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GRAVITY APPLICATION TO ANISOTROPIC SEMICONDUCTOR MATERIALS: FROM HIGH- TO MICROGRAVITY CONDITIONS†

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Abstract—Growth of single crystals under different gravity conditions is of special importance for the development of growth technology for semiconductors. We have studied the properties of tellurium crystals, Te–Se and $Te_{80}Si_{20}$ alloys grown under different gravity levels by a modified Bridgman method using a Te crystal seed. We examined the influence of gravity from the microgravity level up to $10g$ (g is earth's gravity) on the distribution of electrically active intrinsic defects and dopants. The conductivity and the Hall effect, and their variations along the crystal length, were measured over a wide temperature range, 77–300 K. The Se distribution in the Te–Se alloy was determined by X-ray microanalysis. The hole concentration profile in the space-grown crystal of Te corresponded to an almost uniform distribution of impurities. The hole mobility was less than that in the $1g$ sample due to hole scattering on lattice imperfections produced by crystal growth. In the grown crystals and ingots, the hole mobility increased towards the ends of the samples. The higher the gravity, the better the single crystals, the larger the fraction with a constant hole concentration in Te crystals, and the smoother the Se distribution along Te–Se alloys. These effects can be attributed to the anomaly of the liquid Te density near the melting point due to the formation of spiral chains of Te atoms. This anomaly gives rise to additional convection when the melt is heated from above. Mixing of the melt near the solid–liquid interface is intensified under high gravity due to this unusual convection. The situation for the Te–Se alloy is qualitatively comparable to the growth process in Te taking into account some decrease of the melt viscosity with addition of a small amount of Se. The data on solidification of the glassy alloy $Te_{80}Si_{20}$ in space and at normal gravity on earth indicate that microgravity suppresses cluster nucleation during the solidification and promotes ideal glass formation. © 2001 Published by Elsevier Science Ltd.

1. INTRODUCTION

One goal of micro- and macrogravity crystal growth experiments on semiconductors is to determine the role of gravitational and Coriolis forces in the melt on convection, and on crystallization and segregation processes. Centrifugation was used to produce high-gravity conditions, and growth in space to achieve the microgravity level. Tellurium and its alloys proved to be the most convenient materials for such experiments, as the structural and electrical properties of Te are generally influenced by crystal defects and impurities. In addition, the properties of Te–Se and Te–Si alloys are sensitive to the content and distribution of Se and Si along the ingot [1]. Moreover, the relatively low melting temperature of both Te and Se (452 and 221°C, respectively) and the eutectic $Si_{80}Te_{20}$ (450°C) facilitate the technological arrangement of the experiments. In this paper, we outline the main results of studies of single- and polycrystalline Te-based samples grown with a modified Bridgman technique at different gravity levels, from microgravity in the Crystallizator CSK-1 furnace aboard the Mir station [2], to $10g$ using centrifugation of the Meudon furnace [1]. Comparing their properties with the corresponding parameters of terrestrial samples grown with the same temperature conditions, we found a correlation between the gravity conditions and the distribution of structural defects and impurities, and their influence on hole scattering.

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The glassy alloy $Te_{20}Si_{20}$ in the Te–Si system is a member of the chalcogenide eutectic glasses, for which the vitrification range extends from 10 to 27.5 at% Si [3]. The best glass-forming capability corresponds to the eutectic $Si_{17}Te_{83}$. The densities of the two components of the eutectic are considerably different (6.26 g/cm^3 for Te and 4.39 g/cm^3 for Si_2Te_3). So, the solidification process in the melt and the properties of the resulting glass should be gravity dependent. The discovery of such an effect [4] allowed us to choose between two general models for the amorphous metal structure, namely: the random close packing model and the cluster model.

2. EXPERIMENTAL METHODS AND SAMPLES

2.1. *Elemental tellurium and Te–Se alloy*

The crystals of Te and Te–Se alloy were grown in an axial temperature gradient $dT/dx = 30^\circ C/mm$ using a crystalline seed of Te which was oriented parallel to the three-fold C-axis. This axis is a preferential growth direction for single crystals of Te and Te–Se alloy at small Se contents. For these experiments, polycrystalline ingots of Te with a hole concentration of 10^{14} cm^{-3} and Te–Se ingots with $\sim$ 4 at% Se were used. These ingots had been fused with the Te seed in a quartz ampoule container sealed under vacuum. The growth rate was approximately 0.3 mm/min for Te and 0.13 mm/min for Te–Se. For protection, another quartz ampoule was used for the Meudon furnace. An additional steel container was used for the Crystallizator CSK-1 furnace on Mir. The seeded recrystallization experiment with pure Te in space was carried out in the gradient furnace Crystallizator CSK-1 designed for Mir in the program “ALCUTEST-2” [2]. The Meudon furnace was placed within a massive pivotal cabin on the centrifuge so that the resulting acceleration vector was directed along the ampoule axis and opposite to the solid–liquid interface movement. Before the start of crystal growth, the phase boundary position was 2–3 mm below the contact with the seed, which was maintained solid during the growth process. The ingot melting in the Meudon furnace was followed by 2 h of homogenization at 500°C with the centrifuge switched on. Growth began on cooling at a rate of 1.25 and 0.5°C/min for Te and Te–Se, respectively. At 350°C, the centrifuge was switched off and the temperature was kept constant for 2 h annealing.

The electrical properties of the samples, such as the conductivity and Hall effect, were measured over a wide temperature range (from 77 to 300 K) and compared with the properties of $1g$ samples.

2.2. *Te–Si glassy alloy*

The cooling velocity under which glass forms in the Te–Se system must be higher than 10°C/min. Therefore, the following regimen for $Te_{80}Si_{20}$ glass solidification was worked out. A temperature of 700°C was maintained for 4 h along the Crystallizator CSK-1 furnace to melt the compound completely. After that, the capsule with the melt was rapidly quenched by means of switching-off the furnace and removing the capsule from the furnace at the maximum rate of 0.1 cm/s.

The ground-based and space experiments were carried out using the same temperature regimen.

3. EXPERIMENTAL RESULTS

3.1. *Tellurium and Te–Se alloy*

The ingots obtained were selectively etched in 30% HNO_3 to reveal their microstructure. The Te crystals grew in the C-axis direction with the exception of the $5g$ sample, in which a few blocks of different orientations were embedded [5]. The microgravity ingot demonstrated a microblock structure with an average orientation of crystallites along the C-axis in accordance with the seed.

All of the recrystallized Te–Se ingots had a block-like structure. The large crystalline blocks possessed a C-axis orientation inclined by 30° to the ampoule axis for the $5g$ and $10g$ ingots. The number of blocks decreased towards the end of the ingot.

Figure 1 shows the variation of the hole concentration determined from the Hall effect (all the samples were p-type at 77 K), and Hall mobility $R\sigma$ along crystals grown at different gravity levels. The Hall coefficient was measured at a few cross-sections along the crystals in a magnetic field of $H = 0.5$ T. In the recrystallized part of the $1g$ and $5g$ crystals of Te and Te–Se alloy, the hole concentration increased towards the crystal end. In the μg and $10g$ samples, there was a low concentration region that was longer in the μg crystals. The results led to a conclusion about the probability of producing an extended uniform crystal by decreasing or increasing the gravity level. It is necessary to note that the high hole concentration in the first cross-sections of the Te crystals was due to electrically active structural defects, the number of which exponentially decreased with distance from the seed.

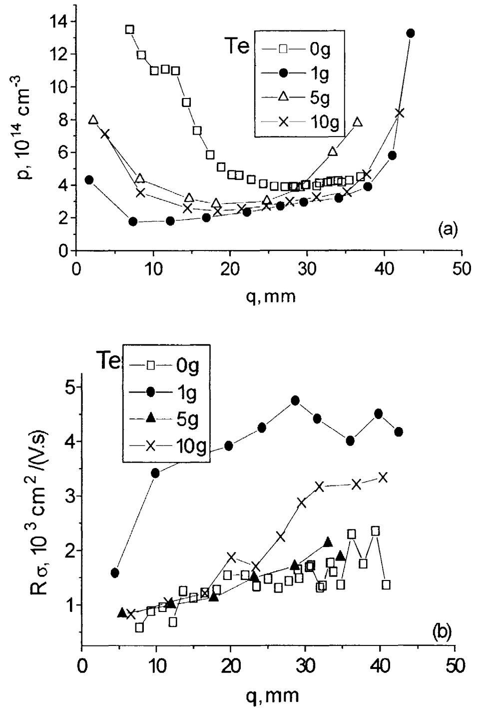

Fig. 1. Variation of hole concentration p (a) and hole mobility $R\sigma$ (b) at 77.4 K along Te crystals grown in space (μg), on Earth ($1g$), and with centrifugation at $5g$ and $10g$. Here q is the distance from the initial seed–ingot boundary.

Figure 2 shows the results for Te–Se. The hole mobility was mainly constant in the Te–Se samples (Fig. 2b) and in the $1g$ sample of Te (Fig. 1b). In the samples grown at the lower and higher gravity, $R\sigma$ appeared to be smaller than in the $1g$ crystal. Nevertheless, the mobility rose in the Te crystals along the crystal length and its temperature dependence was stronger than for the $10g$ sample [4]. That means fewer structural imperfections formed in the Te crystals as the solid–melt interface moved, so the hole scattering on the intrinsic defects became weaker compared to scattering on acoustical phonons at 77 K. A similar crystal perfection dependence on gravity level has been observed in directional solidification of PbTe⟨Ag⟩ [6].

On the other hand, in the Te–Se crystals the hole mobility was one order of magnitude smaller than in the $1g$ Te crystals, and $R\sigma$ decreased with the gravity level (Fig. 2b). The measured hole concentration profile $p(q)$ depended on the relation between impurity and lattice defect concentrations along the ingot. For polycrystalline Te–Se ingots it is difficult to determine the effective segregation coefficient K_{eff} of Se by measuring only the hole concentration profile. Therefore, the Se distribution along the $1g$, $5g$ and $10g$ Te–Se crystals was measured using X-ray microanalysis (Fig. 3). The data corresponding to local Se segregation on grain boundaries were omitted. The Te–Se alloy grown

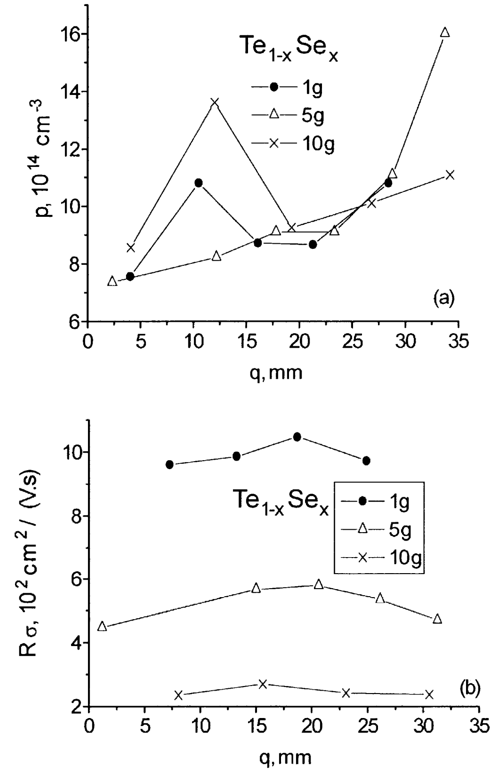

Fig. 2. Variation of the hole concentration p (a) and the hole mobility $R\sigma$ (b) at 77.4 K along recrystallized Te–Se ingots grown at three different gravity levels: $1g$, $5g$ and $10g$. Here q is the distance from the initial seed–ingot boundary.

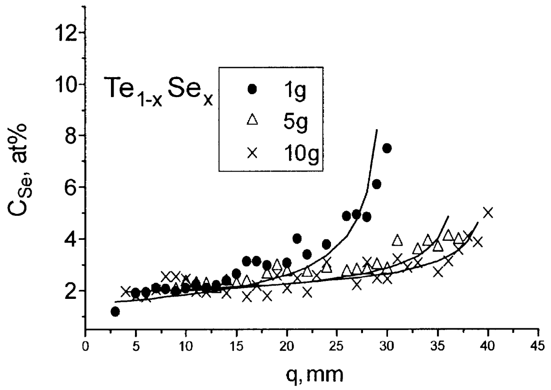

Fig. 3. Selenium distribution in Te–Se ingots grown by directional solidification at different gravity levels. The curves show the calculated dopant distribution for convection-controlled segregation with $K_{\text{eff}} = 0.5$, 0.73 and 0.76 at $1g$, $5g$ and $10g$, respectively. The initial Se concentration in the melt was 3, 2.5 and 2.5 at% for solidifiction at $1g$, $5g$ and $10g$, respectively.

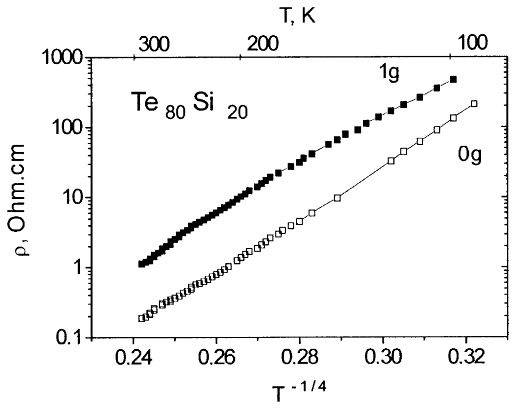

Fig. 4. The temperature dependence of the electrical resistivity of the μg and 1g samples of $Te_{80}Si_{20}$ alloy.

under high-gravity conditions had a more uniform Se distribution, i.e. the rejection of Se during the solidification was less ($K \sim 1$).

3.2. $Te_{80}Si_{20}$ alloy

The $Te_{80}Si_{20}$ obtained in space using the Crystallizator CSK-1 furnace was a vitreous phase with conchoidal and glittering fracture surfaces typical of a glass without crystalline inclusions. It is relevant to note that previously we made an additional experiment on solidification of $Te_{80}Si_{20}$ under normal (1g) and high gravity (5g) in the Meudon furnace on a special centrifuge [1]. Both of these ingots consisted of glassy and polycrystalline parts.

X-ray microanalysis of composition revealed that the space sample consisted of a single phase with a Si content of 20 ± 1 at %, whereas the terrestrial one had a Si concentration that fluctuated about 3 at % from point to point.

The average density of the space samples was slightly higher than that of the terrestrial one. The microhardness of the μg sample was less than that of the 1g sample (136 and 150 kg/mm, respectively).

The electrical resistivity of $Te_{80}Si_{20}$ glassy alloy is very sensitive to a glass-forming regime, especially at low temperatures. In Fig. 4, we compare the data for samples solidified under similar conditions in the Crystallizator CSK-1 at μg and at 1g. Repeated resistivity measurements for the 1g sample differed from point to point by approximately 10%, perhaps due to non-controlled surface decomposition.

Measurements of the μg sample showed electrical uniformity, but the resistivity was less than that of the 1g sample over the whole temperature range of 77–300 K (Fig. 4). Temperatures higher than 300 K were not used in order to avoid the annealing effect. The plots of Fig. 4 permit us to define the activation energy of charge carriers for hopping conductivity with variable hop length of Mott's type, as described by $\sigma = \sigma \exp[-(T_0/T)^{1/4}]$, with $T_0 = 5.75 \times 10^7$ K at μg and 4×10^7 K at 1g. The μg sample correlated with Mott's law up to higher temperatures.

4. DISCUSSION

In Fig. 5, we compare the experimental hole concentration profile in Te crystals (from Fig. 1) with that calculated from the equation for impurity segregation with steady buoyancy-driven convection. The exponential behaviour of the intrinsic structural defect concentration can be described by

$$p(q) = K_{\mathrm{eff}} C_0 \left(1 - \frac{q}{l}\right)^{K_{\mathrm{eff}}-1} + C_{\mathrm{def}} \exp\left(-\frac{q}{q_0}\right). \tag{1}$$

Here K_{eff} is the effective impurity segregation coefficient, q the distance from the initial boundary, q/l the solidified fraction, l the total length of the regrown crystal, C_0 the initial impurity concentration in the melt, C_{def} the initial concentration of defects, and q_0 the defect relaxation length.

These results suggest improvement of the crystal structure towards the end of the Te crystals grown by directional solidification at different gravity levels. An anomaly in the impurity segregation coefficient in Te at 5g was found: $K_{\mathrm{eff}} = 0.16$ instead of 0.5 at the normal condition. The axial Se distributions shown in Fig. 3 were compared with the calculated curves corresponding to directional solidification with partial liquid mixing with a Se segregation coefficient $K = 0.76$ at 10g, 0.73 at 5g, and 0.5 at 1g. In Te–Se, an increase of acceleration up to 10g led to leveling of the Se concentration along the ingot. The segregation coefficient of Se in the 10g ingot approached $K_{\mathrm{eff}} = 1$ over the whole ingot, contrary to the case of 1g, as illustrated in Fig. 3.

These results show that an increase of the gravity level produces a noticeable change in the crystallization process for these materials. The described phenomena may be explained by peculiarities of the solidification process of a Te crystal that contains spiral chains of atoms packed in a hexagonal lattice cell. The bonds between atoms in the chain are covalent, while the bonds between the chains are weaker. Therefore, they will be broken first during the melting process while the covalent bonds persist to higher temperatures. On the other hand, during the crystallization process the chains form first and the coordination num-

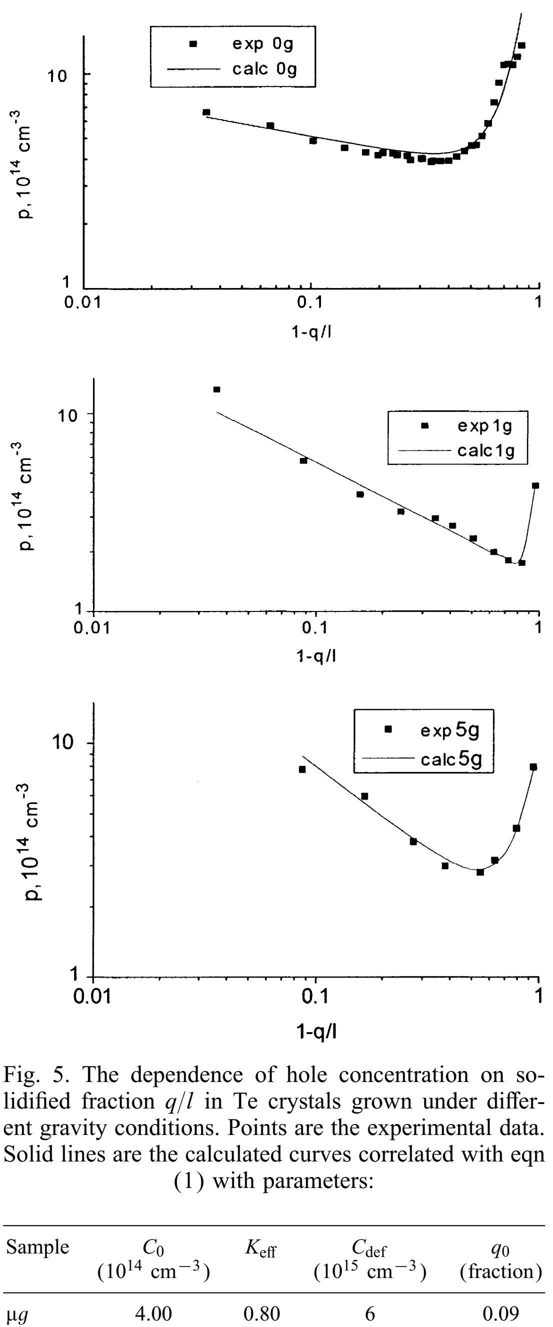

Fig. 5. The dependence of hole concentration on solidified fraction q/l in Te crystals grown under different gravity conditions. Points are the experimental data. Solid lines are the calculated curves correlated with eqn (1) with parameters:

Sample	C_0 (10^{14} cm^{-3})	K_{eff}	C_{def} (10^{15} cm^{-3})	q_0 (fraction)
μg	4.00	0.80	6	0.09
1g	3.55	0.42	0.6	0.05
5g	5.48	0.27	0.85	0.17
10g	3.23	0.60	1.3	0.09

ber of Te atoms near the melting temperature T_{m} turns out to be significantly small ($N = 2$–3). This causes the anomalous temperature behaviour of the melt density; a minimum appears near T_{m}. The complex melt structure of Te near T_{m} changes also the viscosity, which is one order of magnitude larger than that for liquid metals, and decreases with temperature. These anomalies act in different ways on the gravitational convection in the melt. The density inversion in the melt leads to additional convection. But, at the same time the high viscosity near T_{m} would suppress buoyancy flow. With increasing gravity, this unusual convection becomes stronger. The mixing of the melt near the crystallization front is intensified and the effective segregation coefficient K_{eff} decreases (for example, in Te at 1g and 5g in comparison with μg). Then, with further gravity increase, K_{eff} in Te increases under centrifugation again. This behavior is probably connected with a changing convection pattern and vigor [7–16].

The situation near the interface in the Te–Se melt is qualitatively the same, but quantitatively differs due to the melt viscosity decrease caused by the addition of a small amount of Se (less than 5 at%). The inserted Se atoms destroy formation of Te atomic chains in the melt near T_{m}.

Comparing the data for the glassy alloy, we may conclude that the number of defects in $\text{Te}_{80}\text{Si}_{20}$ solidified under microgravity conditions is less than in its ground-based analogue. This conclusion is confirmed by the following arguments:

The compositional homogeneity of the μg sample is better than that of the 1g sample.

The decrease of microhardness also points to a smaller concentration of cluster type defects in the glass.

According to Mott's theory, the activation energy for hopping conductivity through defect states, T_0, is proportional to $1/N_{\text{F}}$, where N_{F} is the density of states at the Fermi level as determined by the defect concentration. The greater T_0 for the space sample means that N_{F} for this sample was smaller and, consequently, the number of defects as well.

5. CONCLUSION

Growth experiments for Te and Te-based compounds ($\text{Te}_{0.96}\text{Se}_{0.04}$ and $\text{Te}_{80}\text{Si}_{20}$) in a centrifuge were complemented by experiments in space for Te and the glassy alloy $\text{Te}_{80}\text{Si}_{20}$. There is considerable evidence that the gravity level is an important factor for crystallization processes in these materials. The increase of K_{eff} in Te–Se with g is attributed to a reduction of the melt convection during growth. To achieve the same segregation coefficient in Te as for the 10g crystal by decreasing the gravity level, a value of $\sim 10^{-3}g$ was necessary. From the microscopic point of view, convection near the melting point T_{m} is affected by the temperature dependence of the coordination number in molten Te, resulting in a minimum of the density and a high viscosity near T_{m}. The Te crystals grown in space exhibited a uniform hole concentration axial profile.

The investigation of material with the amorphous structure $Te_{80}Si_{20}$ obtained in space and on earth showed better glass-forming capability in space. Provided that the defects in the $Te_{80}Si_{20}$ glass are connected with the presence of microclusters formed under solidification, we can conclude that the vitreous semiconductor alloy $Te_{80}Si_{20}$ obtained in space exhibits a suppression of cluster nucleation during solidification. The high-gravity conditions promoted cluster formation and polycrystalline regions in the ingot.

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