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Growth, Characterization and Electrical Anisotropy in Layered Chalcogenide Gallium Monosulphide Single Crystals

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Abstract: Single crystals of GaS were prepared by a modified of Bridgman technique. Measurements of electrical conductivity and Hall-coefficient are performed in a single crystal GaS parallel and perpendicular to c-axis. At room temperature the conductivity ratio $(\sigma_\perp / \sigma_{\parallel})$ is equal to ten. The study covers a wide range of temperature. It was found that the samples have p-type conductivity. In the intrinsic conduction region an energy gap of 2.5eV occured The ionization energy is determined. Very strong anisotropy in the hole mobility parallel and perpendicular to c-axis was observed. The scattering mechanism at low and high temperatures is checked.

1. Introduction

Crystalline materials with high anisotropy of physical properties have attracted ever growing attention recently. For many years, the properties of layered crystals have constituted a major research area in solid state physics.[1] In recent years, a great deal of interest has been focused on semiconducting III-IV compounds. This interest has been driven by their possible device applications.[2,3] GaS is a chalcogenide binary layered compound and the interest in this material is stimulated not only by its fundamental properties, but also by possible practical application. A description of the phase diagram for Ga-S and structural studies of all the solid phases are given by many authors.[4-6] Investigations on GaS have revealed that this compound has interesting semiconducting properties.

GaS is a layered semiconductor[7] of the III-IV with a crystallographic structure similar to the InSe and GaSe. Crystals with layer structure are characterized by strong (covalent) bonding within the layers and weak (probably, of Vander waals type) bonding between the layers. The structure of individual layer differs from crystal to crystal. Semiconductors of A_3B_6 group GaS, GaSe and InSe have a more complex, four-fold[8] structure of a layer. Several works on the crystal structure and optical properties of GaS have been reported.[9-14]

At present the electrical properties and Hall effect of the GaS compound is poorly investigated and the data reported in the literature are ambiguous.

Since a good general picture of the physical behavior of a semiconductor can be obtained by measuring the electrical conductivity and Hall effect. In the present note experimental results on the electrical conductivity, Hall effect, and their dependence on temperature in two crystallographic direction are described, in view of the current interest in this material and its possible practical applications.

2. Experimental Technique and Procedure

Single crystals of the layered compound GaS were prepared, by a modified Bridgman technique. Using a quartz ampoule with pointed lower end to facilitate seeding in the growth process containing a molten charge evacuated to about 10^{-5} mmHg and sealed under vacuum. High purity material (99.999%) were used. The ampoule with its charge was introduced in a three-zone tube furnace. At the beginning of the growth run the ampoule was held in the hot zone of the furnace to about 10 hours for melt homogenization, where the temperature was just above the crystalallization temperature, then allowed to be drawn with a very slow rate (1.7mm/h) to enter the middle zone where the temperature corresponds to the crystallization temperature of the compound.

This temperature is 950°c according to the phase diagram[6]. Finally the ampoule enters the last zone of the furnace where the temperature is just below the melting point. Such process requires a very long time, of at least 15 days to be performed. Since the pointed tip enters the lower part of the furnace first, the charge will start to crystallize there. As the ampoule continues to be lowered, crystallization proceeds to take place until all the contents solidify. The apparatus and procedure for crystal growth are mainly the same as those described in the previous work.[15]

The product- a bright yellow crystal- is identified by X-ray analysis and DTA to be GaS.

In preparing the samples for electrical measurements, care was taken to cut them from region of the ingots in which the layers of the crystal lattice were near to one another.

The samples were 4.3x1.4x1.2 mm (in the $J \mathbin{/\!/} C \perp H$ case) and 6.0x1.5x1.0 mm in the case of ($J \perp C \mathbin{/\!/} H$). The samples had natural mirror faces. Ohmic contact for the conductivity and the Hall coefficient measurements were obtained by painting silver paste into the freshly prepared surfaces of the specimens. The ohmic nature of the contacts was checked by recording the current-voltage characteristics. It is convenient for Hall contacts to be infinitely small so that they do not distort the current flow. Samples are then mounted in a pyrex glass cryostat designed for electrical measurements at different temperatures.

A compensation method is used for measuring voltage without drawing appreciable current. For this purpose a Tensely potentiometer is used. By the aid of two selector terminals the Hall voltage and temperature can be measured simultaneously. This potentiometric method of voltage measurements is a standard method to remove the influence of contact resistance on the specimen properties. Variac transformer is used to control temperature variation. The temperature is recorded by means of a cupper-constantan thermocouple. Using a reversing switch all thermomagnetic effect, with the exception of the Ettingshauasen effect, can be eliminated by suitable averaging of the measured Hall emfs.

In general, the error due to the Ettingshauasen effect is small and can be neglected, particularly if the sample is in good thermal contact with its surroundings.[16] All electrical measurements are carried out under vacuum to a void oxidation of the specimen at high temperature and to eliminate contamination with water vapour at low temperature.

3. Results and Discussion

The temperature dependent behavior of electrical conductivity of gallium monosulphide single crystal samples has been studied in a wide range of temperatures. Figure 1 may serve to illustrate the variation of electrical conductivity with temperature for GaS single crystal. The curves show the typical semiconductor behavior. In general $\sigma_{/\!/}$ is higher than $\sigma_{\perp}$ and the ratio between electrical conductivities $\sigma_{/\!/}/\ \sigma_{\perp}$ is approximately equal to 10. For instance at room temperature $\sigma_{\perp} \approx 10^{-13}$ ohm^{-1}.cm^{-1} and $\sigma_{/\!/} \approx 10^{-12}$ ohm^{-1}.cm^{-1}.

At low temperature the carrier concentration is determined by the number of ionized acceptors and consequently the conductivity increases slowly. When intrinsic conduction becomes important the conductivity rises very rapidly with temperature due to the rapid increase in total carrier density (electron plus holes). This means that the intrinsic conduction becomes more favorable at higher temperature, since the intrinsic concentration increases rapidly with temperature. The energy gap width (ΔE_g) is found to be 2.46 eV. In the extrinsic region the impurity ionization energy (ΔE_a) can be calculated, and it is found that (ΔE_a) approximately equal 0.22 eV for $\sigma_\perp$ and 0.15 eV for $\sigma_{//}$.

We notice in Figure 1 the existence of intermediate region which extends from 200-320K corresponding to the impurity exhaustion range. In this range all the impurity atoms are ionized but no noticeable excitation of intrinsic carriers take place because of that the carriers concentration remains approximately constant and equal to the impurity concentration. The variation of electrical conductivity parallel and perpendicular to c-axis can be attributed to the anisotropy of carrier mobility. The temperature dependence of Hall coefficient is represented in Figure 2. From the results and the curves we can conclude the following:

1- The Hall coefficient for GaS single crystal has a positive sign, indicating that the sample has a p-type conductivity.

2- There are two different values of the Hall coefficients, one which is measured with the magnetic field parallel to c-axis, and the other is measured with the magnetic field perpendicular to c-axis.

3- In the intrinsic conductivity range, Hall coefficient varies linearly and rapidly with temperature, but in the impurity region it varies slowly.

In the intrinsic region the Hall coefficient R_H obeys the relation:

$$R_{\mathrm{H}} = \frac{A}{e}\,\frac{\mu_p - \mu_n}{\mu_p + \mu_n}\left(N_C - N_V\right)^{-\frac{1}{2}} exp\left(\frac{\Delta E_g}{2KT}\right)$$

Since the mobility part $\frac{\mu_p - \mu_n}{\mu_p + \mu_n}$ is independent on temperature, the width of the forbidden gap (ΔE_g) can be determined from the relation between lg $R_H T^{3/2}$ versus $\frac{10^3}{T}$

$$\Delta E_{\mathrm{g}}\left(eV\right) = 0.397\,\frac{lg\left(R_H T^{3/2}\right)}{\left(\frac{10^3}{T}\right)}$$

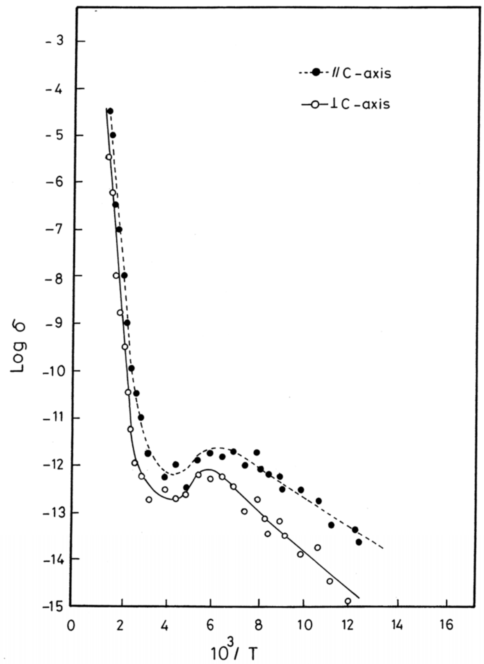

Fig. 1: Temperature dependence of electrical conductivity of GaS single crystal.

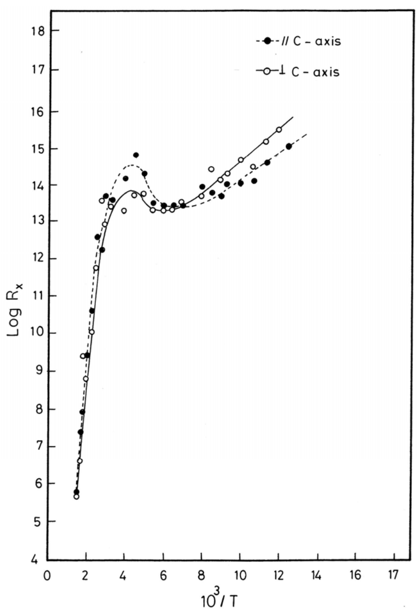

Fig. 2: Dependence of Hall coefficient on temperature for P-type GaS single crystal.

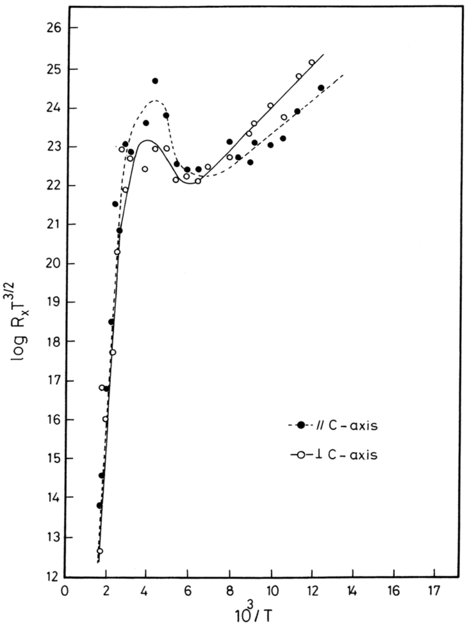

Fig. 3: Relation between $R_H T^{3/2}$ versus $\frac{10^3}{T}$ and for P-type GaS single crystal.

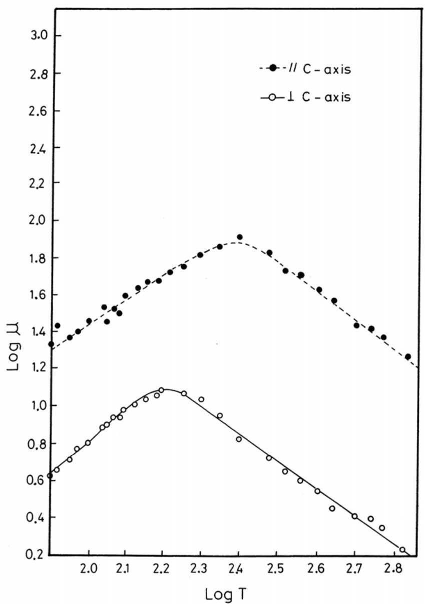

Fig. 4: Variation of charge carrier mobility with temperature.

Figure 3 represents the above relation.

The band width of the forbidden gap as calculated from the slope of the curve in the intrinsic region is approximately 2.54 eV. It appears from the curves that in the extrinsic region, the Hall coefficient is much less temperature-dependent, while in the intrinsic region, the Hall coefficient sharply decreases as the temperature increases.

The Hall constant can be used to determine the Hall mobility.

$$\mu_H = R_H \sigma$$

Thus the mobility of free charge carriers can be determined from measuring both the electrical conductivity and Hall coefficient in extrinsic region.

Experimental measurements of the influence of temperature on the mobility are plotted in Figure 4. From which two regions can be distinguished: At low temperatures, the mobility seems to increase reaching a maximum value $\mu_{\perp}$=12 cm^2/V.sec corresponding to 166 K and $\mu_{//}$=80 cm^2/V.sec corresponding to 250 K.

At low temperatures, it is found that both $\mu_{\perp}$ and $\mu_{//}$ follows a $T^{1.46}$ dependence. In this range of temperatures impurity scattering dominates. At high temperatures both $\mu_{\perp}$ and $\mu_{//}$ have been found to follow a $T^{-1.48}$ dependence, this leads to assumption that lattice scattering dominates and the impurity concentration has little effect on the mobility. The mobility is seem to decrease with increasing temperature. Lattice scattering which is due to thermal vibration of the atoms in the crystal, disrupts the periodicity of the lattice and thereby impedes the motion of free carriers. The difference between $\mu_{\perp}$ and $\mu_{//}$ can be attributed to strong anisotropy of carrier mobility.

From the temperature dependence of the Hall coefficient, temperature dependence of the charge carrier concentration may be experimentally determined.

Figure 5 shows the dependence of charge carrier concentration on temperature. The width of the forbidden gap is calculated and found to be equal to 2.50 eV. From the figure we notice that the concentration of carriers in the intrinsic region increases rapidly with temperature, while it increases slowly with temperature in the impurity region. At room temperature the concentration of free charge carriers lies between 10^4 and $10^5 cm^{-3}$.

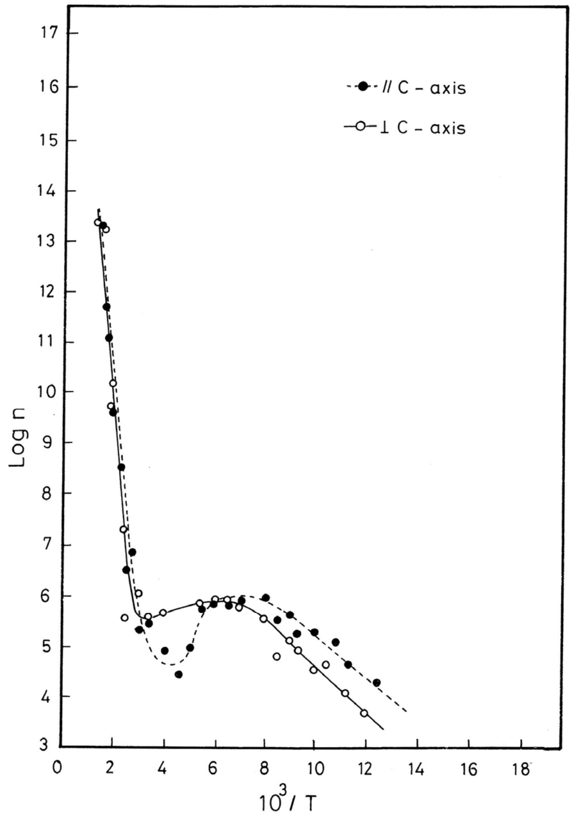

Fig. 5: Temperature dependence of carrier concentration for GaS compound

4. Conclusion

A special design, based on Bridgman technique was used for preparation of single crystals of GaS. The resulting ingots were identified by X-ray and DTA analysis.

Measurements of Hall coefficient and DC electrical conductivity cover a wide range of temperature. The investigated samples have p-type conductivity. The energy gap and the ionization energy ΔE_a were estimated. The scattering mechanism of free charge carrier was checked.

In the present work we describe for the first time the electrical conductivity and Hall effect in two crystallographic directions for gallium sulphide single crystal.

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الإنماء البلوري والخصائص الكهربائية اللاتجاهية لبلورات أحادية شالكوجنيدية طبقية من مركب كبريتيد الجاليوم

رقية حسين العريني

قسم الفيزياء– كلية العلوم للبنات

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المستخلص: استهدف البحث دراسة الخواص الكهربائية لعينة بلورية طبقية، واستخدم لذلك بلورات أحادية من مركب كبريتيد الجاليوم تم تحضيرها باستخدام تقنية بريجمان المطورة. درست الموصلية الكهربائية، ومعامل هول لهذا المركب في مدى حراري واسع، وقد أجريت القياسات في اتجاه المحور البلوري (c-axis) والاتجاه العمودي عليه.

وعن طريق هذه الدراسة أمكن تعيين العناصر الرئيسية لهذا النوع من البلورات الطبقية، مثل اتساع فجوة الطاقة، وتحديد نوعية التوصيل الحادث، والتي وجد أنها تتم بواسطة الثقوب الموجبة، كما تم حساب طاقة تأين الشوائب المستقبلة.

وجد أن الموصلية الكهربائية عند درجة حرارة الغرفة في حدود $١٠^{-١٣}$ أوم$^{-١}$ سم$^{-١}$ ، $١٠^{-١٢}$ أوم$^{-١}$ سم$^{-١}$ في الاتجاه العمودي والموازي للمحور البلوري (c-axis) على الترتيب.

أمكن التعرف على ميكانيكية التبعثر الحادث عن طريق دراسة تأثير درجة الحرارة على انسياقية حوامل التيار.

وعن طريق هذه الدراسة، ألقي الضوء على مميزات هذا النوع من أشباه الموصلات، من حساسية شديدة للتأثير الحراري، وكبر مقاومتها الكهربائية، واتساع فجوة الطاقة، لتفسح المجال للتطبيق العملي المناسب لهذا النوع من البلورات.

وتعتبر هذه الدراسة هي الأولى من نوعها على هذا النوع من البلورات، لتضمنها قياسات في اتجاهين متعامدين للمحور البلوري (c-axis) للخواص الكهربائية.