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Temperature Dependence of the Optical Characterizations of GaTe Single Crystal

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GaTe,
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Abstract: GaTe binary semiconductor was grown by the modified Bridgman-Stockbarger technique. Absorption measurements, XRD, SEM, EDX and AFM were performed for structural, morphological and optical characterizations of the semiconductor. As a result of the XRD analyses, it was observed that GaTe binary semiconductor had monoclinic structure. To define the effect of annealing temperature on structure, the grown crystal annealed in a nitrogen gas environment at different temperatures in determined periods, after annealing XRD analyses were done. For GaTe semiconductor, atomic weight values that were obtained by the EDX technique and the values that were calculated during growth and applied agreed with each other. The absorption measurements of GaTe binary semiconductor was in the range of 10-320 K and these measures were performed for each 10 K steps. Energy band width and absorption coefficients were determined as a function of temperatures variable for GaTe single semiconductors.

GaTe Tek Kristalinin Sıcaklığa Bağlı Optik Karekterizasyonu

Anahtar Kelimeler
GaTe,
XRD,
SEM,
EDX,
AFM,
Soğurma Katsayısı,
Band aralığı

Özet: GaTe ikili yarıiletken bileşikleri, modifiye edilmiş Bridgman-Stockbarger kristal büyütme yöntemi ile elde edilmiştir. Büyütülen kristallerin yapısal, morfolojik, topolojik ve optiksel karakterizasyonları sırasıyla XRD, SEM, EDX, AFM ve soğurma ölçümleri ile gerçekleştirilmiştir. XRD analizleri sonucunda, GaTe ikili kristallerinin monoklinik yapıya sahip oldukları belirlenmiştir. Tavlama sıcaklığının yapı üzerindeki etkisini belirlemek amacıyla büyütülen kristaller çeşitli sıcaklık değerlerinde belirlenen süreler boyunca azot gazı ortamında tavlanmış ve tavlamadan hemen sonra XRD analizleri yapılmıştır. GaTe yarıiletkeni için EDX tekniği ile elde edilen atomik ağırlık değerleriyle büyütme esnasında hesaplanıp uygulanan değerleri birbirleriyle uyum içinde olduğu belirlenmiştir. Bileşiğin soğurma ölçümleri 10-320 K aralığında ve 10 K'lik adımlarla alınmış GaTe ikili bileşiklerine ait sıcaklığın bir fonksiyonu olarak soğurma katsayısı ve yasak enerji aralıkları hesaplanmıştır.

1. Introduction

Group III-VI compounds are suitable for optoelectronic circuit elements such as photon detectors, lasers and nuclear detectors. Layered GaTe from III-VI compounds has a high potential for applications such as optoelectronic devices, radiation detectors, solar cells due to a direct bandwidth of approximately 1.7 eV at room temperature. The chemical bonds between the layers are van der Waals

bonds, while the atoms inside the layers have dominantly covalent bonds. Interactions between strong covalent bonds and weak van der Waals bonds are responsible for structural, electrical and optical properties with two-dimensional characters in this system. GaTe grows in hexagonal or monoclinic form according to the growth method. GaTe grown by the Bridgman technique is usually monoclinic [3,4,5]. Two-thirds of the Ga-Ga bonds of the GaTe crystal are perpendicular to the layer planes. The remaining one is parallel to the plane of the plates. Due to this property, it differs greatly from other III-IV compounds crystallographically and optically. Since GaTe has a direct band gap, it is more advantageous in optoelectronic applications. In addition, GaTe has higher anisotropy than other layered III-IV compounds.

The forbidden energy range of GaTe binary compound at room temperature is 1.67 eV and 1.79 eV at 4K. The GaTe binary compound can be proposed as the optoelectronic material of the future due to its energy range of 1.67 eV at 300 K, strong exciton luminescence emission and significant optical nonlinearity properties. From the optical absorption and passing data, it was found that the GaTe crystal gave a very strong (αmax = 16000 cm^{-1}) and rather narrow (meV) exciton peak at $E_{ex.}$= 1.779 meV energy, the exciton binding energy was 17.5 and 19.5 meV, the refractive index was 2.7. The direct bandwidth is reported as 1.797 eV at 1.6K, 1.7 and 1.667 eV at 300K at 4K, the temperature coefficient of variation of the bandwidth (4.14-4.8 10^{-4} eV / K) and the static dielectric coefficient of 7.3 [6].

In this study, pure GaTe semiconductor single crystal belonging to the group of A^{III}-B^{VI} material and used for many technological and industrial applications have been grown by modified Bridgman-Stockbarger techique and its structural and morphological analyses have been performed. Ga and Te elements of purity 99.999% were used for growing GaTe semiconductor. The X-ray diffraction analysis, energy dispersive X-ray and scanning electron microscopy systems were used for structural and morphological characterization of the crystals. The optical absorption measurements were measured using a 4S Spectrometer which works in the range of 175-1100 nm and has a wavelength with less than ±0.3 error nm at 10 and 320 K. Therefore, bandwidth can be determined with an accuracy of approximately better than 0.6 meV considering the wavelength accuracy of the spectrometer.

2. Materials and Method

The first significant step in acquiring high-quality crystals is the purity of the main materials which are being involved in the structure. These elements were weighed in a stoichiometric ratio accurate to 0.1 mg. The total mass of the materials was about 60 g. The main criteria for this choise were, firstly a sufficient need to justify the cost of one run, secondly minimal loss of the material in the form of breakage.

For this purpose, GaTe binary semiconductor was grown by the Bridgman/Stockbarger technique, which was developed in our current crystal growth laboratory. XRD spectra were taken after annealing GaTe binary semiconducting compounds at different temperatures and different annealing times. Structural and morphological properties of the samples were determined using X-ray diffraction analysis (XRD), scanning electron microscopy (SEM) and energy X-ray spectroscopy (EDX) and Atomic Force Microscopy (AFM) techniques. XRD diffraction patterns were obtained at room temperature, then by annealing at 100, 200, 300, 350, 400, 500, 600 and 700 °C for 10, 20 and 30 minutes. The structural of GaTe single crystal was analysed using a x-ray diffraction analysis system using Cu-Kα radiation with a wavelength of λ=1.54050 A°(Bruker 2D Phaser). The values of 2θ were altered between 4 -90°. In this study, two- and three-dimensional AFM images of the surfaces of the crystals were taken to investigate the morphological structures of the GaTe binary compound grown by the modified Bridgman-Stockbarger technique. The fractions of crystal were chosen to be approximately 1x1 μm^2.

2.1. Optical Properties of Crystals

When light is dropped on a crystal material, many optical events occur within the crystal material. These events are; it is called reflection, refraction, absorption, luminescence, scattering and permeability. The main factor in the occurrence of these events lies in different electronic transitions. By using electronic transitions in semiconductors, information about many characteristics can be obtained. Especially to determine the optical properties of the GaTe binary semiconductor amplified within the scope of this study, absorption measurements were taken and band gap energy range and binding energies were calculated using these measurements.

3. Results and Discussion

Pure GaTe of good quality crystal was grown by using the Bridgman/Stockbarger technique. We submit the conclusion of the well ordered studies on the structural analysis and optical properties of the GaTe. According to XRD results, it was observed that the GaTe samples had monoclinic crystal structure. From XRD data, the lattice parameters are a = 17.404 Å b = 10.456 Å and C = 4.077 Å.

The intensity of the peaks increased and the FWHM of peaks decreased for GaTe crystal anneled at 350°C for 10 minutes and 600°C for 20 minutes. As clearly seen from Figure (1-3) XRD spectra of GaTe. The Miller indices are indicated on each diffraction peak. Some of the crystal properties were calculated for the most intense peak (410) for GaTe crystal. These features; inter plane distance (d), grain size (D), residual strain (δ), dislocation density (ε), number of crystals per unit areas (N) and micro strain (σ) [1,2] were calculated at room temperature and at 100, 300 and 500 °C and tabulated in Table 1 below for some temperatures.

SEM analyzes provide information about features such as nucleation, crystal growth, atomic proportions and crystal structure. Sufrace images of GaTe grown by modified Bridgman-Stockbarger technique were obtained by SEM system. The surface of the sample is covered with gold so that the image is clear and high quality. The gold provides conduction between the electron beam and the sample. SEM images of GaTe obtained at magnification rates of 125.000 and 5.00 kV are shown in Figure 4.

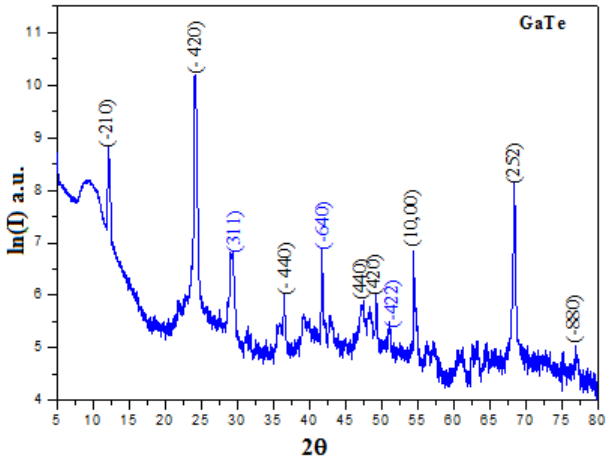

Figure 1. X-ray diffraction patterns of as-grown GaTe crystals.

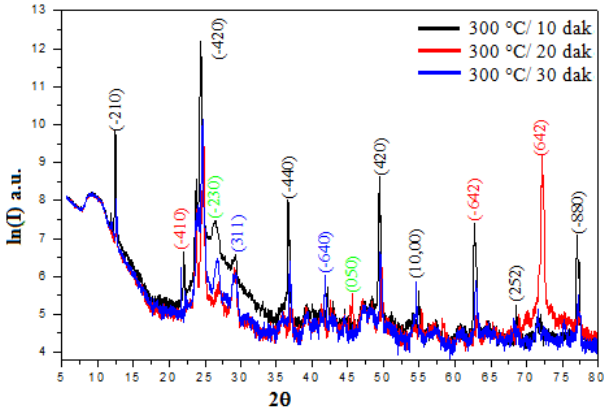

Figure 2. X-ray diffraction patterns of GaTe crystal annealed at 300 ° C/10-20-30 min.

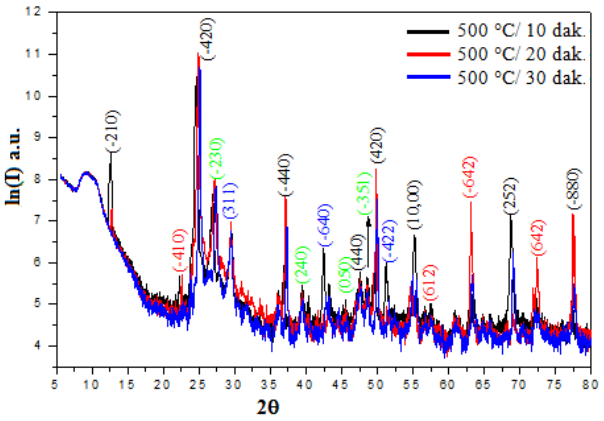

Figure 3. X-ray diffraction patterns of GaTe crystal annealed at 500 ° C/10-20-30 min.

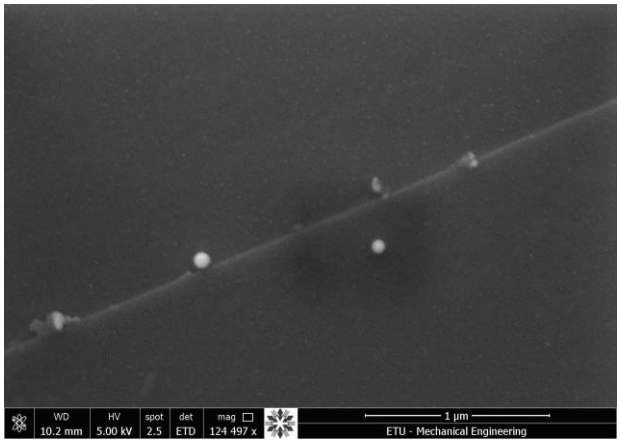

Figure 4. SEM image of GaTe crystal.

As seen in the Figure 4, there is a homogeneous distribution on the surface of the GaTe semiconductor. When the EDX results for GaTe are examined, it is found that the content of Ga is 36.62% by weight, that of Te is 63.33% and that of oxygen is 0.05% in Figure 5.

Table 1. Some crystal properties of GaTe at various temperature and annealing times.

Sample	2θ	FWHM (deg.)	D_{exp} (Å)	ε, x10^{-4} (lin^{-2}m^{4})	δ x10^{14} (lin/m^{2})	N x10^{18} (m^{-2})
GaTe	24.197	0.216	418.2	9.215	5.718	6.973
GaTe 100°C-10 min.	24.699	0.159	534.6	6.777	3.091	2.771
GaTe 300°C-10 min.	224.4311	0.148	574.1	6.311	2.680	2.237
GaTe 500°C-10 min.	24.622	0.152	559.2	6.480	2.827	2.424

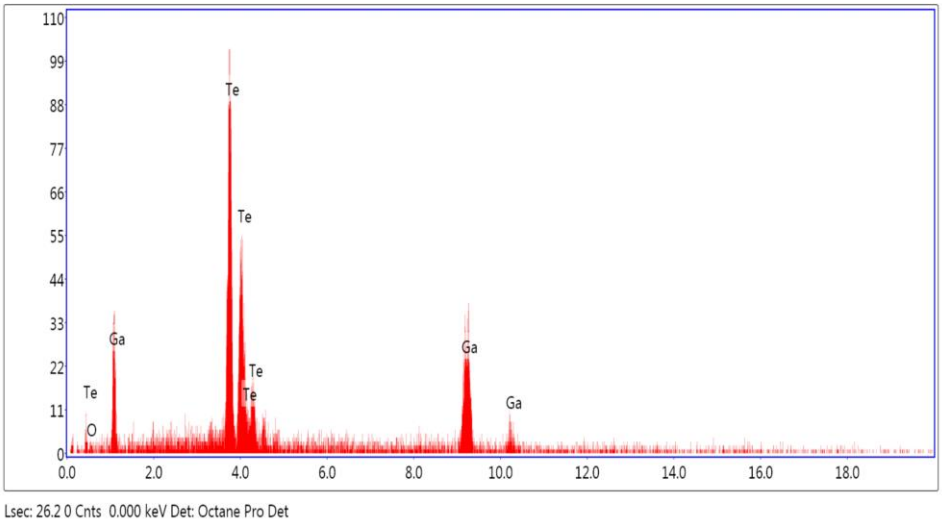

Figure 5. The EDX spectrum of the binary compound GaTe.

AFM was used to investigate the morphological structures of the GaTe binary compound amplified by modified Bridgman-Stockbarger technique. Figures 6-7 show two- and three-dimensional AFM images of the surfaces of GaTe crystal. The height difference between the highest peak and the lowest pore is only 4.7 nm and the mean square root (RMS) surface roughness value is 0.51 nm. This height difference and the RMS value are quite low and the surface of the crystal can be said to be smooth and flat.

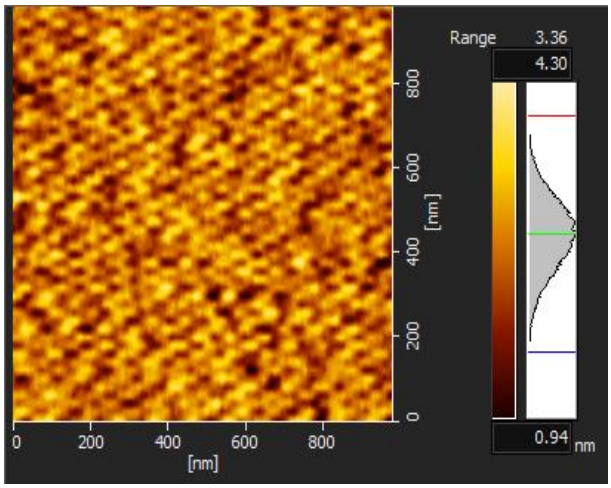

Figure 6. Two-dimensional AFM image of GaTe crystal.

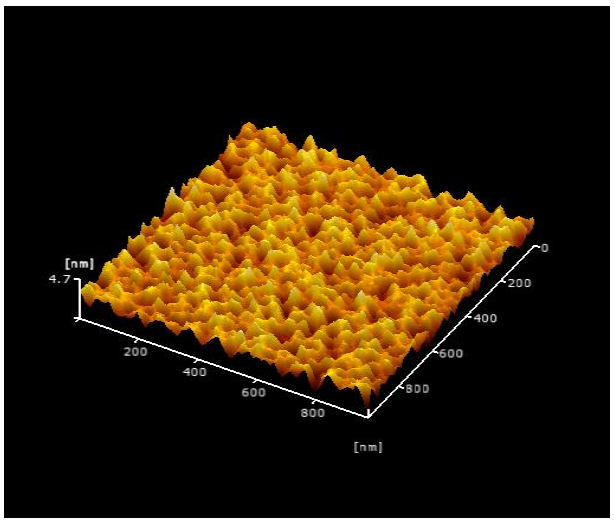

Figure 7. Three-dimensional AFM image of GaTe crystal.

Absorption measurements of GaTe semiconductor was taken depending on temperature. For this, the sample temperature was started in 320 K and decreased in 10 K steps and the last measurement was taken at 10 K temperature. A certain time (10 minutes) was waited to achieve steady state at each temperature value. The absorption data obtained with the help of Perkin Elmer UV/VIS Lambda spectrometer were converted into absorption coefficient values and their wavelength-dependent changes were obtained. By converting the values taken in wavelength into eV, photon energy graphs corresponding to the absorption coefficient were obtained. The variation of the absorption coefficients of the GaTe compound with temperature is given in Figure 8. The thickness of the GaTe binary compound was measured as 58 µm.

When the basic absorption spectrum of the GaTe binary compound was examined, a shift was observed in the spectrum with decreasing temperature. Since the optoelectronic properties of the GaTe binary compound affect the transient property of carriers, it has been reported to be highly dependent on impurity atoms and hence annealing has a significant effect [7]. After annealing the GaTe semiconductor (30 minutes at 350°C), it was seen both a shift in spectrum and a very little change in the absorption coefficient. On the basis of the shift, phonon-defect interactions are likely to occur. When the temperature increases, the result of the increase in the vibration of the crystal lattice causes the crystal lattice to change, and thus the valence band approaches the conductivity band. As a result of this approach, absorption shifts to regions with longer wavelengths [8]. In addition, other factors in changing the band gap are known to be the degree of crystallinity, stoichiometric ratios, Ga vacancy defects [7]. As can be seen in Figure 8, we can say that annealing has an effect on the GaTe binary compound and has made an improvement in the structure. In addition, as a result of annealing, the absorption spectra appear to be steeper. The reason for the steepening of the absorption spectra as a result of annealing may be the reduction of the optically activity of the impurity atoms and the homogenization of the structure (Figure 8, 9).

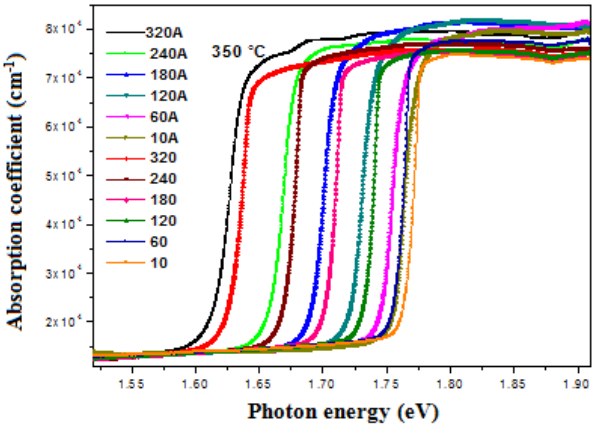

Figure 8. Comparison of the change with temperature of the absorption coefficient of the annealed and non-annealed GaTe semiconductor.

Table 2. Comparison of the band gap energy value of annealed (30 minutes at 350°C) and non-annealed of GaTe for some temperature values.

GaTe		
T (K)	**Annealed**	**Non-annealed**
10	1.7552	1.7550
60	1.7463	1.7467
120	1.7241	1.7234
180	1.6939	1.6930
240	1.6631	1.6606
300	1.6314	1.6288
320	1.6207	1.6167

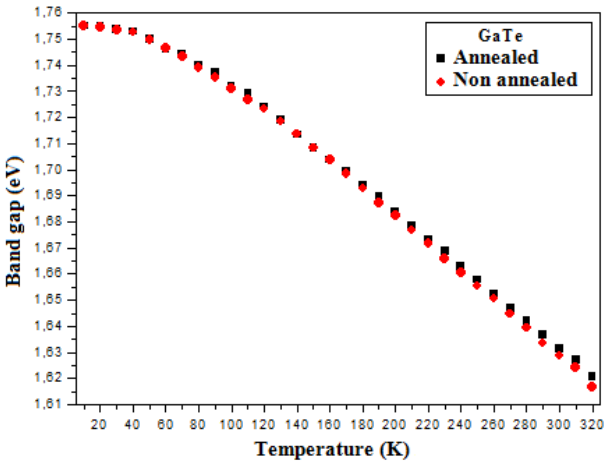

Figure 9. Comparison of the change with temperature of the band gap energy values of GaTe semiconductor .

4. Conclusion

GaTe crystal used in this research was grown by using the Bridgman/Stockbarger technique. The ingots have no cracks and voids on the surface in bulks. There is no process to polish and clean treatments at cleavage faces of these samples because of the natural mirror-like cleavage faces. GaTe has

specific impurities arising from its crystal structure. Samples were cleaved along the cleavage planes (001). The freshly cleaved crystals had mirror-like surfaces even before using mechanical treatment.

For structural analysis of GaTe crystal, XRD spectra was taken for as-grown crystal and the crystal annealed at different temperatures and at different times. When GaTe was annealed at 300 °C for 10 minutes and 500 °C for 20 minutes; the intensity of the peaks increased and the full width at half maximum (FWHM) of peaks decreased. For the as-grown GaTe crystal, the crystallite size (418 Å), residual strain ($9.215x10^{-4}$ lin^{-2} m^{-4}), dislocation density ($5.718x10^{14}$ lin/m^{-2}), number of crystals per unit area ($6.973\ x10^{14}$ m^{-2}) and micro strain (0.599) values have been determined using XRD results (410). From the SEM and AFM results, it was observed that the sample was homogeneous.

The effect of annealing on the band gap energy values shows that there is an increase of approximately 0.01 eV in the band gap energy at high temperature as a result of annealing for the GaTe binary compound. But as the temperature value decreases, the difference is observed to decrease. It was reported that Ga and Te vacancy defects in the GaTe have significant effects on the band structure [14,15]. It was observed that the band gap energy ranges of the annealed and non-annealed sample increased with decreasing temperature. The band gap energy for GaTe is between 1.75 and 1.62 eV and these values have also been reported in the literature [7, 8-13].

Highlights

1. GaTe semiconductor was grown by the Bridgmann-Stockbarger Technique.
2. The structural, optical, surface morphology and composition of GaTe semiconductor were studied.
3. The techniques of XRD, SEM and EDX were used.
4. The band gap value of GaTe decreased with increasing temperature.

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