Functional Materials 17, No.2 (2010)

# TlBr: Carrier transport as influenced by defects and Tl ion migration

*V.Kazukauskas, A.Ziminskij,*
*G.Davidyuk**, *V.Bozhko**, *G.Mironchuk**

Semiconductor Physics Department and Institute of Materials Science and
Applied Research, Vilnius University, 3 Universiteto St, Lithuania
*Volyn National University, 13 Volya Ave., Lutsk, Ukraine

*Received October 7, 2009*

Photoelectrical and current transient properties of TlBr were investigated in the temperature region from 243 K up to 293 K, where the ionic conductivity effect changes significantly. A nonmonotonous conductivity variation with temperature has been identified, demonstrating a mobility-related maximum superimposed on a band-to-band generation conductivity growth. This maximum could be caused by the recharge of the scattering center at about 1.65 eV. Presence of such center was confirmed by the photocurrent spectra. From spectral dependences defect-related transitions at 0.55; 0.83, 1.1; 1.32 and 1.65 eV were identified, being dependent on sample prehistory, i.e., its excitation by light and/or voltage. The transient photocurrent kinetics have demonstrated a complex behavior that could be explained by the combined influence of electron generation/recombination processes superimposed upon the effect of ionic conductivity. The results indicate that ionic conductivity can take place also at 243 K, though its influence is less because of the thermally activated character.

Исследованы переходные фотоэлектрические и токовые свойства TlBr в температурной области от 243 до 293 К, где эффект ионной проводимости значительно изменяется. Обнаружено немонотонное изменение проводимости с температурой, включающее связанный с подвижностью максимум, накладывающийся на рост проводимости, обусловленный межзонной генерацией. Этот максимум может быть обусловлен перезарядкой центров рассеивания с энергией приблизительно 1,65 эВ. Присутствие таких центров подтверждается спектрами фототока. По спектральным зависимостям установлено наличие связанных с дефектами переходов при 0,55; 0,83; 1,1; 1,32 и 1,65 эВ, зависящих от предыстории образца, т.е. от его возбуждения светом и/или напряжением. Кинетика переходного фототока имеет сложный характер, что можно объяснить сочетанием влияния процессов генерации/рекомбинации электронов, накладывающихся на эффект ионной проводимости. Полученные результаты свидетельствуют, что ионная проводимость может иметь место также при 243 К, хотя ее влияние ослаблено вследствие ее термически активированного характера.

## 1. Introduction

Thallium bromide (TlBr) is an attractive and promising material for X- and $\gamma$-ray spectroscopy because of its wide bandgap (2.68 eV), high density (7.56 g/cm$^3$) and high atomic numbers (Tl:81 and Br:35) [1–3]. Such properties ensure a high photon stopping efficiency. The pixelated TlBr $\gamma$-ray detectors had demonstrated energy resolutions of 6.7 keV and 22.3 keV for 122 and 662 keV $\gamma$-rays, respectively [2, 3]. Nevertheless, one of the main problems still hindering practical applications of TlBr is its ionic conductivity, which is appreciably temperature-dependent [4] and causes instability of the device characteristics. This causes, e.g., degradation of spectroscopic performance because of the polarization phenomena if the devices are operated at the room temperature [2].

## 2. Experimental

TlBr crystals were grown by the Bridgman-Stockbarger method. The samples of about 4×3×1 $mm^3$ size provided with the evaporated gold contacts were investigated in the temperature region from 253 K up to 293 K, where the ionic conductivity effect changes significantly [4]. In order to prevent the long-living sample polarization and its degradation, low electric fields of less than 150 V/cm were applied. At 293 K, the sample conductivities were $(3–4)\cdot 10^{-10}\ \Omega^{-1}cm^{-1}$. The IV curves of the samples were symmetrical and linear, evidencing the suitability of the Au contacts.

## 3. Results and discussion

In the temperature region of 258–278 K, the conductivity demonstrated a sharp maximum (Fig. 1). It was superimposed on the conductivity growth due to the band-to-band generation having the activation energy of about $E_G/2$. This maximum could be mobility-related, as it is evidenced in Fig. 1. A similar conductivity behavior was revealed by impedance spectroscopy in [5], though we have not observed it in the samples with lower thermal activation energy of about 0.78 eV [6]. The maximum height and position were dependent on the sample prehistory (Fig. 2). Nevertheless, the maximum, once reached, did not vanish with time (inset in Fig. 2), though long current relaxations took place. Such relaxations might be due to either persistent conductivity in disordered materials [e.g., 7, 8] or ionic conductivity of TlBr.

The thermal activation energy of this mobility-related maximum was up to 1.65±0.15 eV in different samples, evidencing that it was rather caused by the recharge of the scattering center and not by weakening ionized impurity scattering.

The defect levels were investigated by the photocurrent spectra (Fig. 3). They were analyzed using Lucovsky photoionization model [9]:

$$I \sim n_M \Delta E_M^{0.5} (h\nu - \Delta E_M)^{1.5}/(h\nu)^3, \qquad (1)$$

where $\Delta E_M$ is the optical activation energy of the deep trap, and $n_M$ is density of the trapped carriers. A band-to-band generation starts at about 2.75 eV. The current drop at

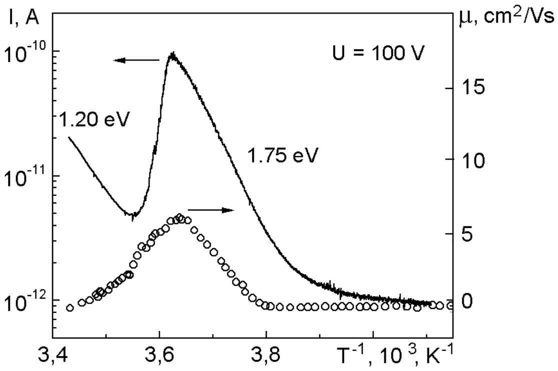

Fig. 1. Temperature dependences of the sample current and Hall mobility.

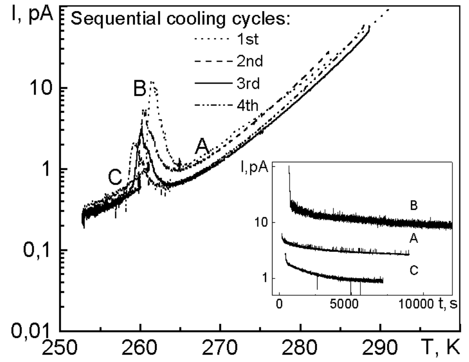

Fig. 2. Change of the current maxima position and height during subsequent cooling cycles. Inset: relaxation of the dark current at different temperatures as marked by the letters A–C.

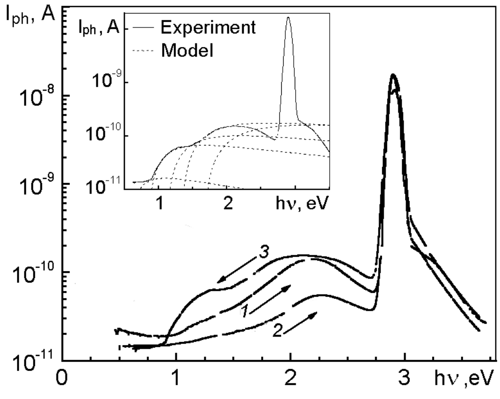

Fig. 3. Photocurrent spectra at 253 K. Inset: fitting of curve *3* by Eq.(1). Curve *1* was obtained after relaxation of the unbiased sample in the dark for 20 h. Curves *2* and *3* were measured after keeping the sample at 60 V bias at room temperature for 6 hs, followed by cooling it down and scanning spectra in different directions. Measurement directions are indicated by the arrows.

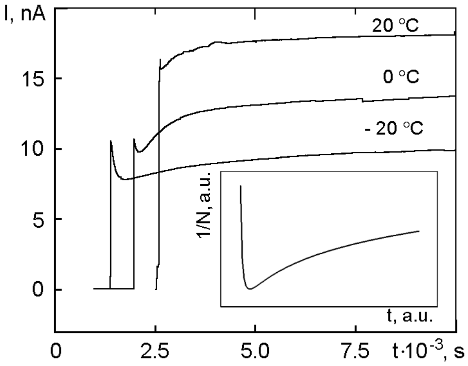

Fig. 4. Current transients at different temperatures, after the onset of the light excitation corresponding to the photoconductivity maximum. Curves are shifted in time for the sake of convenience. Inset: model curve, representing reciprocal number of atoms diffusing from a limited source depending on time — Eq.(2).

the high-energy side is associated with the increasing absorption and intensifying surface recombination. The fitting of the curves has revealed the following photoionization energies: 0.55; 0.83, 1.1; 1.32 and 1.65 eV. The latter value coincides with that obtained from Fig. 1, confirming presence of the defect level that can be neutralized, causing mobility growth. Typically, the defect bands in the region between 1 eV and 2.5 eV were dependent on sample prehistory. The defect-related shoulders at about 0.83 and 1.1 eV appear usually if the spectra were scanned starting from the higher quantum energies. Meanwhile, influence of the levels at 1.32 and 1.65 eV decrease usually as the sample was kept biased for several hours.

A similar complex defect structure was also revealed by photoluminescence in [10]. The luminescence in the range 1.5–2.0 eV was observed under X-ray excitation and was attributed to several recombination centers [10], meanwhile, the absorption band at 1.1 eV was observed in the short-living absorption spectra under pulsed electron beam excitation in [11] and it was explained to be due to hole trapped at cation vacancy ($Tl^{2+}Vc^{-}$). This center may arise if a hole is trapped at a pre-irradiation vacancy, as well as a result of the radiation-induced Frenkel pair formation ($Tl^{2+}Vc^{-}$ and interstitial $Tl_i^0$). Our results indicate that such a vacancy can also be light-induced, even though the light intensity from monochromator is low.

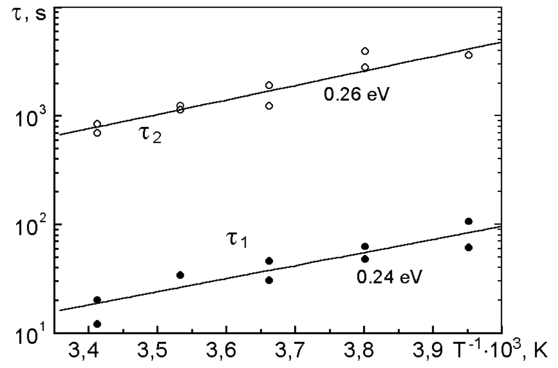

Fig. 5. Dependences of the averaged time constants $\tau_1$ and $\tau_2$, describing current decrease and the following growth, respectively.

Therefore, we have investigated the photocurrent transient effects.

The photocurrent kinetics were measured at different temperatures using excitation by the best absorbed light. Fig. 4 represents general and repeatable tendencies. A similar behavior, though less pronounced, was also observed without light excitation. A notable feature is the presence of two different trends. When the light is turned on, after the sharp jump, the current decrease starts, which is followed by the growth until saturation. These thermally activated processes followed the exponential dependences with the single time constants (Fig. 5). Though the time constants of current decay and its growth were differing by about two orders of magnitude, their thermal activation energy values of about 0.24–0.27 eV were the same within the experimental accuracy. Therefore, the photocurrent kinetics can be supposed to be caused either by two different competitive processes or by a single complex process. In the first case, the current decrease could be ascribed to the faster electronic process, i.e., trapping and/or recombination of light-generated carriers at the defect centers. This process could be similar to the known thermal quenching mechanism. The following current increase might be attributed to the growing ionic conductivity of $Tl^{+}$ ions, as observed in [5].

Nevertheless the similar thermal activation energies of both time constants point that they might be attributed to a single process. The similar non-monotonous behavior is typical of the diffusion from a limited material source [12]. In such case, the total number of extraneous atoms at a certain point is given by:

$$N = At^{-0.5}\exp(-B/t), \qquad (2)$$

where $A$ and $B$ are diffusion- and material-related constants.

A model curve in Fig. 4 depicts the inverse value of $N$. This can be explained, assuming that the transport is governed by electron and/or ion mobility, which is limited by a varying number of scattering centers as $\mu \sim 1/N$.

## 4. Summary and conclusions

We had investigated photoelectrical and current transient properties of TlBr in the temperature region from 253 K up to 293 K, where the ionic conductivity effect is pronounced. The sample conductivities at 293 K were about $(3–4)\cdot10^{-10}$ $\Omega$–1cm$^{-1}$.

The following peculiarities were revealed that could stand for both electronic and ionic conductivities. The non-monotonous conductivity variation with temperature was identified, demonstrating a mobility-related maximum that was superimposed on an intrinsic conductivity growth. This maximum could be caused by the recharge of the scattering center at about 1.65 eV. The presence of such a center was confirmed by the photocurrent spectra.

From the spectral dependences, several defect-related transitions at 0.55; 0.83, 1.1; 1.32 and 1.65 eV were identified, being dependent on sample prehistory, i.e., its excitation by light and/or voltage. The defect-related shoulders at about 0.83 and 1.1 eV intensify usually if the spectra were scanned starting from the higher quantum energies. Meanwhile, influence of the levels at 1.32 and 1.65 eV usually decreases if the sample is kept biased for several hours.

The photocurrent kinetics had demonstrated a complex structure where its decrease was changed by the growth. The thermal activation energy of the time constants for both processes was found to be 0.24–0.27 eV. Such a complex behavior could be explained either by the combined trapping and/or recombination of light-generated carriers to the defect centers followed by the growing ionic conduction, or by the variation of the ion diffusion-related scattering in time. Our results, in contrast to [4], demonstrate that the ionic conductivity may take place also at 253 K, though its influence is less because of the thermally activated nature. Moreover, even low intensity intrinsic light excitation might be effective in capacitating ionic conductivity.

*Acknowledgements.* This work was supported by the Lithuanian and Ukrainian Ministries of Education and Science and the Research Council of Lithuania (projects № TAP-21 and TAP 63. The samples were kindly provided by Brucker Baltic (Dr.V.Gostilo and Dr.M.Shorohov). A.Ziminskij acknowledges Student Research Fellowship Award from the Research Council of Lithuania.

## References

1. P.J.Sellin, *Nucl.Instrum.Meth.Phys.Res. A*, **513**, 332 (2003).
2. K.Hitomi, M.Matsumoto, O.Muroi et al., *IEEE Trans.Nucl.Sci.*, **49**, 2526 (2002).
3. K.Hitomi, M.Matsumoto, O.Muroi et al., *J. Cryst.Growth*, **225**, 129 (2001).
4. T.Onodera, K.Hitomi, T.Shoji, *Nucl.Instrum.Meth. Phys. Res. A*, **568**, 433 (2006).
5. J.Vaitkus, J.Banys, V.Gostilo et al., *Nucl.Instrum.Meth. Phys. Res. A*, **546**, 188 (2005).
6. V.Kazukauskas, A.Jurgilaitis, *Mol.Cryst.Liq. Cryst.*, **485**, 825 (2008).
7. B.I.Shklowskii, A.L.Efros, *Zh.Eksp.Teor.Fiz.*, **61**, 816 (1971).
8. M.K.Sheinkman, A.J.Shik, *Phys.Tekh.Polupr.*, **10**, 209 (1976).
9. G.Lucovsky, *Solid State Comm.*, **3**, 299 (1965).
10. L.Grigorjeva, D.Millers, *Nucl.Instrum.Meth. Phys. Res.B*, **191**, 131 (2002).
11. L.Grigorjeva, D.Millers, *Electrochemi Soc. Proc.*, **25**, 438 (1998).
12. P.V.Pavlov, A.V.Khohlov, Solid State Physics, Vysshaya Shkola, Moscow, 1985 [in Russian].

# TlBr: Вплив дефектів та міграції іонів Tl на транспорт носіїв

***В.Кажукаускас, А.Зиминський, Г.Давидюк, В.Божко, Г.Мирончук***

Досліджено перехідні фотоелектричні та токові властивості TlBr у температурному діапазоні від 243 до 293 К, де ефект іонної провідності значно змінюється. Виявлено немонотонну зміну провідності з температурою, яка включає пов'язаний з рухомістю максимум, що накладається на зростання провідності, зумовлене міжзонною генерацією. Цей максимум може бути обумовлений перезарядкою центрів розсіювання при енергії приблизно 1,65 еВ. Присутність таких центрів підтверджується спектрами фотоструму. Із спектральних залежностей встановлено наявність зв'язаних з дефектами переходів при 0,55; 0,83; 1,1; 1,32 та 1,65 еВ, залежних від передісторії зразка, тобто від його збудження світлом та/або напругою. Кінетика перехідного фотоструму має складний характер, що можна пояснити поєднанням впливу процесів генерації/рекомбінації електронів, які накладаються на ефект іонної провідності. Одержані результати свідчать, що іонна провідність може мати місце також при 243 К, хоча її вплив послаблений внаслідок її термічно активованого характеру.