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Advances in crystal growth, device fabrication and characterization of thallium bromide detectors for room temperature applications

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ABSTRACT

Thallium bromide (TlBr) is a promising room-temperature radiation detector candidate with excellent charge transport properties. However, several critical issues need to be addressed before deployment of this material for long-term field applications can be realized. In this paper, progress made towards solving some of these challenges is discussed. The most significant factors for achieving long-term performance stability for TlBr devices include residual stress as generated during crystal growth and fabrication processes, surface conditions, and the choice of contact metal. Modifications to the commonly used traveling molten zone growth technique for TlBr crystals can significantly minimize the stresses generated by large temperature gradients near the melt–solid interface of the growing crystal. Plasma processing techniques were introduced for the first time to modify the Br-etched TlBr surfaces, which resulted in improvements to the surface conditions, and consequently the spectroscopic response of the detectors. Palladium electrodes resulted a 20-fold improvement in the room-temperature device lifetime when compared to its Br-etched Pt counterpart.

1. Introduction

Thallium bromide (TlBr) is a promising room temperature wide bandgap semiconductor radiation detector material. Compared to other semiconductors, TlBr has higher photoelectric and total attenuation coefficients for gamma rays with energy greater than 20 keV [1]. The cubic crystal structure and fairly low growth temperature of this binary compound (480 °C) significantly simplifies the crystal growth process. Furthermore, TlBr is self-compensated, and shows high electrical resistivity (10^{10}–10^{11} Ω cm) without doping. These provide TlBr a distinctive advantage over other high melting temperature ternary semiconductors (such as CdZnTe). Extensive research has been done on purification of TlBr, mostly employing the zone refining technique; this process improves the charge transport properties by almost two orders of magnitude [2].

The long-term room temperature stability of TlBr radiation detectors is adversely influenced by the electro-diffusion of Br ions towards the anode under applied electric field. The electro-diffusion of Br ions (and to a lesser extent that of the less mobile Tl ions) influences charge collection in the detector and degrades the spectroscopic resolution of the device. More importantly, the diffusing Br ions can react with the contact metal and over time corrode it to the extent that the device fails. Two other factors which also influence the performance of the detectors are residual stress and surface condition of the detector before metallization. TlBr is a soft material and can undergo extensive plastic deformation during growth and in post-growth fabrication steps [3]. Crystalline defects on the crystal surface can act as nucleation sites for channels that accelerate the electro-diffusion of Br [4]. In this paper we report on computer simulation of a modification to the standard TMZ growth process aimed at reducing thermo-elastic stresses during growth. We will also discuss the effect of plasma etching on improving the surface of TlBr, and present data on long-term stability of TlBr detectors with Pt and Pd contacts.

2. Experiments

The detectors used in the experiments described in this paper were fabricated from ultra-high purity TlBr single crystals grown at CapeSym. The starting material undergoes a two-stage purification process. First, the charge is melted and passed through a quartz filter to remove impurities larger than 60 μm. The charge is then subjected to multiple zone refining passes at 5 mm/h. The purified TlBr charge material was then grown using traveling molten zone technique (TMZ) at a rate between 0.5 and 1 mm/h in dehydrating HBr atmosphere. Two different types of TMZ growth setups were used: flowing gas TMZ and closed ampoule TMZ. In the first process, crystals were grown in an open system where a

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Br-rich atmosphere was established by a flowing gas mixture containing HBr. The devices used in the experiments described in this paper were grown using this technique. In a different kind of the closed-ampoule runs, crystals were grown in a sealed ampoule in presence of HBr.

Plasma processing of TlBr devices was performed using a barrel-type low power plasma reactor. In this setup, the TlBr samples were placed in a quartz chamber with external semi-tubular electrodes. Ultra-high purity Argon was introduced into the chamber while RF was applied across the electrodes to generate plasma. The RF power source included a solid state oscillator operating at a frequency of 13.56 MHz. TlBr devices were placed horizontally on the plasma stage (as opposed to the vertical orientation used for larger diameter semiconductor wafers), which resulted in higher uniformity of the polishing process. In the radiation degradation experiments with Pd and Pt contacts, the metals were sputtered on the Br-etched TlBr surfaces with minimum exposure to the ambient.

3. Results and discussion

One of the primary causes of dislocations in semiconductor crystals is thermal stresses during crystal growth associated with unavoidable thermal gradients in the growing crystal. In the TMZ process, the heat of fusion and heat from the melt is transferred through the crystal to the ambient through radiation and gas convection, resulting in large temperature gradients close to the solidification front. The low thermal conductivity (k=0.586 $Wm^{-1}K^{-1}$ at 343 K) and the high thermal expansion coefficient (51×10^{-6}/°C at 300 K) result in high levels of thermal strain in the crystal. TlBr is a soft material with Knoop hardness value of 11.9, similar to that of refrigerated butter. The combined effect of large thermal strains and material's softness suggests that the growing crystal is highly susceptible to plastic deformation and massive dislocation multiplication. We have demonstrated the presence of residual stresses in the TlBr crystals [3], and have shown that plastic deformation and residual stresses can significantly influence the performance of TlBr devices. For example, stress significantly increases the polarization phenomena in the devices and irreversibly disrupts the internal electric field.

We have initiated a program to understand and control thermal stresses during growth of TlBr. As part of this program, we have developed a thermos-fluid model of the growth system. Fig. 1(a) shows a photograph of a standard TMZ furnace. Fig. 1(b) shows a modified furnace, where an afterheater is used to reduce temperature gradients, and thus thermal stresses, in the growing crystal. Fig. 1(c) is a solid model representation of the 3D model of the furnace in Fig. 1(b) used to calculate the temperature field in the furnace and the charge. The model of the TMZ process includes heat distribution in the heater, and conduction-dominated heat transfer through the charge material.

The conduction–radiation simulations were done in ANSYS FLUENT. The material properties used for this study are shown in Table 1. The volumetric heat generation in the heater(s) was adjusted to yield the observed melt zone width, with heat loss around the entire exterior of the furnace and ampoule by convection and radiation exchange with a sink temperature of 300 K.

Fig. 2(a) and (b) shows the temperature and temperature gradient distribution in the charge during growth in standard TMZ process respectively, and Fig. 3(a) and (b), those of the modified one. The temperature distribution in the heater assemblies is not shown for purposes of clarity. Simulation results clearly show that in standard TMZ, the crystal experiences extremely large temperature gradients immediately upon solidification. As at present, data on the high temperature elasto-plastic behavior of TlBr is not available, it is not possible to compare the stresses associated with these temperature gradients with critical stress levels in the crystal. However, the calculated large temperature gradients indicate presence of large driving forces for plastic deformation of the crystal during growth in standard TMZ. The largest temperature gradients occur next to the molten zone location of the growing crystal (delineated by a white isotherm at the melting point temperature). Results of Fig. 3 show that these gradients can be reduced on the crystal side with the addition of the after heater, by three–four times. Although quantitative comparison of prevailing stresses in the crystal with critical stress levels in TlBr is not possible at this point, our observations that the crystal stresses are extremely sensitive to handling and polishing, strongly suggest reduction of thermal stresses during growth is necessary. Whether or not the stress reduction achieved by the after heater is sufficient to substantially reduce the dislocation density and performance effecting stress will be assessed through crystal growth runs under various thermal conditions. Nevertheless, the after heater acts as an in-situ annealing station, which has been shown to reduce the residual stresses in the crystal [4].

The softness of the TlBr also complicates the post-growth device fabrication processes, introducing a large variability in the performance of TlBr devices. For example, in a series of room temperature lifetime tests performed on detectors fabricated from samples cut from adjacent regions in the crystal, the lifetime of 4 TlBr planar detectors processed through identical steps varied between 29 and 62 days. We believe this variability is primarily related to the polishing process which is conducted by hand. To date, hand polishing produces the best results, which in turn

Table 1
Material thermal conductivity values used in the simulations.

TlBr (melt and crystal)	0.586 W/m K
Fused quartz (ampoules)	1.4 W/m K
Heater	2 W/m K
Alumina (solid insulation)	0.045 W/m K@255 K, 0.11 W/m K@1033 K

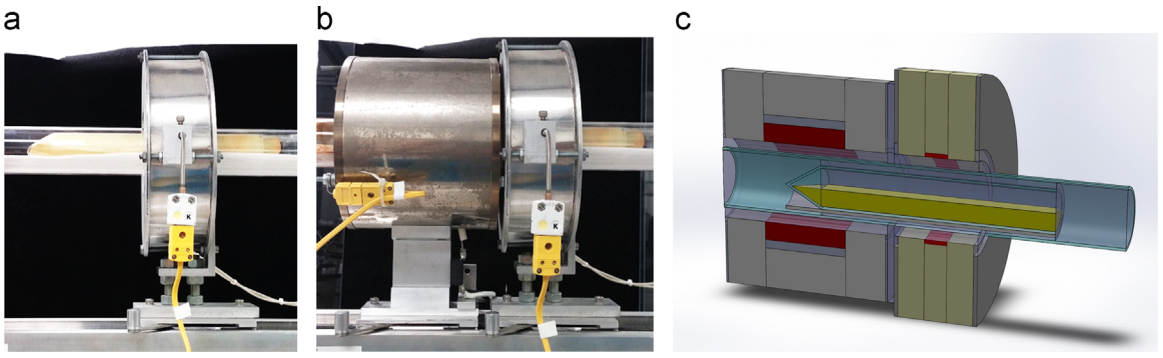

Fig. 1. (a) Standard TMZ furnace; (b) TMZ furnace with an after heater; and (c) simulation model of the TMZ heater and after heater, in a mid-growth position.

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