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Crystal Growth, Characterization and Anisotropic Electrical Properties of GaSe Single Crystals for THz Source and Radiation Detector Applications

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Abstract. The single crystal growth of large semi-insulating GaSe by the vertical Bridgman technique using zone-refined selenium (Se) and HP gallium (Ga) is described. The grown crystals (up to 10 cm long and 2.5 cm diameter) have been characterized thoroughly by X-ray diffraction (XRD), energy dispersive analysis by x-rays (EDAX), optical absorption/transmission, X-ray photoelectron spectroscopy (XPS), charge carrier electrical property measurements, second harmonic test, and radiation detection measurements.

INTRODUCTION

Recently, there has been considerable interest in the properties of layered semiconductors because of their highly anisotropic properties, resulting from strong covalent bonding within the layer planes and weak van der Waals type bonding between them. GaSe, a III-VI semiconductor, is one such compound whose fundamental properties have not been studied in detail, although it's possible applications in nonlinear optics [1], tunable THz sources [2-3], broadband THz detection [4] and radiation detectors [5-6] have been investigated. Since the early 1970's, this material has been the subject of several studies [7], but difficulties in growing large and good quality crystals limited its widespread applications. We report here large device-grade single crystal growth of GaSe and their characteristics as radiation detectors and THz sources.

EXPERIMENTAL

GaSe single crystals (mp 950°C) were grown from stoichiometric amounts of high purity (6N) Ga and EIC's zone-refined (7N) Se using the vertical Bridgman method. Ga was etched in an ice bath with semiconductor grade concentrated HCl followed by repeated rinsing with deionized water and dry in a flow of purified nitrogen. Synthesis of GaSe was first carried out at 1050°C in a sealed quartz ampoule evacuated to 10^{-6} torr using a two zone horizontal furnace. Continuous rotation during the synthesis was used to ensure homogeneity. The polycrystalline product was then placed in a conically tipped thick-walled quartz ampoule and sealed under a vacuum of 10^{-6} torr. The conical tip was specially designed to hold a GaSe seed crystal, which was used to prevent secondary nucleation and to allow growth along a preferred orientation. Low temperature gradients (~10°C/cm) were used to stabilize the solid-liquid interface, minimize stresses resulting from anisotropy of the thermal expansion coefficients and also suppress volatile evaporation of Se. The sealed ampoule was then placed in the Bridgman crystal growth furnace and connected to a slow-speed (0.2 rpm) motor. The polycrystalline material was heated slowly (10°C/hr) to 1050°C in a computer controlled three-zone vertical furnace. After 72 hours, the furnace started "pulling" crystal at a rate of 0.5 cm/day. After the entire ingot was solidified, the temperature was lowered at a rate of 15°C/hr to room temperature.

RESULTS AND DISCUSSION

Following the procedure described above, we have been able to grow up to 10 cm long and 2.5 cm diameter GaSe ingots. X-ray diffraction of the powdered sample confirmed the hexagonal phase of GaSe with a=3.743 Å and c=15.916 Å. Energy dispersive analysis (EDAX) was carried out on three specimens and showed 49.8-50.0% Ga and 50-50.2 % Se. XPS analysis was used to determine the chemical composition from the peak intensities, taking into account the photoionization cross sections measured under identical conditions. The results agreed with the values obtained from EDAX.

Optical observation under an infrared microscope did not reveal any precipitates or microcracks or any formation of second phase Ga_2Se_3. Bulk optical absorption measurements on a grown 10x10x5 mm^3 (z-cut) GaSe crystal showed that the linear absorption was ~0.98 cm^{-1} in the visible wavelength of 0.68-0.80 μm and <0.8 cm^{-1} in the IR range of 1.0 to 18 μm. Preliminary second harmonic generation (SHG) tests (type I) on the same crystal with no antireflection (AR) coatings showed a d value of 54 pm/V and excellent stability of the SHG power output at 4.8 μm.

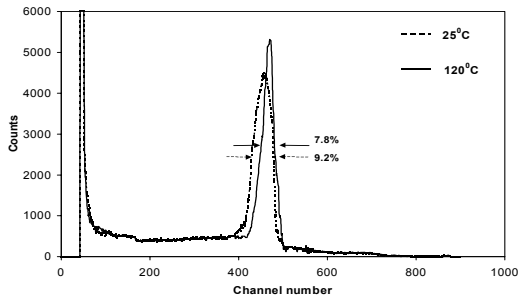

FIGURE 1. ^{241}Am spectrum at a bias voltage of -30V and 5 μs integration time at 25°C and at 120°C.

Thin wafers of about 300 μm with area 5x5 mm^2 have been cleaved from the as-grown ingot, and gold contacts with a circular diameter of 3 mm were deposited on both sides by sputtering. From dark current-voltage measurements we have estimated a bulk resistivity of 4.8x10^8 Ω.cm. Electric fields of up to ±750 V/cm could be applied without causing any electrical breakdown. The leakage current measured was small (~140 nA) at 25°C but increased to 182 nA at 120°C. For α-particle detection performance, a negative bias voltage of –30V was applied to the top gold electrode irradiated with ^{241}Am. As shown in Fig. 1, the pulses observed at 120°C are slightly higher in amplitude than that observed at 25°C. This is probably due to the increase in the charge collection efficiency resulting from the thermal detrapping of electrons in the GaSe crystal. The energy resolution at 120°C is 7.8%, expressed in terms of the full width at half maximum (FWHM), which is better than the energy resolution of 9.2% at room temperature. Therefore, it is concluded that GaSe radiation detectors can be used at temperatures of up to 120°C.

Nuclear detection measurements were carried out with a reversal of the polarity of the applied bias, and the mobility-lifetime product ($\mu\tau$) data for electrons and holes has been extracted using Hecht analysis. The results are presented in Table 1. The $(\mu\tau)_e$ is about an order of magnitude larger than $(\mu\tau)_h$. This is one of the main problems limiting the spectral resolution, due to hole trapping and creating a "tailing" on the low energy side of a photo peak. Our future work will be concentrated on improving the ($\mu\tau$) values by better purification of precursor materials, optimum doping, and more controlled crystal growth.

TABLE 1. Properties of gallium selenide

Property	Value
Bandgap	2.02 eV at 300K
Resistivity (ρ)	> 10^8 Ω.cm
Electron ($\mu\tau$) product	6.8 x 10^{-6} cm^2/V
Hole ($\mu\tau$) product	5.3 x 10^{-7} cm^2/V

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