J. Phys. Chem. Solids Pergamon Press 1967. Vol. 28, pp. 403–404. Printed in Great Britain.

SOME ELECTRICAL PROPERTIES OF THE SEMICONDUCTOR β-Ga_2O_3

M. R. LORENZ, J. F. WOODS and R. J. GAMBINO

IBM Watson Research Center,
Yorktown Heights, New York, U.S.A.

(*Received* 1 *August* 1966; *in revised form* 26 *September* 1966)

Abstract—The wide-band gap semiconductor β-Ga_2O_3 has an electron mobility of the order of 100 cm^2/V-sec at room temperature. Single crystals grown under reducing conditions have about 2×10^{18} free carriers, apparently due to anion vacancies.

INTRODUCTION

Of the group III metal oxides, B_2O_3 and Al_2O_3 are well known insulators, but In_2O_3 has been shown to be a semiconductor.[1,2] In this investigation, some of the electrical properties of β-Ga_2O_3 were measured which demonstrate that this III-VI compound can be either an insulator or a conductor depending on the growth conditions. Optical absorption measurements indicate a gap of 4·8 eV in agreement with earlier results by Tippins.[3] Conductivity measurements have not been previously reported on this material.

EXPERIMENTAL

Chase[4] has reported the growth of Ga_2O_3 crystals using an oxy-hydrogen flame fusion burner. In this work single crystals of β-Ga_2O_3 were grown by the Verneuil method under both oxidizing and reducing conditions: an induction-coupled plasma torch, with argon–20 percent oxygen working gas, was used when an oxidizing growth atmosphere was required, and an oxy-propane torch was used for growth under reducing conditions. The starting material was electronic grade (Eagle-Picher 99·999 percent pure) Ga_2O_3. The angled torch geometry, previously described for the growth of BaO and SrO,[5] was used because of the high vapor pressure of Ga_2O_3 at its melting point. The boules were grown at a rate of approximately 10 mm/hr and usually consisted of several crystals. Single crystal slabs up to 1·5 cm in the longest dimension could be cleaved from the boules. Crystals grown under oxidizing conditions were transparent and colorless, while crystals grown in a reducing atmosphere were light blue.

Small columnar and needle-like crystals were also grown by slowly cooling Ga_2O_3 saturated Ga solutions.[6] Slightly larger single crystals were grown by vapor transport utilizing iodine or gallium suboxide as the transport agent. The vapor grown crystals were also light blue.

RESULTS

The solution-grown and vapor-grown crystals were too small for definitive electrical measurements. It was possible however to make resistivity measurements which indicated that the resistivity was of the order of 1 Ω-cm. The larger crystals grown by the Verneuil technique were investigated by Hall effect measurements. Crystals grown under oxidizing conditions were insulating, i.e. their resistivity was greater than 10^6 Ω-cm. The light blue transparent crystals grown under reducing conditions were conducting. Room temperature measurements on several crystals indicated electron concentrations of about 10^{18} cm^{-3}.

The Hall coefficient and resistivity were measured as a function of temperature, and some results are shown in Fig. 1. The saturation value of the Hall coefficient at both high and low temperatures indicates a net impurity concentration $(N_d - N_a)$ of about $2{\cdot}3 \times 10^{18}$ cm^{-3}.

At temperatures above 200°K the electrons are in the conduction band. Their mobility is about 80 cm^2/V-sec at room temperature and increases with decreasing temperature, reaching a value of approximately 110 at 160°K. At lower temperatures the electrons freeze-out from the conduction band

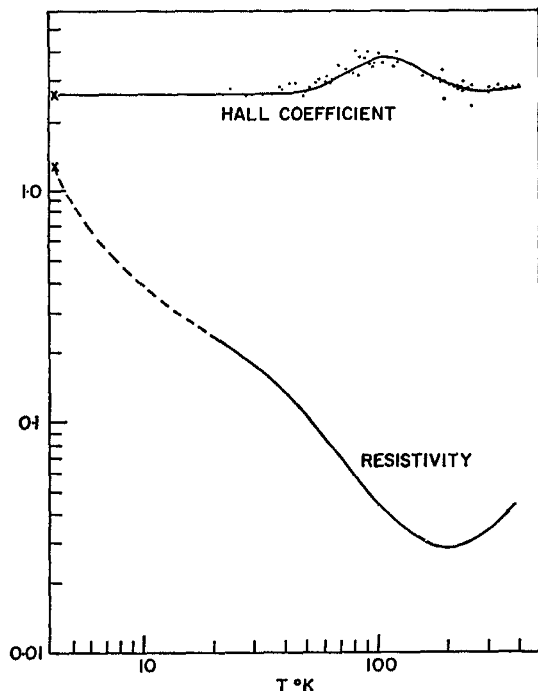

FIG. 1. Temperature dependence of Hall effect and resistivity of single crystal β-Ga_2O_3. The ordinate is in Ω cm for the resistivity and in cm^3/C for the Hall coefficient.

into the impurity band. At 4·2°K the mobility of the electrons in the impurity band is about 2 cm^2/V-sec. At intermediate temperatures there is appreciable conduction in both the conduction band and the impurity band. The Hall coefficient has a maximum at the temperature at which the conduction is equally divided between the impurity band and the conduction band.[7] The height of the maximum is given by $R_{max} = R_0(b+1)^2/4b$ where R_0 is the exhaustion value at high and low temperatures, and b is the ratio of conduction-band mobility to impurity-band mobility at the temperature of R_{max}. In this sample the maximum is 1·4 to 1·5 times the R_0 value. Thus $b \approx 3·5$. This value and the magnitude of the resistivity at the same temperature (110°K) indicate an impurity-band mobility of about 40 cm^2/V-sec and a conduction band mobility of about 140 cm^2/V-sec.

Since the mobility of the electrons in the impurity states is of comparable magnitude to the conduction-band mobility, the rate of change of resistivity is much less than the rate of carrier freeze-out from the conduction band. Detailed analysis of the data gives an approximate value of 0·02–0·03 eV for the activation energy of the donor states. The details of the calculation will be published in a later report.

The optical absorption spectrum of a crystal grown in reducing atmosphere was measured and the spectrum is in good agreement with the results of TIPPINS.[3] The value for E_g at 300°K is about 4·8 eV.

CONCLUSION

β-Ga_2O_3 is another of the wide band gap materials which has been shown to exhibit semiconductor properties. The dependence of the conductivity of the material on the conditions during growth, suggests that the dominant donor species is an anion vacancy. Annealing of conducting crystals at high temperature for several hours in an oxygen atmosphere rendered them insulating. This is additional evidence for the anion vacancy donor model. The possibility of iodine also being an active donor when substituted on oxygen sites cannot be ruled out for the crystals grown by vapor transport with iodine.

Acknowledgments—The authors wish to thank S. BALIOZIAN, L. BUSZKO and R. FLACHBART for technical assistance.

REFERENCES

1. RUPPRECHT G., *Z. Phys.* **139**, 504 (1954).
2. WEIHER R. L., *J. Appl. Phys.* **33**, 2834 (1962).
3. TIPPINS H. H., *Phys. Rev.* **140**, A316 (1965).
4. CHASE A. B., *J. Am. Ceram. Soc.* **47**, 470 (1964).
5. GAMBINO R. J., *J. Appl. Phys.* **36**, 656 (1965).
6. WOLFF G. A., HEBERT R. A. and BRODER J. P., *Phys. Rev.* **100**, 1144 (1955).
7. HUNG C. S. and GLIESSMAN J. R., *Phys. Rev.* **96**, 1226 (1954).