LATVIAN JOURNAL OF PHYSICS AND TECHNICAL SCIENCES
2008, N 3
10.2478/v10047-008-0012-8

SOLID STATE PHYSICS

SURFACE PROCESSING OF TlBr CRYSTALS FOR X- AND γ-RAY DETECTORS

M. Shorohov[a,b], F. Muktepavela[b], J. Maniks[b]

[a]Baltic Scientific Instruments,
26 Ganibu dambis Str., LV-1005 Riga, LATVIA

[b]Institute of Solid State Physics, University of Latvia,
8 Kengaraga Str., LV-1063, Riga, LATVIA

A procedure for surface processing of TlBr crystals to be applied as X-and γ-ray detectors has been developed, providing removal of a mechanically destroyed surface layer by deep chemical etching, allowing the surfaces of good topography and thus the detectors with high energy resolution and stability to be obtained in a repeatable way. The surface quality and structural changes in the near-surface layer are estimated by the optical microscopy and indentation hardness technique.

Key words: *radiation detectors,* TlBr *crystals, surface processing, micro-hardness.*

1. INTRODUCTION

In recent decades, an increasing demand has been observed for new types of X- and γ-ray detectors based on wide-gap semiconductor compounds such as cadmium telluride, gallium arsenide and thallium bromide [1, 2]. TlBr is a promising detector material because of its excellent stopping power for hard X- and γ-rays. The wide bandgap of TlBr permits the low-noise operation of the device at room temperature.

Numerous studies on TlBr as a radiation detector material have been reported recently (see, e.g. [3–10]). It has been established that the purity of raw material, the conditions of crystal growth, crystal processing and making of metal electrodes generally limit the TlBr detector performance. Every stage introduces crystal defects and imperfections that affect the sensitivity and energy resolution of the detector. Much effort was made for improving the purity of TlBr crystals and optimizing the growth methods [3–8]. However, only few reports are devoted to the problems of the surface quality, which strongly affects TlBr application as a radiation detector. The manufacturing of detectors includes crystal cutting, grinding, polishing and chemical etching. However, TlBr is a soft material and its mechanical processing leads to generation of dislocations, vacancies and other structural defects, which affect the electrical resistance, carrier diffusion and trapping, and deteriorate the quality of detectors [11–13]. Depending on the technique of mechanical processing, the depth of the mechanically destroyed layer varies from several tens or hundreds of micrometres up to a millimetre or even greater [12, 14]. The development of the methods for surface treatment in order to obtain high-quality defect-free surfaces of detector crystals is an actual task.

In this work, the procedure of surface processing of TlBr single crystals is developed, which ensures removing the mechanically destroyed surface layer in a controllable way. The surface quality and structural changes in the near-surface layer are estimated by the optical microscopy and indentation hardness technique. The spectrometric performance of detectors is studied.

2. EXPERIMENTAL

For the experiments, TlBr single crystals of 99.99% purity, grown from melt by the Bridgman–Stockbarger method (provided by GIREDMET, Moscow, Russia) were used. Several series (A, L and S) of samples obtained under different growth conditions were investigated. The crystals were cut into slices of thickness ~ 2 mm and of area 5×5 mm^2 using a diamond impregnated wire saw (diameter 0.01″).

A freshly prepared mixture of HBr and high-purity ethyl alcohol (1:10) was used for the chemical etching of crystals. The surface morphology and the microstructure of the crystals were controlled using an optical microscope.

The indentation hardness – as a structure-sensitive technique – was employed for characterization of the crystals and detection of the work-hardened surface layer. The microhardness tests were performed with a square-based Vickers pyramid as the indenter. Vibration damping allowed accurate measurements in the 3.2–500 mN load range. The microhardness H was determined as equal to $1.854\ P/d^2$, where P denotes the load and d is the diagonal length of indentation measured using optical microscopy. For each hardness data point, three impressions were made reaching an accuracy of about 7%.

The thickness of the damaged near-surface layer was estimated from the depth profiles of hardness obtained by variation of the applied load [15]. The indentation depth at each load was attained as $h = d/7$.

The gold or indium electrodes, 4 mm in diameter, were formed on the crystal surface by vacuum deposition. The spectral performance of detectors was studied using ^{55}Fe, ^{57}Co, ^{137}Cs and ^{241}Am γ-ray sources. The detectors were tested in a vacuum chamber through a Be window. The output signals were processed by a MULTISPECTRUM multichannel analyzer. The spectrometric characteristics of the detectors were measured in the temperature range of 230–300 K.

3. RESULTS AND DISCUSSION

3.1. Characterization of the crystal quality

Thallium bromide is a semiconductor compound with a CsCl-type simple cubic crystal structure, which exhibits advantageous for detector applications physical properties, such as the high atomic number (81 for Tl and 35 for Br), high density (7.5 g/cm^3), wide bandgap (2.86 eV) and comparatively low melting temperature (723 K).

The structural defects in TlBr single crystals were studied using optical microscopy. The structure was visualized by chemical etching of samples. The investigation has shown that TlBr crystals have regions with imperfect macro- and microstructure appearing in the growth process. The main growth defects were a block structure of the crystal and the inclusions of impurity phases and decomposition products of TlBr (Fig. 1, *a–b*). In some cases, the grain boundaries were

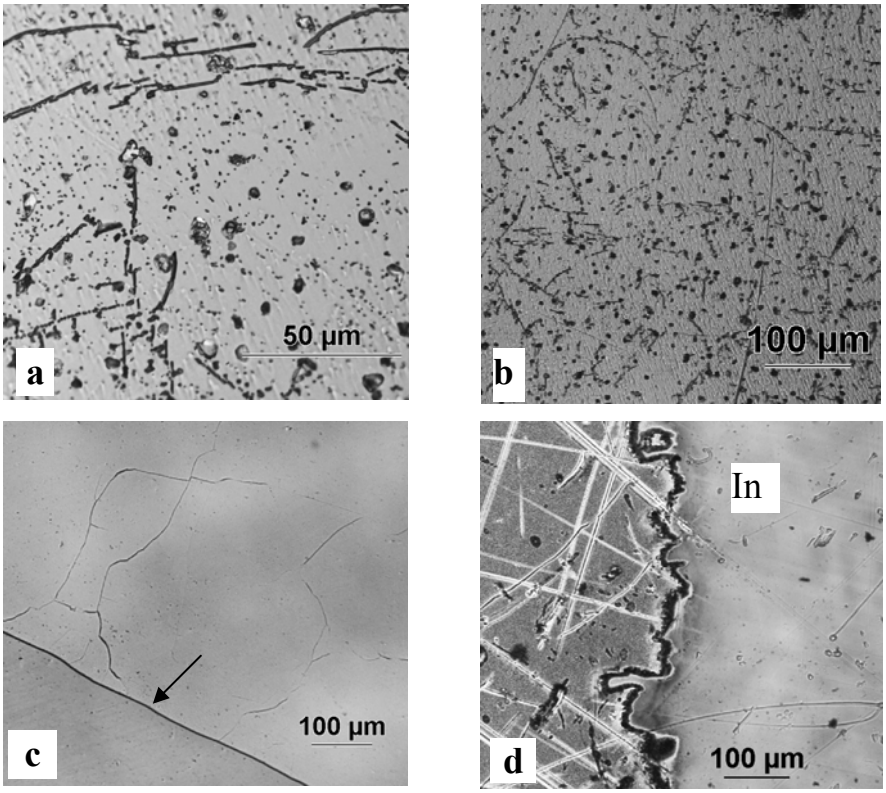

Fig. 1. A view of the impurity phases (*a*, *b*), grain boundaries (*c*) and indium electrode film (*d*) on the etched surface of TlBr.

observed (Fig. 1*c*). The grown-in and deformation-induced structural defects serve as carrier traps and deteriorate the electrical properties of crystals [16]. Since the room temperature corresponds to 0.4 T_m (where T_m is the melting temperature), the diffusion and related processes are facilitated. Dislocations and other imperfections serve as channels for fast diffusion and affect the growth of impurity phases, adhesion and chemical reactions on the interface between TlBr and the metal electrode that could worsen the quality of detectors. Over the defected surface areas, the surface structure and morphology of the metal electrode film is modified (Fig. 1*d*).

The single crystal areas without visible macrodefects were selected for preparation of samples.

3.2. Surface processing

The samples were obtained by cutting the crystal into several slices using a diamond wire saw. To minimize the surface damage, the cutting procedure was performed at a low load and a low cutting velocity in water as a cooling medium. A typical view of the crystal surfaces after cutting is shown in Fig. 2*a*. The traces of cutting are clearly seen. The measurements of the surface hardness after cutting showed remarkable effect of work hardening. The Vickers microhardness of the virgin crystals provided by GIREDMET was in the range from 50 to 90 MPa depending on the growth conditions (Fig. 3). However, TlBr is a soft and highly plastic material, in which the dislocations and other intrinsic structural defects are

easily formed under mechanical treatment. The hardness of surfaces after cutting increased from the average numbers of about 70 up to 180 MPa. The thickness of the work-hardened surface layer was estimated using the extrapolation of log (*H*) – log (*h*) curves to the hardness of a virgin crystal as offered in [15]. The results showed that the depth of the mechanically destroyed surface layer, even under highly accurate conditions of cutting, reaches at least 20 μm. The depth of the surface layer enriched with point defects is even higher. As shown in [17], the vacancy type defects extend in a single crystal more than 150 μm from the cut surface. In severe conditions of cutting by abrasive discs, the damaged layer on TlBr reaches about 1 mm [12].

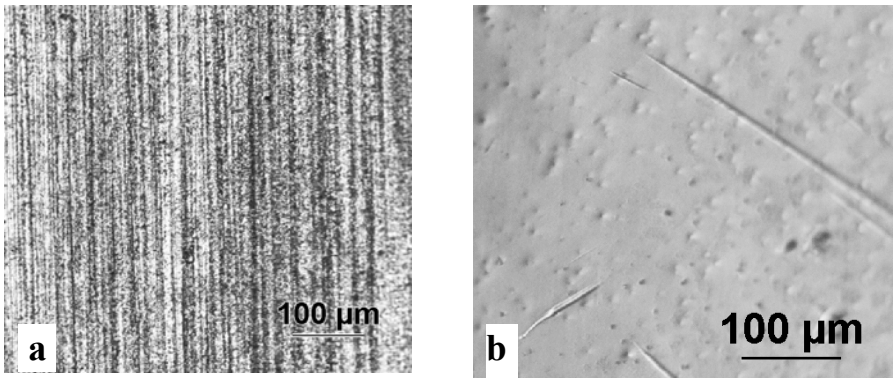

Fig. 2. Optical image of TlBr surfaces after cutting (*a*) and after subsequent chemical etching for 20 min (*b*).

The thermal or hydrothermal annealing procedures are commonly used for structural homogenization and removal of the deformation-induced structural defects in solids. However, in the case of TlBr the annealing procedure was complicated and left residual defects, whose removal required additional mechanical and chemical surface treatments [12].

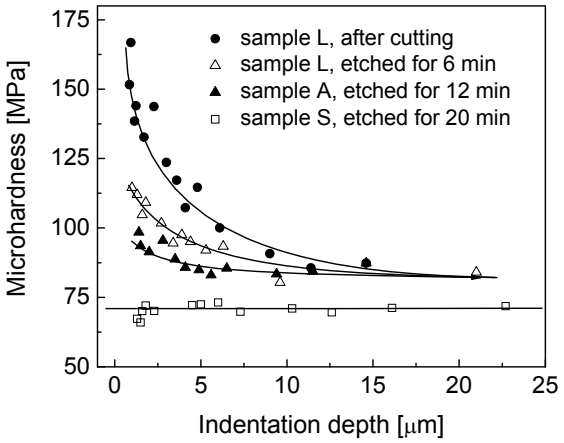

Fig. 3. The surface hardness of TlBr as a function of the indentation depth after different surface treatments.

In the present study, the cutting scum and destroyed surface layer were removed by chemical etching. No mechanical treatments, such as grinding and polishing by abrasives, were used in the further processing of surfaces. Figure 3 shows the depth profiles of hardness at different stages of chemical etching. The etching for 6 min and 12 min reduces the surface hardness. However, even the reduced hardness still exceeds that for a virgin crystal. This means that the mechanically destroyed surface layer is removed only partially. The full removal of the work-hardened surface layer required etching for about 20 min. The etched surfaces were smooth and showed only a small amount of structural inhomogeneities (Fig. 2*b*). The results for different sample series (A, L and S) gave similar results and confirmed that the offered surface processing ensures producing surfaces of a good topography and microstructure as well as low and uniform microhardness in a repeatable way.

It is well established that chemical etching provides high cleanliness of surfaces. As shown by X-ray photoelectron spectroscopy of etched surfaces of pure TlBr, the only contaminants in small amounts are carbon and oxygen [5], which are commonly observed foreign elements on solid surfaces.

3.3. Spectral performance of detectors

The detectors were produced by depositing metal electrodes on both surfaces of the crystal. Gold or indium were chosen as electrode materials in order to minimize the ageing phenomena on the interface between the crystal and the metal film [18, 19].

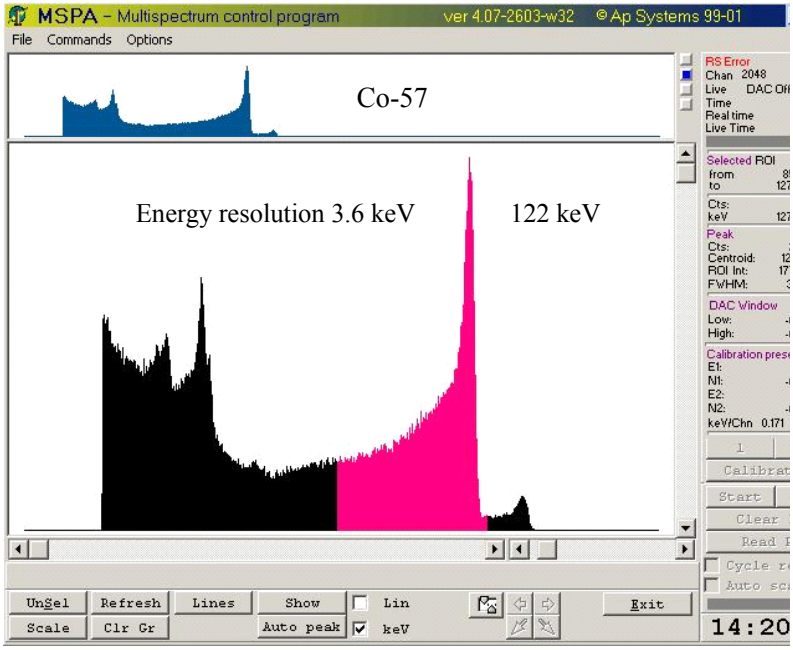

Fig. 4. ^{57}Co spectrum obtained with a TlBr detector at room temperature.

Figure 4 demonstrates ^{57}Co spectrum obtained with a TlBr detector at room temperature. The detector exhibits ~ 20% higher energy resolution compared with

the earlier results [20] and shows a good stability of the parameters during the testing procedure.

Comparison of the results for different sample series (A, L and S) exhibiting different hardness shows that the hardness value plays no decisive role in the detector quality, whereas the removal of the mechanically destroyed surface layer is an obligatory condition for obtaining the detectors with a high energy resolution and stability.

4. CONCLUSIONS

In the present work, the surface processing of TlBr crystals for X-and γ-ray detector applications is developed, which allows us to produce surfaces of a good topography and structural uniformity. The mechanically destroyed and work-hardened surface layer is removed by chemical etching. The surface quality is controlled by the indentation hardness technique. Such preparation of crystal surfaces before deposition of the contact electrodes ensures repeatable properties, higher energy resolution and higher stability of the detectors.

ACKNOWLEDGMENTS

This study was supported by the European Regional Development Fund Project "New materials for Radiation Detectors" Nr. VPDI/ERAF/CFLA/05/ APK/2.5.1/000064/031/ and ESF.

REFERENCES

1. Zaletin, V.M. (2004). Development of semiconductor detectors based on wide-gap materials. *Atomic Energy, 97*, 773–780.
2. Owens, A., Bavdaz, M., Lisjutin, I., Peacock, A., Sipila, H. & Zatoloka, S. (2001). On the development of compound semiconductor thallium bromide detectors for astrophysics. *Nuclear Instruments and Methods in Physics Research A, 458*, 413–417.
3. Oliveira, B.D., Chubaci, J.F., Armelin, M.J.A. & Hamada, M.M. (2004). Purification and crystal growth of TlBr for application as a radiation detector. *Cryst. Res. Technol. 39*, 849–854.
4. Kozlov, V., Leskela, M., Prohaska, T., Schultheis, G., Stingeder, G. & Sipila, H. (2004). TlBr crystal growth, purification and characterization. *Nuclear Instruments and Methods in Physics Research A, 531*, 165–173.
5. Hitomi, K., Muroi, O., Matsumoto, M., Hirabuki, R., Shoji, T., Suehiro, T. & Hiratate, Y. (2001). Recent progress in thallium bromide detectors for X- and c-ray spectroscopy. *Nuclear Instruments and Methods in Physics Research A, 458,* 365–369.
6. Hitomi, K., Onodera, T. & Shoji, T. (2007). Influence of zone purification process on TlBr crystals for radiation detector fabrication. *Nuclear Instruments and Methods in Physics Research A, 579,* 153–156.
7. Kozlov, V., Leskela, M. & Sipila, H. (2005). Annealing and characterisation of TlBr crystals for detector applications. *Nuclear Instruments and Methods in Physics Research A, 546,* 200–204.
8. Kouznetsov, M.S., Lisitsky, I.S., Zatoloka, S.I. & Gostilo, V.V. (2004). Development of the technology for growing TlBr detector crystals. *Nuclear Instruments and Methods in Physics Research A, 531,* 174–180.
9. Kozlov, V., Leskela, M., Vehkamaki, M. & Sipila, H. (2007). Effects of metallization on TlBr single crystals for detector applications. *Nuclear Instruments and Methods in Physics Research A, 573,* 212–215.

10. Hitomi, K., Shoji, T. & Niizeki, Y. (2008). A method for suppressing polarization phenomena in TlBr detectors. *Nuclear Instruments and Methods in Physics Research A, 585*, 102–104.
11. Oliveira, I.B, Costa, F.E., Kiyohara, P.K. & Hamada, M.M. (2005). Influence of crystalline surface quality on TlBr radiation detector performance. *IEEE Transactions. Nuclear Science, 52*, 2058–2062.
12. Kozlov, V., Leskela, M., Kemella, M. & Sipila, H. (2006). Effects of polishing and etching on TlBr single crystals. *Nuclear Instruments and Methods in Physics Research A, 563*, 58–61.
13. Gostilo, V., Gryaznov, D. & Lisjutin, I. (2002). Technological limitations and processing-generated defects at the development of pixel and strip arrays. *Nuclear Instruments and Methods in Physics Research A, 487,* 13–18.
14. Engel, A. (2006). Contributions to the surface preparation of semiconductor materials of low hardness. *Kristall und Technik, 15*, 1439–1446.
15. Manika, I. & Maniks J. (1992). Characteristics of deformation localization and limits to the microhardness testing of amorphous and polycrystalline coatings. *Thin Solid Films, 208*, 223-227.
16. Kozorezov, A.G., Wigmore, J.K., Owens, A., Hartog, R., Peacock, A. & Al-Jawhari, H. A. (2005). Resolution degradation of semiconductor detectors due to carrier trapping. *Nuclear Instruments and Methods in Physics Research A, 546*, 209–212.
17. Hansen, H. E. & Petersen, K. (2006). Surface damage from diamond-saw cutting of high purity Mo studied by positrons. *Phys. Status Solidi* (a), *69*, 625–629.
18. Varchenya S.A., Simanovskis, A.A. & Stolyarova, S.V. (1988). Adhesion of thin metallic films to non-metallic substrates. *Thin Solid Films, 164*, 147–152.
19. Varchenya, S.A., Simanovskis, A.A. & Stolyarova, S.V. Degradation mechanisms of the contact between metallic films and alkali halide crystals. *Thin Solid Films, 192*, 73–78.
20. Gostilo, V., Owens, A., Bavdaz, M., Lisjutin, I., Peacock, A., Sipila, H. & Zatoloka, S. (2001). Single detectors and pixel arrays based on TlBr. *IEEE Nuclear Science Symposium and Medical Imaging, 4,* 2415–2419.

TlBr MONOKRISTĀLU VIRSMAS APSTRĀDE RENTGENA UN γ-STARU DETEKTORU IZGATAVOŠANAI

M. Šorohovs, F. Muktepāvela, J. Maniks

K o p s a v i l k u m s

TlBr monokristāli ir daudzsološs materiāls cieto γ- un rentgenstaru detektoriem astrofizikas u.c. vajadzībām. Darbā izstrādāta uz ķīmisko kodināšanu balstīta metode kristālu apstrādei, kura ļauj iegūt no deformācijas radītiem struktūras defektiem brīvas virsmas. Virsmu kvalitātes kontrolei izmantotas optiskās mikroskopijas un mikrocietības metodes. Izmantojot izstrādāto metodi, iegūti detektori ar augstu stabilitāti un enerģētisko izšķiršanas spēju.

04.05.2008.