JOURNAL OF MATERIALS SCIENCE 4 (1969) 809-813

Vapour Growth of Cu and Li-doped Single Crystal Zinc Oxide in the Resistivity Range 50 to 10^3 ohm cm

J. A. SAVAGE, E. M. DODSON
Royal Radar Establishment, Malvern, Worcs, UK

Received 22 January 1969

A vapour growth technique is described by which copper and lithium-doped single crystal zinc oxide may be grown. Resistivity and drift mobility measurements are reported, together with some discussion on the effect of trapping on drift mobility.

1. Introduction

Zinc oxide crystallises with a hexagonal structure having lattice constants of $a = 3.24$ Å and $c = 5.19$ Å. It is an extrinsic n-type piezoelectric semiconductor with an optical absorption edge of 3.2 eV at room temperature. The electromechanical coupling constant of this material is higher than that of quartz or cadmium sulphide [1], which makes zinc oxide one of the most useful materials for acousto-electric devices, such as acoustic amplifiers. For acousto-electric studies, material is required of resistivity 30 to 10^3 ohm cm and drift mobility 100 cm^2/V sec.

In a previous paper [2] a method was described of growing undoped single crystal needles of zinc oxide up to 20 mm long by 2 to 3 mm diameter, of resistivity 7 to 30 ohm cm and drift mobility 125 cm^2/V sec. In order to provide material of increased resistivity, experiments were initiated to dope the zinc oxide during growth with an acceptor type impurity such as Li or Cu. It has been shown by Lander [3] that Li dissolved in ZnO can act as a donor if in an interstitial lattice position, or as an acceptor if substituted directly for zinc ions. Univalent copper ions would be expected to act in a similar manner. The aim of this work was to increase the resistivity of the vapour crystals by impurity compensation during growth, utilising Li or Cu ions acting as acceptors.

2. Experimental Details

A schematic diagram of the growth furnace is shown in fig. 1. Sintered, polycrystalline zinc oxide, contained in the tube furnace, was first reduced by hydrogen to zinc vapour, which was then reoxidised to form single crystal needles of zinc oxide in the hot zone. Details of the apparatus were given previously [2] but the following improvements were made. The furnace temperature was maintained by a stepless solid state controller, which gave $\pm$ 1.5° C control of the temperature. In order to reduce the possibility of iron contamination which sometimes occurred with mullite reaction tubes, the furnace tube A in fig. 1 was replaced by an aluminous porcelain tube, and B and C were replaced by purox alumina tubes. The oxygen tube C, extended 10 cm beyond B instead of the previous 7.5cm, thus yielding extra source material for growth. The gases used in this work were commercial oxygen, white spot nitrogen and pure hydrogen.

The morphology of the crystals was determined by etching [4, 5] and Laue X-ray diffraction. Resistivity profiles were obtained with an accuracy of $\pm$ 10% by probing along a central 5 mm length of crystal surface, and drift mobilities were obtained from IV plots [2]. For the drift mobility measurements, pieces of crystal 5 mm long by 1 mm square, with their longest dimension in the direction of the c-axis, were electroplated with indium to provide ohmic contacts. The impurity analysis shown in table II was determined with $\pm$ 30% accuracy on a mass spectrometer.

The crystals were chemically polished to remove any surface contamination before resistiv-

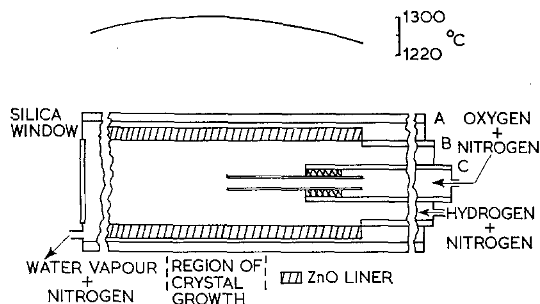

Figure 1 A schematic diagram of the growth furnace.

ity measurements were made or any specimens analysed for impurity. Concentrated orthophosphoric acid was found to be the most useful polish for several crystal planes, depending on the temperature as shown in table I.

3. Results

3.1. Growth of Doped Single Crystals

To avoid the necessity of a separate auxiliary hot zone to control the vapour pressure of the dopant during growth, it was decided to utilise existing equipment and add a solution of the dopant to the zinc oxide source material. The most successful compounds used for doping had small vapour pressures at the growth temperature of 1300° C, so that the dope was continuously present in the vapour for the duration of the growth period. If the compound was too volatile, the high vapour pressure at the start of the growth experiment led to the nucleation of zinc oxide particles in the vapour until the dope was exhausted, when undoped single crystal growth occurred.

Initial experiments [2] with LiOH solution soaked into the source zinc oxide before growth, showed that while some crystals of resistivity up to 50 ohm cm were obtained, more resistive material could not be obtained due to problems with nucleation in the vapour-phase caused by the dope. Lithium fluoride gave better results but this raised problems due to fluoride attack on the alumina oxygen tube C, which was exposed to the fluoride vapour. However, crystals could be grown of resistivity up to 300 ohm cm and occasionally up to 800 ohm cm but here fluoride corrosion was a serious problem. The analytical reagent grade lithium fluoride was added as a powder to the surface of the zinc oxide source material before crystal growth commenced. Typical results of lithium doping experiments are shown in table II.

Doping with a copper compound using this method was found to be more satisfactory, yielding reproducible results. Experiments with copper chloride showed that the vapour pressure was too great at the reaction temperature leading to nucleation in the vapour-phase. However, copper sulphate or nitrate solutions added to the source zinc oxide were satisfactory in that little vapour nucleation occurred and a wide range of dope concentrations in the crystals was possible. Most of the results were obtained using copper sulphate solution of the appropriate concentration, made from "Analar" cupric sulphate or spectrographically standardised copper dissolved in "Aristar" sulphuric acid. In each experiment 20 to 50 ml of copper sulphate solution were added to the source zinc oxide, and table II shows the results of copper doping experiments. The results were similar for "Analar" and "pure" copper sulphate solutions. At concentrations of 4000 ppm of source dopant, vapour nucleation was evident so that difficulty was experienced in growing the crystals. This level probably represented the maximum at which useful crystals could be obtained with the present doping technique but no higher concentrations were attempted.

TABLE I Single crystal ZnO polishing conditions in H_3PO_4

Crystal plane	20° C 20 min	50° C 10 min	100° C 1 to 2 min	150° C 1 min	200° C 1 to 2 min
(0001) zinc face	hexagonal pits	large hexagonal pits	large hexagonal pits	reasonably good smooth polish	—
$(000\bar{1})$ oxygen face	smooth surface with small pits	smooth surface with small pits	smoothing action plus very small pits	rapid etching plus many small pits	—
$\{10\bar{1}0\}$	slow polish rate 7×10^{-4} mm/min	excellent polish	excellent polish	excellent rapid polish	
$\{11\bar{2}1\}$	little effect	—	some smoothing action	reasonable polish after 2 min	reasonable polish but surface
$\{10\bar{1}1\}$	little effect	—	excellent polish	rapid polish ½ min	uneven

In all experiments where solution was added to the zinc oxide source material, the furnace temperature was held at 200° C until the water was removed, after which growth was commenced at 1300° C. When the furnace temperature had stabilised, growth was started at gas flows of 500 cm^3/min N_2 plus 4 cm^3/min H_2, and 50 cm^3/min N_2 plus 6 cm^3/min O_2 for approximately 5 h. The H_2 and O_2 flows were then progressively increased to 12 cm^3/min and 18 cm^3/min respectively. Some of the crystals were the product of several 8 h growth periods with rest periods overnight, but as discussed below, continuous growth runs were started to improve the uniformity of the crystals.

3.2. Physical Properties of the Crystals

The copper-doped crystals were pale yellow-brown in colour due to a shift in the absorption edge (for 1.9 mm thick specimens) from 390 mμ for undoped material to 420 mμ for material containing 900 ppm copper. An absorption also appeared in the infra-red spectrum at 1.6 μ, the intensity of which increased in proportion to the copper content of the crystals. On visual and microscopic examination of these crystals, bands of darker coloration were seen as shown in fig. 2. Each of these bands outlined the crystal surface at the end of one of the intermittent growth periods and probably resulted from extra pick-up of copper dope during each overnight rest period, but it was not possible to detect excess copper or zinc by X-ray microprobe analysis. This effect was obviously undesirable so that all subsequent growth experiments were continuous, yielding macroscopically uniform crystals.

The banding effect also occurred in discontinuously grown undoped crystals but this was only detected during resistivity and Hall coefficient measurements [6]. The resistivity of plates cut from these crystals measured along the *a*-axis differed by several orders of magnitude from that measured along the *c*-axis. Results of this type can be explained by the existence of high conductivity bands aligned in the direction of the *c*-axis. These striations were detected by probing across a crystal slice cut perpendicular to the *c*-axis. The current between the planar and point electrode varied by orders of 10^4 or 10^5 over 20 μm regions of the crystal slice, indicating the positions of the conducting bands. This effect could be explained by the diffusion of a donor type impurity into the crystal surface, or by the loss of oxygen from the crystal surface during each overnight rest period. No bands were visible and none were detected by probing across continuously grown crystals.

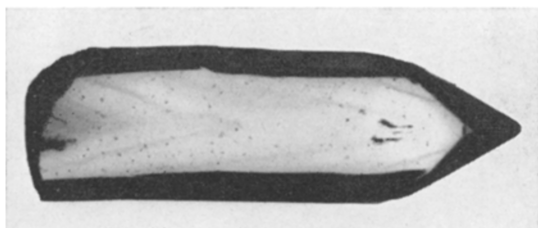

Figure 2 A section through an intermittently grown copper doped crystal showing possible enriched impurity bands (× 5).

The results of electrical measurements on the as-grown lithium- and copper-doped crystals are summarised in table II. The reproducibility of resistivity of the copper-doped crystals from run to run was ± 25% and the variation in resistivity amongst crystals from a single run was 10 to 20%. Resistivity profiles along the length of needles showed them to be uniform within the error of measurement up to a resistivity value of 1000 ohm cm. Above this value, the resistivity changed by a factor of two or more along the length of individual crystals. Profiles for uniform and non-uniform crystals are shown in fig. 3. There was a much greater scatter of resistivities on the lithium-doped crystals so that little systematic work was done on these. The drift mobility of all the doped crystals was below 20 cm^2/V sec indicating that trapping was occurring.

Lander [3] found that Li would diffuse into ZnO and react to form acceptor centres very readily at temperatures above 300° C. Due to the high temperature of crystal growth in the present work, most of the Li ions would therefore be expected to occupy acceptor lattice sites rather than donor substitutional sites in the grown crystals. Subsequent heat-treatment of these resistive crystals in air at 800° C until equilibrium was attained [3], occasionally increased the resistivity by no more than 10%, confirming that most of the lithium was already occupying lattice sites. The position of univalent copper in the zinc oxide lattice was also mainly substitutional for the same reasons, but some of the copper was also in the divalent form. Qualitative epr measurements on the Cu^{63} and Cu^{65} lines of divalent copper compared to a standard trivalent

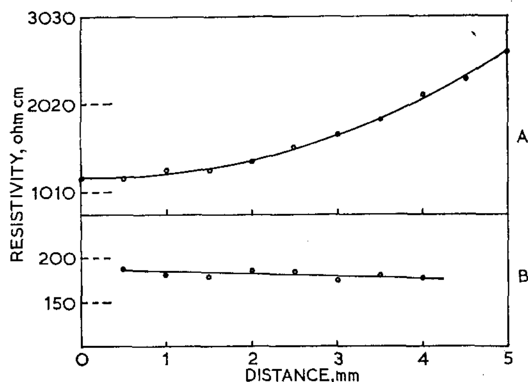

Figure 3 Resistivity profiles along the centre 5 mm of two copper doped crystals: (a) non-uniform, (b) uniform.

chromium reference line for ruby showed that the divalent copper concentration increased approximately linearly with the resistivity and total copper content of the crystals.

4. Discussion

Undoped zinc oxide was grown with adequate drift mobility but was too conducting, while copper- or lithium-doped zinc oxide was grown with useful resistivity but the drift mobility was below 20 cm^2/V sec, due to trapping. A resistivity of 30 to 10^3 ohm cm and drift mobility in excess of 100 cm^2/V sec have not been achieved together in an individual crystal of zinc oxide. The question arises as to the origin of the trapping.

Seitz and Whitmore [7] have measured electronic drift mobilities and space charge limited currents in lithium-doped zinc oxide. In this work, the resistive material was found to have a drift mobility of 2 to 8 cm^2/V sec at 300° K. The observed exponential temperature dependence of mobility indicated that the drift mobility of electrons was primarily controlled by thermal release from trapping states, of estimated density 10^{16} cm^{-3} laying in a region 0.29 eV below the conduction band. This trapping level could not be associated with any specific impurity found from spectrographic analysis of the specimens measured. In addition, these authors obtained a private communication from 3M Company suggesting the existence of discrete traps at 0.28 to 0.29 eV below the conduction band. These energies were derived from thermoluminescence measurements on fine grain polycrystalline "pure" zinc oxide. The agreement between the results of these two rather different experiments suggests that the traps located at an energy value 0.29 eV below the conduction band are characteristic of bulk zinc oxide and not the result of surface or impurity effects. Seitz and Whitmore suggest that such electron traps are likely to be point or line imperfections in the crystal, but no definite evidence for this was available.

If these traps are present in the "pure" undoped zinc oxide, they are ineffective in reducing the drift mobility because the Fermi level must be above the trap level. However, as a result of doping, the Fermi level moves below the trap level so that the traps became effective in reducing the drift mobility. Assuming the impurity analysis in the above work to be correct, thus eliminating common impurities as the cause of the 0.29 eV trapping level, two other causes are possible. The first as postulated by Seitz and Whitmore would be an unspecified line defect, the second might be a point defect associated with interstitial zinc impurity. This impurity would not be detected in spectrographic analysis and is present in all samples of zinc oxide powder as shown by Norman [8], who has developed an improved chemical method for determining excess zinc in zinc oxide. Samples of analytical reagent grade powders were found to

TABLE II Results of lithium and copper-doping experiments

Dope added to liner	Concentration in liner ppm	Concentration in crystals ppm	Concentration in crystals atoms/cm^3	Resistivity of crystals at 300° K ohm cm	Drift mobility at 300° K cm^2/V sec.
Li as LiF	1500	10	4.9×10^{18}	50 to 100	< 10
Li as LiF	3000	N.D.	N.D.	100 to 200	< 10
Cu as $CuSO_4$	250	45	2.4×10^{18}	100	< 20
Cu as $CuSO_4$	500	150	8.1×10^{18}	240	< 20
Cu as $CuSO_4$	1000	260	1.4×10^{19}	500	< 20
Cu as $CuSO_4$	2000	900	4.8×10^{19}	1200	< 20
Cu as $CuSO_4$	4000	1400	7.0×10^{19}	1000 to 2000	< 20

N.D. not determined

contain excess zinc ranging from 1.0 to 7.3 ppm by weight or approximately 5×10^{16} to 4×10^{17} atoms/cm^{-3}. It is also likely that the vapour grown zinc oxide crystals contain a similar amount of excess zinc because it is generally agreed that zinc oxide is a metal excess *n*-type semiconductor with interstitial zinc as the main point defect. This value is in good agreement with the estimated trap density of 10^{16} cm^{-3} obtained from electrical measurements [7], but further work will be necessary in order to associate particular imperfections with observed trap levels.

Acknowledgement

The authors wish to thank Mr B. Kinsman, BDH Ltd, for the supply of the zinc oxide liner tubes, and Miss P. J. Penny, RRE for some of the crystal growth work. Thanks are also due to Dr F. G. Marshall, Dr R. A. Stuart, Mr R. J. Heritage and Mr S. D. McLaughlan of RRE for the assessment of the crystals and to Dr W. Bardsley for helpful discussions.

Contributed by permission of the Director of RRE, Copyright Controller HMSO.

References

1. A. R. HUTSON, *Phys. Rev. Lett.* **10** (1960) 505.
2. E. M. DODSON and J. A. SAVAGE, *J. Materials Sci.* **3** (1968) 19.
3. J. J. LANDER, *J. Phys. Chem. Solids* **15** (1960) 324.
4. A. N. MARIANO and R. E. HANNEMAN, *J. Appl. Phys.* **34** (1963) 384.
5. A. KLEIN, *Zeit fur Physik* **188** (1965) 360.
6. D. G. MOULD, M.Sc. Thesis, Brighton College of Technology (1968).
7. M. A. SEITZ and D. H. WHITMORE, *J. Phys. Chem. Solids* **29** (1968) 1033.
8. V. J. NORMAN, *Analyst* **89** (1964) 261.