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Very high quality crystals of wide-gap II-VI semiconductors: What for?

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ABSTRACT

A review of some of the most important applications of the wide-gap II-VI semiconductors is presented, the key parameters of the crystals for specific applications are emphasized, and the necessity of growing crystals of very high quality is substantiated. Modern methods of growth of high-quality wide-gap II-VI semiconductor crystals are shortly described. The results of the physical vapor transport method, chosen by the authors for ZnTe and CdZnTe crystals, are shown.

Keywords: wide-gap II-VI semiconductors; high-quality crystals; applications of II-VI semiconductors; technology of semiconductor crystals

1. INTRODUCTION

The physics of the wide-gap II-VI semiconductors has been developing during last fifty years, but technical applications are spreading fast only recently. The development of applications is determined by the progress in the technology of crystals. In this review we are going to show why in many applications of the semiconductor crystals the wide-gap II-VI semiconductor crystals are the best choice and that numerous applications require very high quality crystals. The quality requirements for particular applications will be emphasized. Finally, the leading technologies, which enable the growth of very high quality wide-gap II-VI semiconductor crystals, will be discussed with special attention payed to the technology chosen by the authors. Among important applications of the wide-gap II-VI semiconductor crystals one can name:
- X-ray and gamma-ray detectors.
- Substrates for IR detector structures.
- Photorefractive elements for optoelectronics.
- Electro-modulators.
- Optical isolators (CdMnTe).
- Green diodes and lasers (ZnTe).

In all these cases the quality of the crystals plays a crucial role.

2. SELECTED APPLICATIONS OF THE WIDE-GAP II-VI SEMICONDUCTOR CRYSTALS

2.1. X-ray and gamma-ray detectors

Semiconductor detectors of X and gamma radiation are used in many areas of life, science, and technology, like common X-ray diagnostics, nuclear medicine, national security, environment protection, physics of elementary particles and nuclear physics, astrophysics, cosmic-ray physics, material sciences and monitoring of the industrial processes, to mention only a few of them.

The semiconductor detector of X or gamma rays consists of a piece of *properly* chosen semiconductor crystal of *proper* quality with the electrodes for detecting currents. The names "X-rays" and "gamma-rays" describe different ranges of electromagnetic spectrum, i.e. — different ranges of photon energies. Usually we call the photons with energies 1keV - 100keV — "X-ray" photons, and the photons with energies above 100keV — "gamma-ray" photons.

Inside the crystal the photons interact with atoms, giving away all or part of their energy and the final result - the mobile charges - can be detected by the electric circuit. The first required step is the creation of at least one fast charged particle, which subsequently produces many free electrons (and/or holes) through ionization. Different processes of interaction, characterized by a different effectivness of production of current carriers, dominate different ranges of the photon energy:

- 1keV - 400keV — photoelectric effect
- 400keV - 5MeV — Compton scattering
- 5MeV - 100MeV — creation of electron-positron pairs.

The generation of current carriers by photons due to these processes is proportional:
to Z^n $(4 < n < 5)$ — for photoelectric effect,
to Z — for Compton scattering,
to Z^2 — for creation of electron-positron pairs
It is obvious that the crystals for the detectors should have the average value of the atomic number Z as large as possible. For some crystals these values are: HgJ — 66; CdTe — 50; GaAs — 32; Ge — 32; Si — 14. One can see the adventage of chosing II-VI's - CdTe and HgJ.

In the detectors measuring the total intensity of radiation — the current for a given rate of generation of charge carriers (say - only electrons, for simplicity) — is proportional to the product of electron lifetime, electron mobility and the applied electric field. In the photon counting detectors (e.g. - spectrometers) — the magnitude of a current puls for a given number of created charge carriers is proportional to the product of electron mobility and the applied electric field, and the electron lifetime must be long enough to ensure the effective charge collection. Large values of electron mobility, electron lifetime, and the maximum allowed electric field are required for reasonable sensitivity. If the mobility is to be high — the crystal must be pure, with low concentration of carrier scattering impurities and defects, no grain boundaries and twinning. If the lifetime is to be high — the concentration of defects and residual impurities acting as recombination centers must be low. High electric field may be applied only to a crystal of high resistivity if the noise caused by the thermally excited carriers is to be lower than the observed signals. High resistivity implies low concentration of defects (like vacancy related complexes in CdTe) and impurities, responsible for shallow levels. Compensation by the opposite type of impurities is not very good, as it decreases mobility. In the photon counting detectors — the high resistivity is necessary to avoid neutralization of the mobile space charge, during its transit, by the existing carriers. Usually the resistivities of the order of 10^{10} $\Omega \cdot$cm are required. Very often the detector crystals or the detector arrays are of quite a large size. For obvious reasons — the properties of the crystal must be uniform in the whole volume. When the ternary crystal is used, the homogeneous composition is required. Last but not least — the crystals for radiation detectors have to offer possibility of making reliable electric contacts.

High quality CdTe and $Cd_{1-x}Zn_xTe$ $(x < 0.2)$ crystals find increasing application as the crystals for semiconductor detectors. The high average atomic number of CdTe was already mentioned. Zinc is added to increase the energy gap in order to achieve very high resistivity without the necessity of excess compensation. Vast information on semiconductor X-ray and gamma-ray detectors can be found e.g. in Refs. 1-6.

2.2 Substrates for IR-detector structures
Mercury-cadmium telluride ("MCT" or "CMT") is still the basic material for construction of IR-detectors and IR-detector structures. Usually $Hg_{0.8}Cd_{0.2}Te$ is used because its energy gap at room temperature matches the "atmospheric window" and the photon energy of the popular CO_2 laser. The detector structures are fabricated by Molecular Beam Epitaxy (MBE), Metalo-Organic Chemical Vapour Deposition (MOCVD) or Liquid-Phase Epitaxy (LPE). High quality substrate crystals are required for all of these processes.

$Cd_{0.96}Zn_{0.04}Te$ has the same lattice constant as that of $Hg_{0.8}Cd_{0.2}Te$ and is used as the substrate for IR-detector structures based on $Hg_{0.8}Cd_{0.2}Te$. The substrate crystals must be single crystals with no grain boundaries and twins. Definite crystallografic orientation is required for the substrate surface. For example, the substrate surface parallel to the crystallografic plane (001) is used frequently for the MBE processes and (111) - for LPE. Extended defects in the substrate crystal spreading towards the interface give rise to defects detrimental to the detector layers. Density of dislocations in the substrate crystals must be kept below 10^4 cm^{-2}. The diffusion of impurities from the substrate crystal to the detector structure has to be excluded, as in some cases it results in the concentration of unwanted impurities inside the layer of the detector crystal much higher than that in the substrate. Thus, very high purity of the substrate is a must. It is often necessary to illuminate the detector structure through the substrate which has to be transparent for the IR radiation, so the concentration of any absorbing centres and the concentration of free carriers must be low. The high quality single crystals intended for substrates must be large enough to allow the substrate plates of the size of at least 20 mm × 20 mm to be cut off. The last process in the preparation of the substrate plates is the preparation of the perfect ("epi-ready") surface, which is able to avoid

degradation (e.g. fast oxidation) in the period of time between the fabrication of the surface plate and the beginning of the epitaxy process. Many references to the papers dealing with the problems discussed above can be found e.g. in the article by Rogalski[7].

2.3 Electro-modulators and photorefractive elements

The physical phenomenon which underlies the operation of these devices is the Pockels effect: the refraction coefficient of a crystal is modified by the electric field. In electro-modulators — an external field is applied. In photorefractive elements — the electric fields inside a crystal result from the rearrangement of the charges caused in turn by illumination with a certain pattern. The carriers are photoexcited from the localized states to the extended states and migrate towards nonilluminated regions, where they are captured into empty deep centers. Local space charge electric fields are formed and the refractive index is modulated locally by these fields.

For example — a photorefractive optical grating (consisting of stripes with different n) can be created inside a crystal containing suitable impurities by interference of the two laser beams resulting in stripes of strong illumination. The carriers excited inside the stripes migrate outside, where they are captured and the stripes of charges and fields are created. As the electric fields modulate the refractive index — the optical grating is formed.

The CdTe:V (and CdZnTe:V), GaAs:Cr, or InP:Fe are studied as promising photorefractive crystals. CdTe:V is good as a photorefractive material owing to its high (5.5) effective electro-optic coefficient. The figure of merit of a photorefractive material is the product of the electro-optic coefficient and the refractive index, n_0. For cadmium telluride this product is twice as high as for the two other compounds mentioned. Very high quality of the crystal structure, absence of precipitates, and very low concentration of residual impurities are required for the CdTe:V or CdZnTe:V crystals meant to be used as photorefractive crystals, since the residual optical absorption must be below 0.1 cm^{-1}. High resistivity must be achieved by a reasonable compensation. High concentration of vanadium of $10^{17} \div 10^{18}$ cm^{-3} must be accompanied by its homogeneous distribution. The basic knowledge of the photorefractive materials can be found in in the book edited by Garmire and Kost[8] and in the references cited therein. The topics specific to CdZnTe and CdTe can be found in the references to the articles of Triboulet et al[9] and Marfaing et al[10].

2.4 Optical isolators (CdMnTe)

The role of an optical isolator used for a laser is to allow the laser beam to go out but to forbid its coming back inside after external reflections. The Faraday rotation of the polarization plane of the electromagnetic wave inside a crystal in the magnetic field is utilized in the construction of an optical isolators. The crystals of a semimagnetic semiconductor $Cd_{1-x}Mn_xTe$, where the giant Faraday rotation[11] occurs for the wavelengths close to the free exciton line, are used for this purpose. For the IR-lasers working in the wavelength range $1 \div 1.5$ μm — the $Cd_{1-x}Mn_xTe$ crystals with $x \approx 0.1$ are suitable. The rotation of the polarization plane must be uniform for the whole volume of the crystal working as an optical isolator. Thus, the composition x must be uniform. As the scattering of light must be avoided, the single crystals of $Cd_{1-x}Mn_xTe$ must have no grain boundaries and twins, and very small amount of any precipitates. As the power of the laser beam going through the optical isolator is often very high, *very* low absorption coefficient, i.e. very low concentration of any absorbing species, is required.

2.5 Green diodes and lasers (ZnTe)

ZnTe with its room-temperature energy gap of 2.27 eV (546 nm) is considered to be the best candidate for manufacturing optoelectronic structures working in the green region of the spectrum. The pure green light emitting diodes based on phosphorus-doped p-type ZnTe plates were realized in Japan Energy Corporation by a simple thermal diffusion process. According to the authors[12], the success in overcoming the compensation effect in a II-VI material was due to the use of high quality p-type ZnTe single crystals with low dislocation densities of the level of 2000 cm^{-2} grown by the vertical gradient freezing (VGF) method and the suppression of the compensating point defects by low temperature annealing with the surface of the substrates covered by the deposited layer of aluminum (n-type dopant). The intrinsic p-n junctions were formed and the bright 550 nm electroluminescence from these p-n junctions was reproducibly observed at room temperature, with the lifetime exceeding 1000 hours. A more complex ZnTe structure produced by homoepitaxy on the ZnTe substrate is probably required for the construction of a green laser.

The poor quality of the heteroepitaxial (grown on alien substrates) layers of ZnTe results mainly from the lattice misfit, thermal misfit (different expantion coefficients), and from the diffusion of impurities from the substrate. Homoepitaxy of

ZnTe structures on ZnTe substrates is preferred! The ZnTe substrate crystals intended for manufacturing laser structures by homoepitaxy have to be large-size (50 mm in diameter) single crystals with perfect crystal structure, characterized by the FWHM (full width at half maximum) of the rocking curve below 20 arcsec, and the density of dislocations below 5×10^3 cm^{-2}. Low-resistivity (0.01 ÷ 0.1 Ω·cm), p-type (e.g. phosphorus-doped) ZnTe substrate crystals are much-desired. As it has been shown in the text above — many important applications of the II-VI semiconductors require the crystals, which are of very high quality, at least with respect to some parameters. Before going to the technology of high quality crystals, it may be convenient to list the requirements appearing in the text above. A group, usually quite wide, of requirements from the following list applied to every discussed use of the II-VI semiconductor crystals.

- large single crystals — the diameters of about 50 mm
- no grain boundaries, no twins, perfect crystal stucture, characterized by the FWHM of the rocking curve below 20 arc sec
- very high resistivity , above 10^{10} Ω·cm
- very low resistivity, below 0.1 Ω·cm
- uniform doping
- uniform distribution of intentional impurities
- low concentration of unintentional impurities
- homogeneous composition of the ternary compounds
- low concentration of point defects
- low density of dislocations, below 5×10^3 cm^{-2}
- low concentration of precipitates
- "epi-ready" surface

3. THE TECHNOLOGIES OF HIGH-QUALITY II-VI SEMICONDUCTOR CRYSTALS

The technology of high-quality II-VI semiconductor crystals is difficult because of many unpleasant phenomena. Twinning may take place easily due to the temperature fluctuation during crystal growth. Softening quartz tubes become a source of contamination and hinder obtaining the crystals of large diameter. Dislocations are easily generated due to the stress from the container and the thermal stress during crystal growth. It is difficult to control the melt/solid interface shape as desired, because the heat released during solidification cannot be duly dissipated. These phenomena are the consequences of some parameters of the II-VI compounds, which are unfavourable for the technology: low stacking fault energy, high melting point, low critical resolved shear stress and low thermal conductivity.

Nowadays — the following methods of crystal growth are considered to be appropriate for the growth of high quality wide-gap II-VI semiconductor crystals:
- Modified Bridgman Methods
- Travelling Heater Method
- Cold Travelling Heater Method
- Physical Vapour Transport

We are going to describe shortly merits and demerits of those methods.

3.1 Modified Bridgman methods

A growth method called "vertical gradient freezing method" (VGF) has been described by Asahi et al.[13,14] as applied to CdZnTe. VGF method is the Bridgman method modified in such a way that neither the furnace nor the ampoule containing the crystal are moved but the temperature profile of the furnace is continuously shifted by a proper electronic control of the temperature as a function of position and time in a multiple-zone furnace. The absence of the relative movement of the ampoule and furnace ensures more stable conditions at the crystallization front. The second modification was the use of a Cd reservoir outside the crucible made of pyrolytic boron nitride, in which the crystal was growing. Both the crucible and cadmium reservoir were sealed in one quartz ampoule, and the pressure of cadmium vapours in the crucible was controlled by the temperature of the cadmium reservoir (the temperature of the appropriate zone of the furnace) in order to regulate the stoichiometry of the melt. It was possible to achieve low concentration of cadmium vacancies. Because of the very low thermal conductivity, low growth rate of 1 mm/h was used.

The results were very promising - large (100 mm in diameter) single crystals were free of twins and grain boundaries, the density of dislocations was $4 ÷ 6 \times 10^4$ cm^{-2}, the FWHM of the rocking curve — 8 ÷ 13 arcsec, resistivity — 30 ÷ 35 Ω·cm, concentration of holes — 2.2×10^{15} cm^{-3}, and their Hall mobility — 80 ÷ 100 cm^2 V^{-1}s^{-1} for the whole ingot. The authors did

not discuss the segregation of zinc (composition homogenity) along the ingot and the concentration of Te precipitates. The problem of zinc segregation is especially important for $Cd_{1-x}Zn_xTe$ crystals with $x > 0.1$. Such crystals are used for X-ray and gamma-ray detectors and optical modulators.

A very promising version of the VGF method has been applied to ZnTe by Seki, Sato, Oda and Matsuda[15,16]. They used sapphire (Al_2O_3), with the surface parallel to the (0001) hexagonal crystallographic plane, as a hetero-seed for the growth of ZnTe. The sapphire does not dissolve in ZnTe and has a much higher melting point than ZnTe. There is a peculiar match between the crystal structures of sapphire and ZnTe - the (001) plane of ZnTe can be put on the (0001) plane of sapphire in such a way that some of the ZnTe atoms nearly hit the sapphire atoms. Just in this way ZnTe started to grow on the sapphire. The diameter of the growing crystals was up to 50 mm. The growth was performed either in stoichiometric conditions or as a growth from the tellurium-rich solution. The crystals grown in the stoichiometric conditions were of very high quality. In particular, the density of dislocations measured as etch pit density (EPD) was of 2000 cm^{-2}. In the crystals grown from the tellurium-rich solution the density of dislocations was higher — $10^5 \div 10^6$ cm^{-2}, and a large amount of precipitates has been found, but the purity of crystals was better owing to the purifying effect of the solvent. The growth rate was 4.5 mm/day and 1 mm/day for the stoichiometric and non-stoichiometric growth, respectively.

The phenomenon which plagues the growth of the tellurium-based crystals by a Bridgman method or by any method of growth from the liquid phase is the precipitation of tellurium. According to Uchida et all.[17] — the number of tellurium precipitates can be diminished only after crystallization, by the annaealing of the crystal wafers in the cation vapor under controlled pressure. The wafers prepared in such a way have been succesfuly used in the manufacturing of the ZnTe-based green diode[12].

3.2. Travelling heater method
In the widely known "travelling heater method" (THM), developed by Triboulet and Didier[18], the zone of hot liquid (tellurium in the tellurim-based crystals) travells slowly (a few milimiters per day) along a batch of previously synthesized polycrystalline material. High purity of the crystals grown by THM results from the refining effect of the travelling zone of liquid. The tellurium based crystals contain always tellurium precipitates. Usually it is difficult to obtain the whole cross-section of the ampoule filled with one single crystal.

3.3. Cold travelling heater method
In this method, elaborated by Triboulet, Pham Van and Didier[19] for CdTe and ZnTe, the zone of liquid Te travels along a batch of elements (not a polycrystalline compound) in the forme of pieces or powder. "The crossing of the solvent zone through this charge, at a temperature lower than the melting point of the compound, induces the fractional synthesis of the compound in Te solution, its growth and purification as well. Synthesis, growth and purification are thus achieved at low temperature, at the same time, in a simple and inexpensive furnace, in contrast to other processes." The best pair "growth temperature - growth rate" has been found to be 780 ^0C — 2.5 mm/day for CdTe and 980 ^0C — 3mm/day for ZnTe. The single crystals (large fragments of a rod, 20 mm in diameter) obtained with this method showed very high mobility of free carriers and low concentration of residual impurities but were apt to contain tellurium precipitates.

3.4. Physical vapour transport
The "physical vapour transport" (PVT) is a process, in which the previously synthesized compound ("source material") evaporates, goes to the region of a little lower temperature and condenses, causing the growth of the crystal. The advantage of all the vapor-phase methods of growth of the II-VI compounds is the low temperature, which is usually 250 $\div$ 400 ^0C below the melting point. Thus, the tendency to twinning and contamination is greatly reduced. Another good point of these methods is the effect of "self purification". The impurities, which are less volatile than the crystallizing compound, remain at the place of the source material.

The contact between the growing crystal and the wall of the quartz ampoule poses very serious problems (contamination, stress etc.). The "contactless" PVT growth method has been elaborated for CdS by Markov and Davydov[20]. Grasza et al.[21-23] have developed the "contactless" method for CdTe and ZnTe using a very peculiar procedure to achieve self-seeding at low supersaturation. The method is complex, requires a great operational skill, but results in the single crystals of very high quality.

The main disadvantage of the crystallization from the vapour phase is the slow pace of the process. Usually the rate of the crystal growth is below 10 mm per day.

4. THE HIGH-QUALITY CRYSTALS OF ZnTe AND CdZnTe GROWN BY THE AUTHORS

4.1. The method of growth
We have chosen[24,25] the simple horizontal vapour transport method, described by Piper and Polich[26] in the first paper on the PVT technique. The process of crystallization proceeded in a closed horizontal quartz ampoule with a conical tip at the colder end. The temperature profile of the furnace was presented in one of our papers[27]. The design of the furnace allowed us to observe the process of nucleation in the tip of the ampoule. Typical growth rate for good quality crystals was of $3 \div 10$ mm/day. The crystal rods 25 mm in diameter and $30 \div 50$ mm long were grown. Because the quality of the source material, which should be stoichiometric (very important!), pure, and free of trapped gases, turned out to be one of the fundamental factors influencing the process of growth and the quality of the crystals — the source material was the object of characterization nearly as extensive as that used for the final crystals.

4.2. Methods of characterization of the crystals
The quality of the crystal structure was checked by X-ray rocking curve measurements with a Philips High Resolution Diffractometer, by the reciprocal space mapping, by the etch pit density (EPD) measurements (to determine the density of dislocations) and by the measurement of the width of the free exciton structure in the reflection spectrum. The composition of the ternary $Cd_{1-x}Zn_xTe$ crystals was studied by the energy dispersive X-ray fluorescence (EDXRF) measurements, by the measurements (at 2 K) of the position of the free exciton structure in the reflection spectrum and of the position of the bound exciton line in the luminescence spectrum[28]. The impurities were investigated by the luminescence, reflectivity, conductivity, and Hall effect measurements.

4.3. Results of characterization
The FWHM of the rocking curve was of about 17 arcsec for both $Cd_{0.89}Zn_{0.11}Te$ and ZnTe crystals. The EPD was in the range $5 \times 10^3 \div 10^4$ cm^{-2} for $Cd_{1-x}Zn_xTe$ crystals and about 10^4 cm^{-2} for ZnTe. The reciprocal space mapping of the crystals has shown that the stress (related to the chemical disorder) in the ternary crystals was very small. The distance between minimum and maximum of the free exciton structure in the reflectivity spectrum was only 1.5 meV for ZnTe crystals and the free exciton peak in luminescence was clearly seen in the vicinity of the free exciton structure in reflection.

The homogeneous composition of the CdZnTe crystals was a very important achievement. Very small decrease of the Zn content could be seen in the growth direction, but there was usually a "plateau" in the middle of the rod, indicating a large, homogeneous piece of crystal.

While the lines belonging to excitons bound to neutral acceptors: Ag_{Zn} and Li_{Zn} and the DAP band corresponding to Na-acceptors could be detected, the Cu-related DAP band and the characteristic oxygen- related band were below the detection limits. The concentration of Cu impurity was estimated to be well below 10^{15} cm^{-3}. At room temperature the crystals of ZnTe and $Cd_{1-x}Zn_xTe$ were of p-type. The concentration of holes in the $Cd_{1-x}Zn_xTe$ crystals was, for example, of 10^{16} cm^{-3}, according to Hall effect measurements (resistivity of about 10 $\Omega \cdot$cm). The high resistivity CdZnTe crystals, transparent to the infrared light up to the wavelength of 20 micrometers, were prepared by annealing in Zn vapor ambient. The room temperature resistivity of the annealed crystals was $10^6 \div 10^7$ $\Omega \cdot$cm.

5. CONCLUSIONS
The wide-gap II-VI semiconductors begin to be extensively used in many important fields of technology because various properties of those crystals make them, for specific applications, superior to the other ones. But very often the great advantage of the application of those semiconductors can be revealed not before the crystals of very high quality can be grown. This is the reason why the technology of the *very high quality crystals* of the wide-gap II-VI semiconductors has to be developed.

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