Preparation and properties of a novel near infrared photovoltaic detector single-crystal material

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Abstract. A new photoelectronic semiconductor crystal, mercury indium telluride (MIT), with dimensions of 15mm in diameter and 175mm in length has been successfully grown by using the vertical Bridgman method (VB) at the optimized growth conditions. The crystal was determined through the power X-ray diffraction to be defect zinc-blende structure with the space group $\text{F}4\overline{3}m$. The transmittance spectra from 2.5 to 25 $\mu$m shows high middle and far-infrared transmittance of 50–55%, which decreases gradually with the increase of wavenumber due to the lattice absorption and free carrier s absorption. Hall measurements at room temperature show that the resistivity, carrier density and mobility of the MIT crystal are $4.79 \times 10^2 \, \Omega \, \text{cm}$, $2.83 \times 10^{13} \, \text{cm}^{-3}$ and $4.60 \times 10^2 \, \text{cm}^2 \, \text{V}^{-1} \, \text{s}^{-1}$, respectively. The reduction of carrier mobility and the increase of the resistivity are related to the adding of In$_2$Te$_3$ into HgTe, which changes the energy band structure of the crystal.

1. Introduction

Hg$_{(3-3x)}$In$_{2x}$Te$_3$ ($x=0.5$) is a novel photoelectronic semiconductor material for photovoltaic devices, which is an equimolar solid solution of Hg$_3$Te$_3$ and In$_2$Te$_3$ and crystallizes in the defect zincblende structure [1-3], where the sites of the anion are occupied by Te ions and the sites of the cation by Hg ions, In ions and structural vacancies. Because of the valence difference of Hg$^{2+}$ and In$^{3+}$ ions, high concentration of neutral vacancies (about $10^{21}$ $\text{cm}^{-3}$) is introduced into the structure of Mercury indium telluride (MIT) material. The number of structural vacancies is proportional to the content of In$_2$Te$_3$, which has large effects on the properties of the crystals. In In$_2$Te$_3$-HgTe system MIT is a compound of chemical inertness that shows wide spectral photosensitivity, electrical inertia of introduced impurities, and high resistance to gamma and neutron radiation [4-6]. MIT photodiode remains operating even up to temperature of $T \approx 85 \, ^\circ\text{C}$. This makes MIT especially attractive for the application of fast and efficient photodetectors, optical filters, visible and infrared radiation sensors, X-ray detectors and temperature sensors, etc [4]. There are a few previous papers concerning the reaction kinetics in view of material chemistry and elastic behavior from mechanical properties and so on [3, 7]. So far, few works on single crystals growth, optical properties and electrical properties of MIT is reported. In this paper we report on the growth and characterization of MIT crystals as well as the optical and electrical properties.
2. Crystal growth and measurements
The single crystals of MIT (x=0.5) were grown by vertical Bridgman method with a quartz crucible (15mm in diameter). The starting materials of the high purity elements (of at least 7N purity) of Te, In, Hg were charged into the dried quartz crucible with a stoichiometric ratio corresponding to the compound to be grown, then evacuated to about 10⁻⁴ torr and sealed. The crucible was designed to be sharp-pointed cone tip to form a seed crystal in the initial region and had been well treated with the aqua regia and acetone to acquire clean inner surface and to decrease the chance of side wall nucleation. The starting materials in the crucible were synthesized in a rocking furnace. The crystal growth was carried out in the same crucible in a vertical Bridgman furnace to avoid extraneous impurity pollution. Mixtures to be grown were fused in the VB furnace and annealed at 1040K for 24h to obtain homogeneous melts, then gradually lowered the crucible from the high temperature zone to the cold zone in the temperature gradient of about 10K/cm. The crucible translation speed was less than 1mm/h. The as-grown MIT crystal of Ø 15mm×175mm with good quality and free crack is shown in figure 1.

Parts of the as-grown crystal of MIT were crashed and finely ground into powders for X-ray diffraction analysis, which were carried out in the 2θ range of 20°∼100° using an X’Pert MPO Pro X-ray diffractometer with the step of 0.0330°. The X-ray source was CoKα, which has the wavelength of 1.79021Å. The accelerating voltage was 35KV and the current was 40mA. The X-ray diffraction data were indexed using the DICVOL programs.

The MIT wafer with 1mm thick was cut from the as-grown crystal. The FT-IR transmission spectrum was analyzed using NICOLET NEXUS FT-IR spectrometer in the region from 2.5μm to 25μm.

The conduction type as well as resistivity, carrier density and mobility of the MIT crystal was examined by a H7000 type Hall measurement apparatus in the Van der Pauw configuration. The magnetic field Bz applied was 2k Gauss and the measurement temperature was 300K. The good ohmic contacts were obtained by indium painting on the surface of the MIT sample. The wafers for the measurement were chemo-mechanically polished and etched with 5% Br-MeOH solution to eliminate the damaged layer.

3. Results and discussions
3.1. The structure of MIT crystals
The MIT compound can be considered as being derived from HgTe by replacing every three mercury atoms by two In ions plus one vacancy. The zincblende structure of HgTe is composed of two
equivalent face-center sublattice of Te ions and Hg ions. When In$_2$Te$_3$ is added into HgTe, neutral vacancies are produced:

$$\text{In}_2\text{Te}_3 + \text{HgTe} \rightarrow 3\text{Te}_{\text{Hg}} + 2\text{In}_{\text{Hg}} + V_{\text{Hg}}$$  \hspace{1cm} (1)

The structural vacancies locate in the cation sublattice inhabiting the lattice sites and are proportional to the content of In$_2$Te$_3$. When In atoms are incorporated into the HgTe lattice, vacancies of Hg are formed in the cation sublattice. If MIT crystallizes in zincblende structure, there predicatively exist structural vacancies in the cation sublattice of the defect zincblende structure of MIT material.

![Figure 2. Powder X-ray diffraction spectrum of MIT crystals.](image)

The structural investigation of the as-grown MIT crystals was performed by means of powder X-ray diffraction. Figure 2 shows the X-ray diffraction pattern (XRD) of the as-grown crystal measured at room temperature. The diffraction indices of the crystal are also shown in figure. 2. The pattern measured on MIT compound can be interpreted as that of a face-centered cubic lattice. The data indexed by the DICVOL programs indicate that the structure of MIT crystal is similar to that of sphalerite ZnS. The pattern shows that the as-grown crystal is a single phase of zinc-blende structure with high cation vacancies, which belongs to space group F43m. The unit cell parameters was determined to be $a = b = c = 6.2930\text{Å}$, $\alpha = \beta = \gamma = 90^\circ$. The volume of the unit cell is $249.21\text{Å}^3$.

3.2. Optical properties of MIT crystals

FT-IR was used to analyze the infrared transmittance of the crystals. The result is shown in figure 3. The transmittance in the value of 50–55% indicates that the as-grown crystal has good quality and low defect density. Because the MIT crystal is a direct band-gap semiconductor compound, the electrons in the valence band cannot intrinsically absorb the photons with wavelength in the range of middle and far infrared band. Therefore, the transmittance is higher in this range. In figure 3, the transmittance curve is descending gradually in the region from $400\text{cm}^{-1}$ to $4000\text{cm}^{-1}$, which is likely to be caused by the absorption of the lattice and free carrier. On one hand, with the increase of the frequency, the stronger absorption of the lattice leads to the decrease of the transmittance of the MIT crystal.

On the other hand, the free carriers are scattered by the phonons at the infrared radiation and transfer the energy to the lattice, which will reduce the intensity of the transmittance of infrared light. The absorption coefficient, $\alpha$, of the free carriers can be denoted by:
\[ \alpha = \left( \frac{Nq^2 \nu}{4\pi^2 \nu m^* \varepsilon_0 \epsilon c} \right)^2 \]  

where, \( N \) is the free carriers concentration, \( N = 4.96 \times 10^{13} \text{cm}^{-3} \); \( q \) is the electric charge of the free carriers; \( \nu \) is the scattering frequency; \( n \) is refractive index, \( n = 3.17 \); \( m^* \) is the effective mass of the free carriers, \( m^* = 0.8 m_0 \) (\( m_0 \) is the electron mass); \( \varepsilon_0 \) is vacuum dielectric coefficient; \( c \) is vacuum propagation velocity of the light and \( \lambda \) is the wavelength of the infrared light. It is found that the absorption coefficient of the free carriers is proportional to the square of wavelength (\( \lambda \)). With the decrease of the wavelength, the transmittance of the crystal increases.

In conclusion, the transmittance is higher at low wavenumber than at high wavenumber due to the stronger lattice absorption at high frequency and less free carrier absorption at low frequency. Some text.

Figure 3. Infrared transmission spectrum of MIT crystals.

3.3. Electrical properties of MIT crystals

The typical I-V curve for the MIT crystal is shown in figure 4. From the curve, we can see that the I-V curve agrees well with the Ohmic Law and can be used to calculate the resistivity of the MIT wafer. Hall Effect measurements on the electrical properties at room temperature in the Van der Pauw configuration were used to find out resistivity, carrier density and mobility of the MIT crystal.

In n-type semiconductors, Hall coefficient can be expressed as

\[ R_H = -\gamma \frac{1}{ne} \]  

where, \( R_H \) is Hall coefficient, “-” represents n-type conductivity, \( \gamma \) is scattering parameter, which is related to energy band-gap, lattice scattering, ionized and impurities scattering, \( \gamma \approx 1 \), \( n \) is the carrier electron density, and \( e \) is the electron charge. In general, \( R_H \) is the summation of low-resistivity grains and high-resistivity boundaries while the measured Hall coefficient \( R_H \) is approximately equal to that of low-resistivity grains due to the extremely small dimensions of boundaries compared with that of grains.

The electron mobility \( \mu_e \) and the resistivity \( \rho \) are, respectively, defined as

\[ \mu_e = |R_H| \sigma \]  

where, \( \sigma \) is the electrical conductivity.
\[
\rho = \frac{1}{\sigma ne\mu_e}
\]  

(5)

where, \(\sigma\) is conductivity. Hall measurement at room temperature revealed that the MIT crystal was n-type conduction with \(R_H = -5.58 \times 10^5 \text{cm}^3\text{C}^{-1}\). The resistivity, carrier density and mobility of the MIT crystal at room temperature were \(4.79 \times 10^2 \Omega\text{cm}\), \(2.83 \times 10^{13} \text{cm}^{-3}\) and \(4.60 \times 10^2 \text{cm}^2\text{V}^{-1}\text{s}^{-1}\). As comparison, the main electrical properties of HgTe are also listed in table 1.

![Figure 4. The typical I-V curve for the MIT crystal.](image)

| Parameters | Energy band-gap (eV) | Electrons Mobility (cm²V⁻¹s⁻¹) | Intrinsic carrier concentration (cm⁻³) | Resistivity (Ωcm) |
|------------|----------------------|-------------------------------|--------------------------------------|------------------|
| MIT (x=0.5) | 0.73                | 460                           | \(2.83 \times 10^{13}\)              | 478.5            |
| HgTe [8]   | -0.11               | 30000                         | \(3 \times 10^{17}\)                | 6.94\times 10^{-4} |

From table 1, we can conclude that after adding 50mol% In₂Te₃, the resistivity increases six orders of magnitude while carrier density and electrons mobility reduces. It is obvious that the energy band-gap become larger, which may be the main reason that results in the increase of resistivity and the decrease of mobility. HgTe itself is a semimetal in consequences of a small band overlap with an extremely high electron mobility and low resistivity, whose energy band-gap is negative. Even the conduction band is much lower than the valence band. The addition of In₂Te₃ into HgTe causes the energy band overlap to decrease until it goes through zero and become positive, which means that the band edges become parted. Therefore, the resistivity increases and the carrier mobility and carrier density become smaller. In the mean time, the addition of In₂Te₃ introduces high concentration of vacancies, which act as acceptors in the crystal and lead to the reduction of carrier density and the increase of resistivity.

4. Conclusions

We have successfully grown mercury indium telluride (MIT) crystals with dimensions of 15mm in diameter and 175mm in length by the vertical Bridgman method (VB) at the optimized growth conditions. The results of power X-ray diffraction show that MIT crystals have defect zinc-blende structure with the space group F43m. The infrared transmittance of MIT crystal in the region from
400cm\(^{-1}\) to 4000cm\(^{-1}\) was determined by FT-IR to be 50–55\%, which decreases gradually with the increase of wavenumber due to the lattice absorption and free carriers absorption. As compared to semimetal HgTe, alloying In\(_2\)Te\(_3\) improves the semiconducting properties of MIT crystal. The resistivity, carrier density and mobility of the MIT crystal determined by Hall measurements at room temperature are \(4.79 \times 10^2\ \Omega\text{cm}\), \(2.83 \times 10^{13}\ \text{cm}^{-3}\) and \(4.60 \times 10^2\ \text{cm}^2\text{V}^{-1}\text{s}^{-1}\), respectively.

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