing. The pulse height of the W-7 detector was around three times higher than that found in W-4 and W-5. On the other hand, the detector W-6 presented a poorer resolution compared to that of the other detectors polished and etched, W-4 and W-5. This may be attributed to the remainder scratches of polishing process, visible in Fig. 12(b).

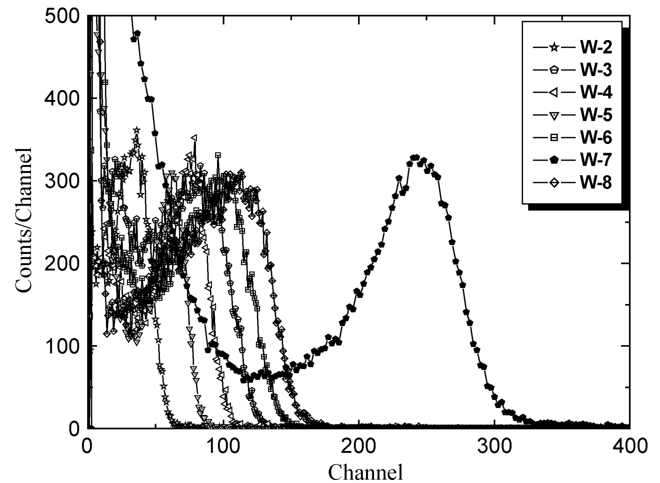

Fig. 14. ^{241}Am spectrum obtained from TlBr detectors prepared at different procedures. Maximum pulse height values are indicated in Table I.

TABLE I
PULSE HEIGHT AND ENERGY RESOLUTION VALUES OF THE EIGHT DETECTORS PREPARED BY DIFFERENT PROCEDURES: EXPERIMENTAL UNCERTAINTIES FOR RESOLUTION ARE 15%

Detector	Pulse Height	Resolution (%)
W-1	-----	-----
W-2	36	66
W-3	79	54
W-4	78	33
W-5	73	27
W-6	100	45
W-7	245	26
W-8	110	44

The better results obtained for detector W-8 compared to the detector W-3 indicate that annealing improves the detector performance, supporting the results observed for W-7, in which a substantial enhancement was obtained compared to other wafers submitted to the same treatment, without annealing (W-4 and W-5).

The results obtained for W-2 may be due to the defects and no-uniformity of the wafer surface, as it can be seen in Fig. 11(a). For the W-1 detector, surface without polishing or etching [Fig. 10(a)], it was possible to observe the radiation response, although no energy photopeak was obtained in its spectrum.

Fig. 15(a) presents the pulse height spectra of the W-7 detector under ^{241}Am (59.5 keV), ^{133}Ba (80 keV) and ^{57}Co (122 keV) gamma radiation excitations. A good linearity of the energy in function of the pulse height is shown in Fig. 15(b).

The importance of the thermal, chemical and mechanical treatments was demonstrated from the results obtained in this work. However, further studies should be carried out in order to have the accurate information on the contribution of each one of the several variables that can affect the surface uniformity. Besides, the experiments performed to verify the influence of the surface quality in the detector response and the structural defects, like chemical impurities, have been studied. The influence of chemical impurities on TlBr detector performance was shown in our previous work [11]. Comparing the resolution found in that work to the one obtained in this study, an improvement in the resolution was achieved for the detector with surfaces treated by more suitable procedures (W-7).

Nevertheless, to obtain a better resolution, a complete charge collection is necessary [12], what was not completely observed

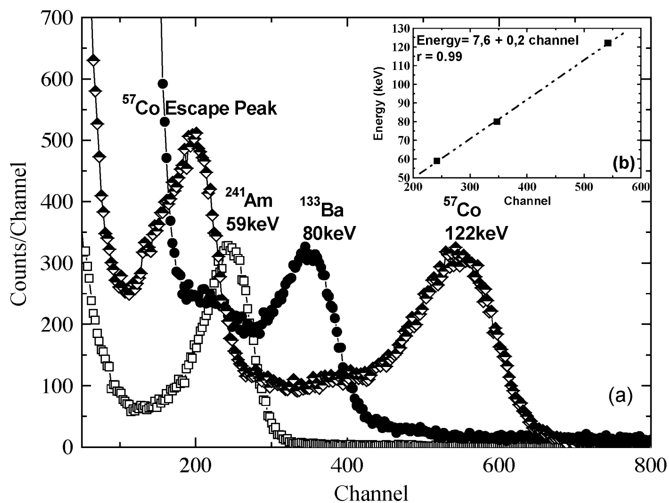

Fig. 15. (a) ^{241}Am, ^{133}Ba and ^{57}Co spectra obtained from W-7 detector. (b) Energy fitting of calibration curve.

in our measurements, not even for W-7. The energy resolution was deteriorated by the tail on the lower energy side of the peak, owing to the incomplete charge carrier collection. One of the causes of the charge trapping is believed to be a direct consequence of the relative softness of TlBr. According to Owens *et al.* [13], [14], any mechanical treatment, like cutting and polishing, generates a high concentration of intrinsic structural defects by local deformation, limiting the performance of a TlBr detector. Therefore, careful handling and suitable surface treatment procedures are necessary for detectors production.

In the recent literature [1], [4], [13], it is observed that, despite considerable performance improvement in the TlBr detectors, several problems remain limiting the progress. The best radiation response has been achieved at low temperatures. The latest results obtained with this detector [4] have been achieved at an optimal temperature range from 0 °C to −30°C. However, our studies are being carried out toward a direct application at room temperature, without cooling system.

Despite not having accomplished an optimum spectroscopic resolution, for applications where a radioisotope with well-known energy is used, like in surgical probes for nuclear medicine, the pulse height result, as well as the resolution obtained for the developed TlBr detector showed to be suitable. Another important parameter that should be evaluated for this application is the detector stability. The decrease in the leakage current was observed along the measurement, accompanied by the deterioration in the energy resolution. This behavior may be attributed to the polarization effect [1], [12]–[14]. Further studies are required to establish the optimal surface processing conditions and the detector stability.

IV. Conclusion

All wafers presented similar morphology before surface treatment and an improvement in the uniformity of the crystalline surface was observed after the treatment in the resulting image from optical microscopy evaluation. The images obtained by the SEM micrograph analysis presented a better resolution, revealing also the cracks and/or scratches in the surface.

The best result of radiation response was found for the detector W7, which was polished, etched and annealed. Substantial improvement in the pulse height value and in the energy resolution was achieved with the annealing. A good linearity of the detector response in function of the gamma source energy was found. On the other hand, the wafer without polishing or etching resulted in the decrease of the charge collection efficiency and no spectrometric results were obtained. These results demonstrate the need of a better understanding of the effects of surface processing and crystalline defects.

The importance of polishing and etching in the TlBr crystalline surfaces, for application as a radiation detector, was demonstrated by the spectrometric results.

Acknowledgment

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