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Photoelectric studies of gallium monosulfide single crystals

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Abstract

Photoconductivity (PC) studies were carried out on GaS single crystals prepared from melt by directional solidification. We studied the effect of light intensity, applied voltage on both the PC and the lifetime of carriers. The V-I characteristics and the absorption spectra were checked for different sample thickness. The present investigation was extended to study the spectral distribution of the photocurrent for GaS. It was found that the photocurrent curves are practically independent of the bias voltage. The energy gap for GaS was found to be 2.5 eV. © 2004 Elsevier Ltd. All rights reserved.

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1. Introduction

The GaS compound is representative of A^{III} B^{VI} crystal. It crystallizes in the same hexagonal lattice as β -GaSe [1]. The lattice parameters are a=0.3578 nm and c=1.547 nm and it was also reported [2] that the single layer is arranged in the S-Ga-Ga-S chain along the hexagonal c-axis. GaS has attracted many authors because it is a promising semiconductor. For example, intensive work has been performed on GaS in the form of thin films [3–6]. Other publications were about low temperature-photoluminescence [7], Raman scattering [8] and thermal conductivity [9]. However, some papers were focused on the optical studies in a limited wave length range or on the glass form of the compound [10]. An increase in the low frequency dielectric constant of GaS under hydrostatic pressure was observed by Segura and Chevy [11]. Thermoelectric power measurements of GaS were previously published [12]. From the literature survey there is no data concerning the influence of thickness on the I-V characteristics or on the absorption spectra. From the point of view of elucidation of the data and according to the progressive interest in the material and in the possibility of its optical applications, the work is presented.

2. Experimental details

The crystal growth and crystal identification work were done in the Chemical Engineering Department of the Clarkson University, NY. The eutectic GaS (68.5% Ga and 31.5% S) was produced from gallium (Aldrich 99.9999% pure) and sulfur (BDH 99.999% pure). The weighed components were sealed in a 10-mm inside diameter pointed lower end quartz ampoule with 10^{-5} Pa. The materials were melt at 1373 K. According to the phase diagram, this temperature was reduced to 1188 K (i.e. the crystallization temperature). Then, the melt was directionally solidified in a vertical Bridgman-Stockbarger furnace. The temperature profile was determined in a similar empty ampoule, yielding a temperature gradient at the eutectic temperature of ~25 °C/cm, with the temperature increasing with height throughout the molten region. So, the ampoule was translated downwards at a constant rate of 2 mm/h. The product ingot length was about 5.8 cm. It was of a layer nature with a bright yellow color. The crystals were identified at the same University by means of the following technique:

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Scanning channeling electron microscopy (type JSM 6300 Jeol mark).

- Computer program (voyager), which is a microanalysis and digital imaging system for electron microscope.
- Transmission electron microscopy with energy dispersive X-ray spectroscopy by NORAN instrument (USA) [13,14].

The V-I characteristics of the compound at four different thickness of the sample, i.e. GaS were examined. The thickness was measured by means of highly precision traveling microscope, Man Company (Burlington). We selected the following thickness values: 0.60, 1.22, 2.51, and 3.75 mm. In the whole experiment, the samples were cleaved from the virgin ingot and silver conducting paste was employed as an Ohmic contact. A Keithley electrometer (610C) was used for recording the current values. For the AC photoconductivity (PC), the samples were connected in series with a highly stable DC power supply and a load resistance equal to $12 \times 10^4 \Omega$. The variation of the voltage across the load resistance due to the modulated (PC) was observed on a double beam oscillograph. The light source was a 1000 W tungsten lamp. Also, a chopper controller (SR520) used in the AC (PC) measurements has a square pulse of monochromatic light. The applied light intensity doses were evaluated by means of a Lx-101 Luxmeter. A monochromator Hilger & Watts 6186.3 has been used for the absorption spectra, the spectral distribution and the photocurrent variation measurements.

3. Results and discussions

In the present investigation, we studied M-GaS-M structure in a sandwich form. The bistable, or memory

switching phenomenon is observed during the work of the current-voltage characteristics (CVC) of the virgin GaS sample.

The dependence of the switching behavior of the active thickness between the electrodes is shown in Fig. 1 at room temperature. The curves present a characteristic shape for each different thickness of the sample, consisting of two sections, a pre-switching portion (off state) and a region of sharp current growth with subsequent switching to the low resistance state. The CVC as a whole is shifted towards higher potentials with reducing the thickness of the sample. After switching to the low resistivity state, the samples remain in this state under zero bias for some hours. This effect is known as switching with memory. The thickness of the sample varied from 0.6 to 3.75 mm. It was observed during the work and from the figure that the holding current and the voltage are affected with the thickness of the crystal. This was also noticed in a previous work done for ZnS crystal [15]. It is evident from Fig. 1 that the threshold potential required for striking, increases with the thickness. This result can be explained clearly in terms of Ovshinsky model [16] in which injection and impact ionization are believed to play important roles in such process. This was previously observed in other III-VI single crystals [17,18], and also in the ternary $ZnIn_2S_4$ crystal [19]. The linear dependence of $V_{\rm th}$ on the thickness d shows that switching is a bulk effect and a critical field is needed. The threshold current ith also increases with increasing sample thickness. So the threshold power, calculated as $E_{\rm th} = i_{\rm th} \cdot V_{\rm th}$, increases with the sample thickness too, according to the law $E_{\rm th} \sim d^{0.73}$. This relation



Fig. 1. Current-voltage characteristics of GaS at different sample thickness.



Fig. 2. Dependence of threshold current, threshold voltage and threshold power on sample thickness for GaS single crystal.

shows a linear proportionality between the active thickness and the required power for switching; see the inset in Fig. 2 (top left). As the thickness of the device increases, a large power for switching is required. This work is also important because it enables us to select the proper thickness and bias of the corresponding voltage for studying the PC of the crystal. A symmetrical square monochromatic light pulse for PC excitation was used in case of AC PC measurements. The chopper frequency varied from 20 to 400 Hz. The PC, as a function of chopping frequency of the modulation of the incident light, was registered directly at different values of light intensity. Fig. 3 represents the dependence of PC, as a function of chopping frequency F, at a bias voltage of 60 V and sample thickness of 3.73 mm. The selected values of light intensities were 500, 750 and 1000 Lux. From the obtained dependence we observe that the behavior of the curves in all the figures is similar and they have a general shape in which the PC decreases with increasing frequency in the whole range of investigated frequencies. The behavior of these curves obeys the relation [20]:

$\Delta \sigma_{\sim} / \Delta \sigma_{\rm st} = \tanh(1/4F\tau)$

According to this relation, and making use of such curve, we can derive the lifetime of the carriers at different light intensities. So, the relation between the carrier lifetime τ and the light intensity can be obtained. The lifetime τ is inversely proportional to the illumination intensity. The value of τ was found to be of the order of 10^{-3} s. In view of the high density of the vacant acceptor levels, photocarriers generated by illumination were captured almost immediately by these levels. Therefore, phototransport could occur either by jumps between random centers or could involve capture by traps.

The same work was repeated whilst changing the voltage in order to establish the effect of the applied bias voltage on the photoconduction behavior of the GaS single crystals. This work was done at bias voltage values of 60, 80 and 100 V. The ratio $\Delta \sigma_{\sim} / \Delta \sigma_{st}$ decreases with increasing frequency as shown in Fig. 4. At high chopping frequencies,



Fig. 3. Variation of AC photoconductivity of GaS with chopping frequency at different light intensities.



Fig. 4. Relation between AC photoconductivity of GaS and chopping frequency at different bias voltages.

the photoconductivity ratio decreases more slowly than in the low-frequency range. The effect of the bias voltage on the PC ratio $\Delta \sigma_{\sim} / \Delta \sigma_{st}$ is evident from these curves. The derivation of the carrier lifetime leads to the fact that τ is inversely proportional to the bias voltage. This can be accepted only if we consider the trapping processes of the carriers, which are activated as a result of increasing the bias voltage. Fig. 5

depicts the PC spectral distribution of p-type GaS single crystal in the wavelength range (350–750 nm) at room temperature. This study was done without a change of the incident light intensity. The shape of the spectral distribution was practically independent of the applied bias voltage. An upward shift towards higher values of the photocurrent with the increasing of the applied bias voltage is observed.



Fig. 5. The spectral distribution of the photocurrent for GaS at different bias voltages.



Fig. 6. The absorption spectra of GaS single crystal at 300 K at different sample thickness.

The photocurrent rises continuously with photon energy, and reaches a certain maximum value at 460 nm, then a steep fall is found at high photon energy. The spectral dependence of the photocurrent agreed with previous measurements of the DC PC of similar compound [21]. By applying the half-maximum value [22], we could evaluate the average energy gap as 2.5 eV.

The absorption spectra of gallium sulfide at 300 K is shown in Fig. 6 for different sample thickness (0.6, 1.22, 2.51 and 3.73 mm). The samples for these measurements were obtained by cleavage of the large single crystals perpendicular to the *c*-axis.

The absorption coefficient is extremely low at $hv < E_g$ and the excitation involves transitions from impurity states to band states. For photon energies larger than the gap, the absorption coefficient increases rapidly. Therefore, the cross-section for transition involving impurities becomes negligible and the dominant transitions are band-to-band transitions. Regarding Fig. 6, the following definite comments can be considered:

- The absorption edges extend over a considerable range of energies, which leads us to believe that this arises from indirect transitions.
- Near the fundamental absorption edge, there are absorption lines, after that the absorption sharply decreases.
- The large absorption coefficient of the line, its position in the neighborhood of the fundamental absorption edge

and the reproducibility of the results for all samples, permit one to assume that this line is due to exciton absorption.

The fundamental absorption edge in most semiconductors follows an exponential law. Above the exponential tail, the absorption coefficient of semiconductor has been observed to obey the equation

 $\alpha \hbar \omega = B(h\omega - E_{\rm g})^n$

where $\alpha \hbar \omega$ is the absorption coefficient of an angular frequency of $\omega = 2\pi v$, *B* is a constant, and *n* is an index which can assume the values 1/2, 3/2, 2, and 3, depending on the nature of the electronic transition responsible for the absorption. It is well established that n = 1/2 corresponds to the direct allowed transition (high-energy part of the spectra), n = 3/2 to a forbidden direct transition, n = 2 to an indirect allowed transition (low-energy part of the spectra) and n = 3 to a forbidden direct transitions [22,23].

For the determination of the energy gaps, E_g , of the GaS substance from the absorption spectra, we have plotted $K^{1/2}$, K and K^2 (where K is the experimental absorption coefficient at 300 K), against the photon energy $E=h\nu$. We only found that $K^{1/2}(E)$ approaches a straight line over much the largest range of E values. When this line is extrapolated to zero, which corresponds to the thicknesses: 3.73, 2.51, 1.22 and 0.6 mm and these yields' energy gap values: 2.49, 2.56, 2.55, 2.58 eV, respectively.

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