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γ-Radiation Stimulated Structural Transition of Monoclinic $TlInS_2$ to Hexagonal Phase

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Temperature dependent dielectric function and conductivity, as well as room temperature photoconductivity have been investigated on monoclinic $TlInS_2$ subjected to γ-radiation in a wide range of radiation doses. The structural changes have been detected by XRD performed after every stage of γ-irradiation. Frenkel pairs (vacancies and interstitial sulfur atoms) have been assumed to appear in $TlInS_2$ at irradiation doses below 100 Mrad through well-known Klinger's "residual charged impurity assisted electrostatic" mechanism. These defects eventually lead to the formation of neutral impurity complexes responsible for the observed sharpening of the anomalies in dielectric function and conductivity at the temperature of the well-known ferroelectric phase transition in $TlInS_2$. The last anomalies become smeared out at irradiation doses above 200 Mrad. Finally, the transformation of the monoclinic $TlInS_2$ to the one with hexagonal structure has been witnessed in a thin surface layer at high fluencies (1000–1500 Mrad) of γ-radiation. © 2011 The Japan Society of Applied Physics

1. Introduction

$TlInS_2$, like any other representative of $A^3B^3C_2^6$ (A, B: metal, C: chalcogen) family of semiconductors can crystallize in crystal structures with different symmetries such as monoclinic (M), triclinic, tetragonal, orthorhombic, and hexagonal (H).[1–4] The growth conditions for any of the above-listed modifications of $TlInS_2$ are already known.[5,6] Almost all $A^3B^3C_2^6$ crystals with layered or chain structure undergo a ferroelectric phase transition (FPT) accompanied by anomalies in temperature dependencies of the various parameters including dielectric function, $\varepsilon(T)$, and conductivity, $\sigma(T)$. It has been shown[7] that various $\varepsilon(T)$-dependences observed so far on different samples of M-$TlInS_2$ are due to its different polytypes. Other factors which can influence FPT and, hence, $\varepsilon(T)$ and $\sigma(T)$ dependencies are impurities[8] and intrinsic defects. Defects, as well as impurities can even cause structural changes in $TlInS_2$.[6,9] For example, increased concentration of interstitial S-atoms in the basic polytype with lattice parameter $c = 15$ Å can eventually bring about a polytypes of M-$TlInS_2$ with evenly increased lattice parameter. As a result, a narrow dielectric anomaly observed at $T = 203$–205 K noticeably broadens and additional maxima emerge on $\varepsilon(T)$. Note that growing concentration of vacancies and interstitial atoms can frequently lead to amorphous state, too.[10] For M-$TlInS_2$, crystal-to-amorphous (c–a) transition has also been reported.[11]

One of the most effective tools for creation of intrinsic defects is known to be γ-irradiation (γ-IR).[12–15] The effect of γ-IR with $\hbar\omega = 1.23$ MeV (Co^{60}) on the room temperature $\varepsilon(T)$ and $\sigma(T)$ dependencies was already studied in some of the layered M-$A^3B^3C^6{}_2$, including M-$TlInS_2$.[16–19] However, the obtained experimental results were insufficient to built up a comprehensive and self-consistent picture of the influence of intrinsic defects on FPT in M-$TlInS_2$.

Here we extend our experimental approach up to X-ray diffraction (XRD) and photoconductivity (PC) examinations, which, as well as $\varepsilon(T)$ and $\sigma(T)$ measurements, have been carried out in a broader range of radiation fluencies in comparison with previous studies.[16–19] XRD and PC have been selected to monitor sample structure and shallow impurity states near the band gap, respectively.

We focus on the mechanisms responsible for radiation-induced defect formation, and on structural transition to H-phase we disclosed in M-$TlInS_2$ at high irradiation fluencies.

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2. Experimental Procedure

In our experiments more than 10 samples obtained from the same ingot of M-$TlInS_2$ grown from the stoichiometric melt were used. After XRD, PC, $\varepsilon(T)$, and $\sigma(T)$ measurements the samples were put in evacuated glass ampoules to avoid oxidization during γ-IR. After every stage of γ-IR and XRD measurements the Ag-contacts were made to the samples and PC, $\varepsilon(T)$ and $\sigma(T)$ measurements were then performed. The contacts were removed after the measurements prior to a next stage of γ-IR.

Radiation doses were counted as a sum of γ-IR fluencies received by a sample at each stage of irradiation. XRD, PC, $\varepsilon(T)$ and $\sigma(T)$ measurements were carried out with the aid of a DRON-2 X-ray spectrometer, an MDR-23 optical spectrometer and E7-21, respectively. For dc $\sigma(T)$ measurements T-ohmmeter E6-13A was used.

3. Results and Discussion

The influence of γ-IR on structure and physical properties of M-$TlInS_2$ depends of the radiation dose. As shown in Fig. 1 (curve 1), all XRD reflexes from (001) surface parallel to the layer plane of non-irradiated M-$TlInS_2$ (Fig. 1, curve 1) can be identified as $(002n)$.[20] Strong (004)-reflex that corresponds to the reflection from Tl and In atomic planes is becoming narrower and its intensity is growing with subsequent increase of the radiation fluency from 0 to 200 Mrad (Fig. 1, curves 1–3). On the other hand, the (002)- and (008)-reflexes bound to the sulfur atoms are getting weaker and broader. It is then suggestive that the intrinsic defects which emerge in M-$TlInS_2$ under above-specified γ-IR doses are related with sulfur atoms only. The results of room temperature PC and low-temperature $\varepsilon(T)$ and $\sigma(T)$ measurements are shown in Fig. 2.

By making comparison between curves 1 and 2 in Fig. 2, and considering shallow impurity (SI) levels, one can notice that PC value at photon energy ($\hbar\omega$) approaching band gap (E_g) is higher for irradiated samples while the ratio $\Delta\sigma(\hbar\omega \approx E_{SI})/\Delta\sigma(\hbar\omega \approx E_g)$ where E_{si} is the energy position of SI level, is larger for non-irradiated samples. In other words, PC of M-$TlInS_2$ subjected to relatively weak radiation fluencies behaves as if concentration of the residual charged SI centers is decreased. It is therefore possible to conclude that some SI centers are neutralized by sulfur

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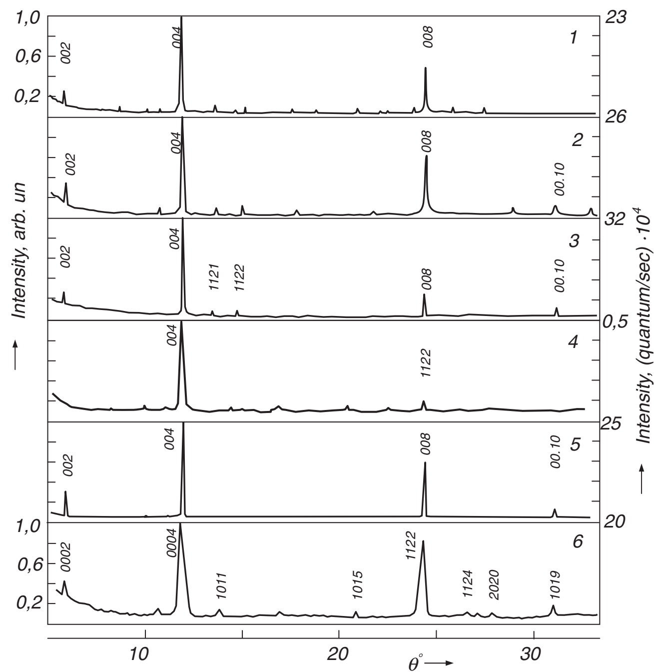

Fig. 1. XRD from (00l) surface of γ-irradiated M-$TlInS_2$; 1 — before irradiation of polytype $c = 15$ Å with small admixture of other polytypes, 2 — 100 Mrad, 3 — 200 Mrad, 4 — 300 Mrad, before removal of the irradiated surface layer; 5 — 300 Mrad, after removal of the irradiated surface layer; 6 — 1500 Mrad, before removal of the irradiated surface layer (all reflexes in 6 correspond to H-$TlInS_2$).

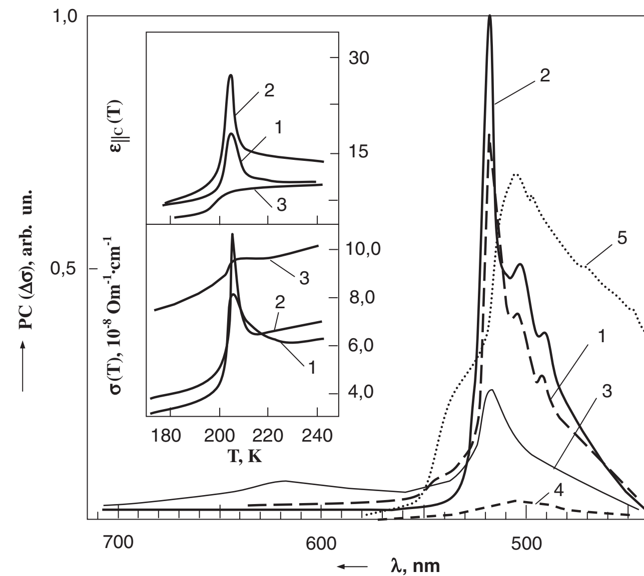

Fig. 2. PC spectra, $\varepsilon(T)$ (inset, top part) and $\sigma(T)$ (inset, bottom part) dependencies of γ-irradiated M-$TlInS_2$ samples: 1 — 0 Mrad; 2 — 100 Mrad; 3 — 200 Mrad; 4 — 300 Mrad, before removal of the irradiated surface layer; 5 — 300 Mrad, after removal of the irradiated surface layer.

defects (vacancy and interstitial sulfur) introduced during irradiation of the samples. Strong sample's purity dependence of the upper limit of irradiation dose at which PC, dielectric anomaly, and anomaly in $\sigma(T)$ still continue to increase with increasing γ-IR fluency supports such a conclusion. As we found, this limit is conditional and varies from tens of Mrads for samples cut from central part of the ingot to hundreds of Mrads for samples cut from edge part. Note that normally, concentration of the residual impurities is always higher in the latter part.

Let us now turn to the mechanisms responsible for the formation of intrinsic defects in M-$TlInS_2$ under γ-IR. The first is thought to be impact elastic-shifting mechanism (IESM), according to which some part of the energy, E_e, of an electron photo-ionized by γ-IR at elastic collision with a regular (R) lattice atom of the mass, M_{at}, is transferred to this atom. The maximum value, E_{max}, of the transferred energy is $E_{max} = 4E_e m_e M_{at}/(M_{at} + m_e)^2 \approx 4E_e(m_e/M_{at})$[21] and intrinsic defects are formed when threshold energy of defect formation is less than E_{max}. Since S is much lighter than Tl or In, the energy transferred to sulfur atoms is much bigger and S-defects (vacancy and interstitial S) are preferably formed through IESM in M-$TlInS_2$.

Let us now discuss the details of the formation of intrinsic defects in M-$TlInS_2$. There are two electrostatic mechanisms which can produce intrinsic defect, i.e., a vacancy (V) and an interstitial atom (I). The first one does not consider impurities and ascribes the underlying physical origin of the shifts of the atoms from their regular positions in the structure to the repulsive interaction between these atoms ionized by γ-IR.[12] But, more appropriate to our case is thought to be Klinger's impurity assisted electrostatic mechanism (IAEM)[13,14] due to attractive (repulsive) interaction between ionized acceptor (donor) and ionized regular atom. As shown by Klinger,[13,14] the presence of the residual charged impurities near the ionized regular atoms leads to more effective defect formation. Besides, IAEM is usually accompanied by the formation of neutral complexes which consist of V or I and charged shallow impurity.[14] Such complexes are evidently formed in M-$TlInS_2$ under γ-IR, as mentioned earlier in this section. Note that IAEM in M-$TlInS_2$ is supposed to be responsible for the formation of V and I of S-atoms in the first place. This is apparent from the following simple consideration.

If the atoms of residual or doped impurity would not replace regular atoms in M-$TlInS_2$, the former atoms would occupy only empty places in the structure. These places in M-$TlInS_2$ are found only in hollow octahedrons with S atoms in the corners.[4] In other words, S rather than Tl or In would be close to an impurity atom and would be involved in IAEM in the first place. Besides, the light mass of S makes it easier to shift this atom from its regular position by Coulomb repulsion (attraction) force. Therefore, IAEM with assistance of shallow impurity atoms is very likely to be the main mechanism responsible for intrinsic defect formation in M-$TlInS_2$.

A clear evidence of the decrease of the concentration of the charged shallow impurities in irradiated M-$TlInS_2$ can be found in Fig. 2. Both ε (Fig. 2, inset, top part, curve 2) and σ (Fig. 2, inset, bottom part, curve 2) anomalies, accompanying the ferroelectric phase transition are stronger and narrower than those in non-irradiated samples (Fig. 2, insets, curve 1), because of the decreased damping factor $\omega\tau^{-1}$ (ω-measurement frequency: 10^3 Hz, τ: scattering time) in irradiated samples. Note that $\sigma(T)$ anomaly, which both dc and ac measurements have disclosed, is very likely to be bound with a drastic decrease of the ionization energy of

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the shallow impurities at a temperature, T_{DA}, of dielectric anomaly. Indeed, ionization energy at T_{DA} is $E_i(T_{DA}) = E_i\varepsilon_0^2/\varepsilon^2(T_{DA})$ or $\varepsilon_0^2/\varepsilon^2(T_{DA})$ times its value (E_i) in paraphase. By considering that static dielectric constant $\varepsilon(T_{DA})$ is very large in comparison with that (ε_0) taken at a temperature far from phase transition point, a sudden release of the carriers caught by impurities or trap centers should occur, giving rise to the observed $\sigma(T)$ anomaly. The $\varepsilon(T_{DA})$ in the expression for $E_i(T_{DA})$ is closer to $\varepsilon_{\perp c}(T_{DA})$, which is much greater than $\varepsilon_{\parallel c}(T_{DA})$ given in the insert of Fig. 2.[22]

Thus, XRD, PC at $\hbar\omega > E_g$ and $\varepsilon(T)$ measurements show that small doses of γ-IR improve sample parameters. The amount of this dose depends on residual concentration of shallow impurities and is small for pure samples, for which room temperature band edge exciton lines are observed. The decrease of PC in pure samples occurs at irradiation levels below 10 Mrad while less pure samples exhibit such decrease at higher doses such as up to 100 Mrad and more.

Raising γ-IR dose above 200 Mrad leads to broadening of $\varepsilon(T)$- and $\sigma(T)$-anomalies at phase transition (Fig. 2, inset, curve 3). Besides, a broad line with maximum at $\lambda \approx 0.62$ μm (Fig. 2, curve 3) appears in PC spectra. The origin of the line is apparently bound with sulfur defects.

XRD pattern, as well as PC data obtained for 300 Mrad irradiated sample before and after removal of the exterior layer are different. The (002)-reflex disappear from XRD pattern and (004)- and (008)-reflexes become 40 times weaker (Fig. 1, curve 4) once the IR-dose is raised to 300 Mrad. After removal of the surface layer on the irradiated side of the sample, XRD data are back to those obtained for non-irradiated samples (Fig. 1, curve 5). For a 300 Mrad-irradiated sample, PC signal falls down very much and is almost undetectable (Fig. 2, curve 4). But, after removal of the surface layer PC signal recovers and becomes comparable with that in non-irradiated sample. However, PC maximum corresponding to band gap is now blue-shifted as compared to its position in non-irradiated samples and a clear-cut shoulder caused by shallow impurity levels appears in PC spectra (Fig. 2, curve 5).

As compared to non-irradiated ones, the samples received large dose (>200 Mrad) of γ-IR show much higher (up to several orders of magnitude) values of dark conductivity and do not exhibit $\sigma(T)$ anomaly in both parallel- and perpendicular-to-the layer directions of the measurements. In our opinion, this accounts for by Mott transition, taking place in defect subsystem with increasing concentration (N_{V-I}) of vacancies and interstitial atoms. When Debye screening radius r_s ($r_s \sim N_{V-I}^{-0,5}$) is becoming equal to localization length, a_{V-I}, i.e., $r_s \approx a_{V-I}$, the condition of Mott transition $N_{V-I}^{1/3}\, a_{V-I} > 0{,}26$ is fulfilled and all localized carriers are ionized even at temperatures distant from phase transition point. As a result, $\sigma(T)$-anomaly, which was bound just with ionization of the shallow impurities at a temperature of dielectric anomaly, now disappears since impurities are already ionized at all temperatures. Note that the position of $\varepsilon(T)$ anomaly in the samples received up to 400 Mrad dose of γ-IR remains unchanged though decrease and broadening of this anomaly at phase transition become already considerable.[19]

The doses of γ-IR larger than 1000 Mrad lead to qualitatively new structural changes in M-$TlInS_2$. In fact, such changes can be noticed at an earlier stage of γ-IR as well. However, XRD patterns taken from a sample received high irradiation dose provide a better evidence of the structural changes (Fig. 1, curve 6). It is important to mention that the color of the surface of the crystal received 1500 Mrad of γ-IR turns from yellow to black and the maximum of PC is observed at $\hbar\omega \geq 1{,}1$ eV (Fig. 3, curve 1). The last value is very close to the energy of band gap of H-$TlInS_2$.[6] The thickness of the surface layer with H-$TlInS_2$ is about 10 μm. After removal of H-$TlInS_2$ from the surface, the sample's color turns back to yellow and PC spectra become identical to that of M-$TlInS_2$ with PC maximum at $\hbar\omega \approx 2.35$ eV (Fig. 3, curve 2).

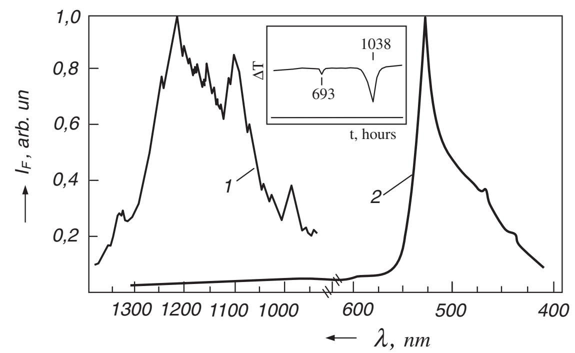

Fig. 3. PC spectra of $TlInS_2$ after γ-irradiation with a dose of 1500 Mrad: 1 — PC before removal of H-$TlInS_2$; 2 — PC after removal of H-$TlInS_2$. Inset: DTA of H-$TlInS_2$ crystal (obtained with 0.1 at. % Tl excess) with H → M phase transition at 693 K.

Differential thermal analysis (DTA) we performed for H-$TlInS_2$ crystal grown with excess of Tl (0.05 at. %) atoms shows the irreversible transformation of H-$TlInS_2$ to M-$TlInS_2$. As it is seen from DTA curve in the inset of Fig. 3, such transformation takes place at $T \approx 695$ K and is accompanied by heat absorption for 10 min. Thus, H-$TlInS_2$ is a ground state variety among the structural modifications of $TlInS_2$.

According to synergetic principle, energy inflow brings about stucturization of the random system and the system turns into a state with smaller free energy. This also implies that a transition from meta-stabile M- to stable H-structure might be possible. The question to answer is how such transition might occur; via intermediate amorphous phase or as a consequence of regrouping of the S interstitial atoms around metal atoms (Tl and In) so that In atoms would occupy the centers of the S_6 octahedrons, which were empty in M-phase. Preliminary analysis of the data obtained in this work points to simultaneous realization of both possibilities. However, further investigations are needed to finalize this conclusion.

4. Conclusions

We have shown that γ-IR influence on $TlInS_2$ properties can be conditionally divided into three stages, depending on γ-IR dose and sample perfection. Small doses of γ-IR lead to "healing" of M-$TlInS_2$ through neutralization of charged residual shallow impurities due to IAEM. Increased intensity of XRD reflexes, PC signal, and $\varepsilon(T)$ and $\sigma(T)$ anomalies at phase transition are all the result of IAEM at this early stage.

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The next stage corresponds to higher doses which intensify formation of sulfur defects predominantly on the surface and lead to crystalline-to-amorphous phase transformation in a thin surface layer. As a consequence, broadening and, finally, disappearing of XRD reflexes, PC signal, and $\varepsilon(T)$ and $\sigma(T)$ anomalies at phase transition are observed. At the same time, the properties of the inner part of the irradiated samples remain practically the same as those of non-irradiated samples. At last, irradiation doses above 1000 Mrad further increase concentration of sulfur defects on the surface and stimulate regrouping of interstitial S atoms around Tl and In atoms so that M-$TlInS_2$ transforms into H-$TlInS_2$. The last transformation is a very slow process diffusively spreading over the inner part of the crystal at a rate of 10 µm/year for γ-IR intensity of ~50–60 rad/s. The obtained results open a gate for preparation of H-$TlInS_2$/M-$TlInS_2$ hetero-junctions with band gap difference of ~1.5 eV by using γ-irradiation.

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