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Vapour Growth of Single-Crystal Zinc Oxide

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A vapour technique is described by which single-crystal zinc oxide may be grown. Sintered, polycrystalline zinc oxide, contained in a tube furnace, is first reduced by hydrogen to zinc vapour, which is then re-oxidised to form single-crystal zinc oxide in the furnace hot-zone. The effect of temperature and gas flow on the crystal type is reported, together with some crystal properties, including resistivity and drift mobility.

1. Introduction

Recent work on the acousto-electric effect in CdS has stimulated interest in single-crystal ZnO, a material which possesses a much higher electromechanical coupling constant [1]. To exploit the full potential of this material, crystals are required of high perfection and semiconductor purity, with a preferred resistivity in the range 30 to 10^3 Ω cm, and drift mobility in excess of 100 cm^2/V sec. The minimum useful size is 1 mm cube, but ideally 1 cm cube ZnO crystals would fulfil present needs.

ZnO has a melting point of 1975° C inside a closed container [2], and it is reported to have a high vapour pressure especially in the presence of water vapour. Consequently, no attempt has yet been made to pull crystals from the melt. The three growth techniques which have been used to grow ZnO are flux, hydrothermal, and vapour methods, of which, the latter two have been the most successful. Crystals 2 cm^3 in size and 1 to 10 Ω cm resistivity have been grown by the basic hydrothermal technique, but lithium-doping during growth is possible, yielding crystals of higher resistivity [3]. The vapour growth technique usually involves the oxidation of zinc metal vapour or ZnS [4] or $ZnCl_2$ [5] vapours, and the size of the crystals varies from sub-millimetre to several millimetre diameter needles or platelets. It is to be expected that a chemically purer product of greater crystalline perfection can be obtained by the vapour process, and future needs will be for thin films or epitaxial layers, so that the vapour technique has been employed in the present work.

Scharowsky [6] reported the growth of small ZnO needles, typically 0.3 mm diameter and several millimetres long, by a vapour method. Zinc metal vapour from a source at 600° C was carried into a refractory air oven at 1150° C on a carrier gas stream of nitrogen and hydrogen. The ZnO needles were formed on the walls of the oven. In an improved method, Nielsen [7] reduced sintered ZnO with hydrogen to provide the zinc stream, thus more easily achieving control over the rate of supply of zinc vapour. ZnO at 1300° C was reduced by hydrogen carried in a stream of nitrogen, and the resulting gas mixture was passed into a sintered ZnO cone 10 to 15 cm diameter at the larger end. Oxygen was passed into the laboratory oven containing the ZnO cone, in the mouth of which grew single-crystal hexagonal needles, up to 15 mm long and 2 to 3 mm diameter. However, no detailed study of the growth mechanism was attempted and no information was available on the effects of parameters such as gas flow and temperature. The latter method has the merit of simplicity and does not involve the use of an easily oxidisable zinc metal source; therefore it was decided to adopt this particular vapour technique in the present work.

2. Experimental Details

Kinetic data are available for the two following chemical reactions [8]:

$$ZnO_{(s)} + H_2 = Zn_{(v)} + H_2O_{(v)} \qquad (1)$$

$$2Zn_{(v)} + O_2 = 2\ ZnO_{(s)} \qquad (2)$$

The ΔG values for reactions 1 and 2 are plotted

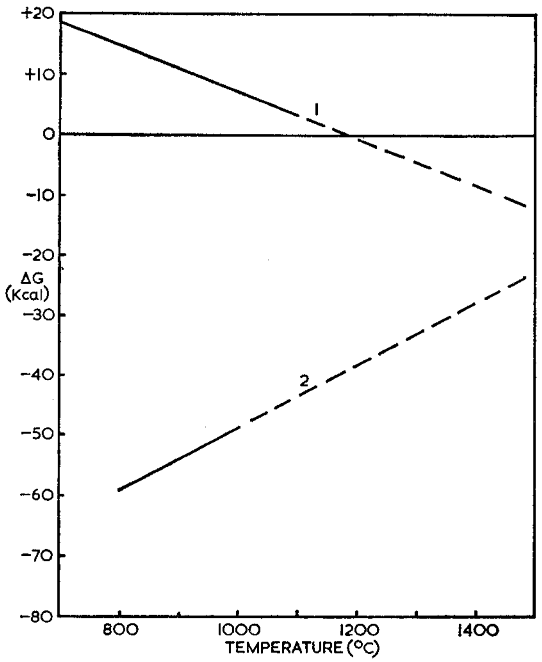


Figure 1 ΔG against temperature for reactions 1 and 2. The unbroken line represents experimental data.

against temperature in fig. 1, where it can be seen that the reduction of ZnO by hydrogen has a negative ΔG value above 1180° C, indicating a spontaneous reaction in this temperature region. Reaction 2 is spontaneous over the whole range plotted in the diagram. For single-crystal growth in a vapour process, it is necessary to achieve sufficient mobility of atoms on the crystal surface, ideally by heating to a temperature near its melting point. However, temperatures of two-thirds of the melting point are usually sufficient, so that, in the case of ZnO, 1200 to 1400° C should be suitable.

In preliminary trials, silica reaction tubes were shown to be unsatisfactory owing to rapid devitrification and penetration by the ZnO, leading to cracking and failure. The diffusion of zinc in alumina at the temperatures concerned is very rapid with the formation of zinc aluminate [9], a process which leads to tube failure. Commercial mullite ($3Al_2O_3.2SiO_2$ plus impurities) was found to react very slowly with ZnO, so that reaction tubes of this material were used. The crystals were grown in a circular tube furnace within a ZnO lining in order to minimise the pick-up of impurities from the mullite reaction tubes. The apparatus shown in fig. 2 consisted of three, concentric, mullite refractory tubes of internal diameters 65, 40, and 15 mm, respectively. The smallest and largest of the tubes were 91.5 cm long, while the middle tube was 62 cm in length. A ZnO liner tube, 20 cm long and 0.5 cm wall, made from purified ZnO powder (dry-moulded and sintered at 1100° C), was placed in the centre of the 65 mm mullite tube. The 40 mm tube was butted against this, and the 15 mm tube was mounted along the axis of the main tube so as to project 7.5 cm

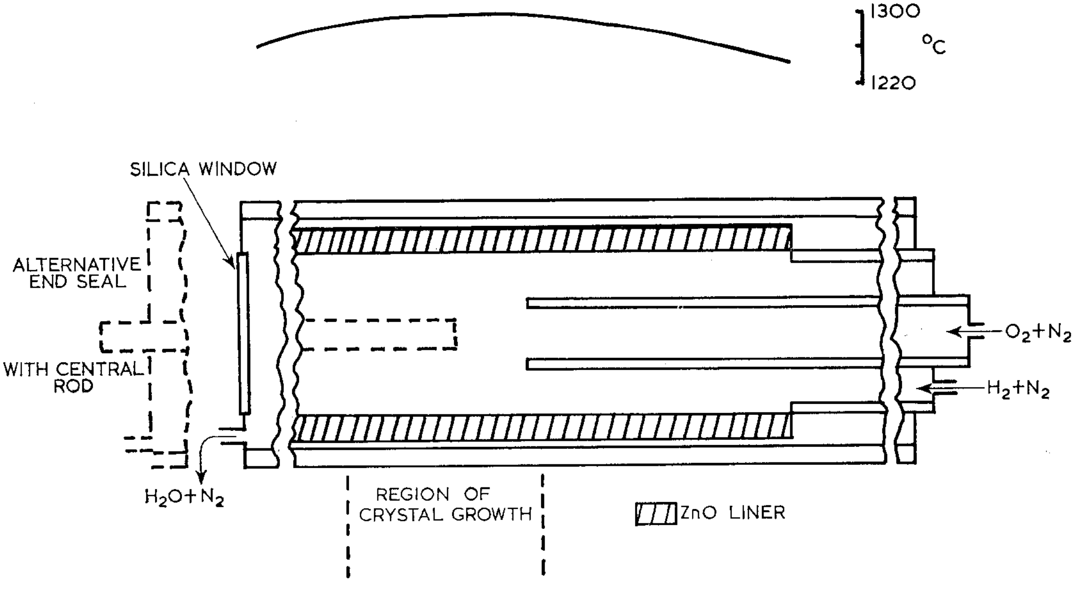


Figure 2 A schematic diagram of the growth furnace.

into the ZnO liner tube. The joints and ends of the tube were sealed with water-cooled brass and duraluminium screw fittings made gas-tight by silicone rubber seals. As shown in fig. 2, the exit-end fitting of the reaction tube contained a silica viewing-port or a brass plate carrying an 8 mm diameter mullite rod along the axis of the furnace. This concentric mullite tube system was heated externally by a thermally insulated, six-rod crusilite furnace, whose temperature was maintained by an Ether Transitrol controller. A temperature profile for the growing region at a furnace temperature of 1300° C is shown in fig. 2.

The gases used in this work were commercial oxygen, white spot nitrogen, and pure hydrogen; they were not dried or further purified in any way, but were passed through calibrated flowmeters before entering the furnace. Hydrogen in nitrogen carrier gas was passed through the 40 mm tube and liner, reducing the ZnO in the first 7.5 cm of liner to zinc metal vapour and water vapour. Oxygen in nitrogen carrier gas was added to this mixture through the 15 mm, projecting, central, mullite tube, in order to oxidise the zinc vapour to ZnO in the central region of the furnace, shown in fig. 2. The exhaust gases from the furnace were passed through a water seal into the laboratory.

The morphology of the crystals was determined by etching [13, 14] and Laue X-ray diffraction. Electrical measurements were made on pieces of crystal 0.5 cm long by 0.1 cm square with their longest dimension in the direction of the c axis. The ends were electroplated with indium, which provided ohmic contacts, and dc pulses of up to 5 kV were applied to these end contacts. Each voltage pulse provided a single spot on an IV plot on an oscilloscope. In this way, an IV plot was obtained from a series of voltage pulses of increasing magnitude. When acousto-electric interaction occurred above a threshold voltage, the IV plot deviated from Ohms law and consisted of two straight lines forming a "knee" at their junction. From the IV curve and the crystal dimensions, the resistivity at room temperature was calculated. The value of the critical voltage at the "knee", E_c, enabled the drift mobility, μ, to be calculated from the equation

$$\text{velocity of sound} = \mu E_c$$

3. Results and Discussion

3.1. The Effect of Temperature upon Crystal Growth

The results of the effect of temperature and gas flow (section 3.2) on crystal growth are given in table I. Experiments were commenced at a temperature of 1150° C, and the hydrogen and oxygen flows were fixed at 4 and 5 cm^3/min, which were the minimum stable flows obtainable from the meters in use. In order to obtain growth in the hot zone, it was found that the minimum, independent, carrier gas flow through the oxygen or hydrogen tubes was 250 cm^3/min. At flows lower than these, back-diffusion of oxygen occurred, leading to growth before the gas stream entered the hot zone. Both carrier gas flows were then adjusted to 500 cm^3/min and a series of experiments was carried out at progressively increasing temperatures. A 3 to 4 h period was sufficient to assess the growth at any

TABLE I The effect of temperature and gas flow upon crystal growth.

Effect of temperature

Temperature (° C)	Gas flow (cm^3/min)				Remarks
	H_2	N_2	O_2	N_2	
1150 to 1255	4	0 to 500	5	0 to 500	Whisker growth
1255	4	0 to 500	5	0 to 500	Start of large-grain, polycrystalline growth
1270 to 1325	4	0 to 500	5	0 to 500	Polycrystalline growth from which single crystals grew
Effect of gas flow					
1295	0 to 16	0 to 500	0 to 20	0 to 500	Heterogeneous nucleation of ZnO on furnace walls
1295	> 16	0 to 500	> 20	0 to 500	Nucleation of ZnO particles in the vapour
1295	> 4	500 to 2500	> 5	500 to 2500	Nucleation in the vapour

temperature by removing and examining the 8 mm central rod, shown by the dashed lines in fig. 2. The furnace was cleared and a further experiment was then carried out at a higher temperature. At 1150° C, many thin, elongated whiskers grew on the rod and ZnO liner tube. The growth of these whiskers was very rapid in the direction of the *c* axis but minimal at right-angles to it. The results were similar at 1195 and 1225° C, but at 1255° C a fine-grain, polycrystalline growth occurred on the 8 mm rod, from which grew thin, sub-millimetre whiskers. Above 1270° C, no whiskers were produced, but large-grain, polycrystalline growth occurred on the ends of the oxygen tube, adjacent liner tube, and 8 mm rod. If the duration of the growth experiment was increased, single-crystal hexagonal needles grew from this polycrystalline layer. It was noticeable that, as the growth temperature was increased from 1270 to 1325° C, the number of crystals grown was smaller but their diameters were greater. The diameters of crystals grown at 1270° C were on average 0.5 mm, and, at 1295° C, the average was greater than 1 mm with several crystals of 2 mm diameter. At 1325° C, none of the crystals was less than 2 mm in diameter. This was due to the reduced supersaturation at higher temperature making nucleation more difficult, so that most of the growth took place on the surfaces of existing crystals. The rate of growth at the higher temperatures was reduced in $<0001>$ direction and increased at right-angles to it.

3.2. The Effect of Gas Flow upon Crystal Growth

The temperature was now held at 1295° C, the hydrogen and oxygen flow rates were increased to 8 and 10 cm^3/min respectively, to allow a faster growth rate for quicker assessment, and the carrier gas flows were progressively increased to 2500 cm^3/min. The growth type was assessed in 2 to 3 h utilising the 8 mm central rod. Each experiment was repeated for a few minutes with a silica window in the end seal so that the interior of the furnace could be observed. In the range of carrier gas flows 0 to 500 cm^3/min, polycrystalline growth occurred on the 8 mm rod leading to single-crystal needle growth. When either of the carrier gas flows was increased above 700 cm^3/min, the growth type changed, once more becoming the whisker type, with some white, fine ZnO powder accumulating at the end of the furnace. At total flows of 2000 cm^3/min or above, ZnO "wool" grew in the hot zone, accompanied by much powdered ZnO at the end of the furnace. The greater the total carrier gas flow above 1000 cm^3/min, the greater was the nucleation of ZnO particles and whiskers in the furnace.

When the interior of the furnace was viewed through the silica window, in the range of carrier gas flows 0 to 500 cm^3/min, nothing was visible in the furnace. At flows above 700 cm^3/min, a mist appeared, indicating homogeneous nucleation in the vapour, and steady streaming lines were visible down the length of the furnace. Utilising carrier gas flows of 500 cm^3/min, which resulted in single-crystal growth, the hydrogen and oxygen flows were progressively increased. At hydrogen and oxygen flows greater than 16 and 20 cm^3/min, a mist of ZnO particles was seen in the furnace, resulting in a coating of ZnO powder on the silica window. The homogeneous nucleation of ZnO particles in this case was initiated by a hydrogen flow greater than 16 cm^3/min and was due to too great a supersaturation of zinc vapour in the furnace.

To allow more room in the furnace for crystal growth, the 15 mm diameter, oxygen, tube was replaced by a 5 mm internal-diameter mullite tube. It was found that the flow of carrier gas through the 5 mm tube had to be reduced from 500 to 50 cm^3/min in order to avoid nucleation in the vapour. At this flow rate, the velocity of gas through the 5 mm tube was equivalent to that through the 15 mm tube at 500 cm^3/min carrier gas flow. Therefore, the critical gas velocity through either oxygen tube, above which vapour nucleation occurred, was 5 cm/sec. The most likely explanation of the vapour nucleation at high, total, carrier gas flows is that the gas stream had insufficient time to heat up to the reaction temperature, so that reaction 2 took place at a lower temperature than the furnace walls. This would result in an increase in the supersaturation and much more nucleation, as observed at lower furnace temperatures.

Deckker [10] has studied the stability of concentric laminar mixing in a tube and found that pseudo-turbulent velocity profiles were observable for certain combinations of Reynolds number, even when the total Reynolds number was less than 2300. However, this effect occurred at flow rates much in excess of those used in the present work, in which streaming lines were visible in the furnace, and the calculated Reynolds numbers did not exceed 12. It is therefore concluded that streamline flow occurred at all flow rates used in this investigation.

3.3. Growth of Single Crystals

Crystal-growth experiments were carried out in the temperature range 1280 to 1325° C, using the tube furnace shown in fig. 2. Single-crystal hexagonal needles grew from the end of the oxygen tube and adjacent liner. To allow more room for these crystals to grow, the 15 mm diameter, oxygen, tube was replaced by a 5 mm diameter tube as previously described, and the remainder of the growth experiments were carried out using this arrangement. When the furnace had stabilised at the set temperature, the growth experiments were commenced with gas flows of 500 cm^3/min of nitrogen plus 6 cm^3/min of hydrogen, and 50 cm^3/min of nitrogen plus 8 cm^3/min of oxygen, for approximately 5 h. The hydrogen and oxygen flows were then increased to 8 and 10 cm^3/min respectively for a further 5 to 10 h. During this initial period, a layer of polycrystalline ZnO was deposited on the end of the oxygen tube and adjacent liner from which grew single-crystal needles. The number of crystals nucleated could be controlled to some extent by temperature; fewer crystals were produced at higher temperatures. When the crystals were seen to have nucleated and started to grow, the hydrogen and oxygen flow rates were increased to 16 and 20 cm^3/min respectively, to increase the rate of growth. Experiments were not continued overnight, so that the crystals were the product of four 8 h growth periods.

If ZnO is to be electrically useful, crystals must be produced within the range of resistivities specified in section 1. Lander [11] diffused lithium into small ZnO needles by coating their surfaces with lithium hydroxide and heating in air to 300° C or higher. He was able to show that lithium acted as an acceptor. A preferable method would be to dope during the crystal growth using a volatile lithium source. Van Arkel *et al* [12] have postulated the reaction

$$Li_2O_{(s)} + H_2O_{(g)} \rightarrow 2\ LiOH_{(g)} \qquad (3)$$

to account for the loss in weight of Li_2O when heated at 1000° C in the presence of water vapour. In the present work, the reduction of the ZnO liner tube by hydrogen produces zinc vapour and water vapour. If lithium were present in the liner, then gaseous LiOH would be formed and transported into the growing region to be incorporated in the crystals. Therefore, doping experiments were carried out in which LiOH solution (50 cm^3) of varying concentrations was soaked into the ZnO liner tubes before their insertion into the furnace. The furnace temperature was held at 200° C until the water was removed, after which a normal growth run was completed. The resulting crystals were of higher resistivity than those produced from undoped liner tubes.

3.4. Physical Properties of Single Crystals

The crystals grown in this work were clear, colourless needles, whose sides terminated in six faces $\{10\bar{1}0\}$. The growth axis was $<0001>$ and the crystal tips terminated in six faces $\{10\bar{1}1\}$ or $\{11\bar{2}1\}$ or a mixture of the two, as shown in figs. 3a, 3b, and 3c. The $\{10\bar{1}0\}$ faces were generally smooth, exhibiting no particular growth features, and occasionally the $\{10\bar{1}1\}$ and $\{11\bar{2}1\}$ faces were also smooth, as shown in fig. 4a. However, the latter faces on the growing tips of the crystals usually showed steps over part or all of their surface, as seen in fig. 4b. A general view of crystals grown between 1270 and 1325° C is shown in fig. 5. The visible and infrared spectrum of a crystal in the $[10\bar{1}0]$

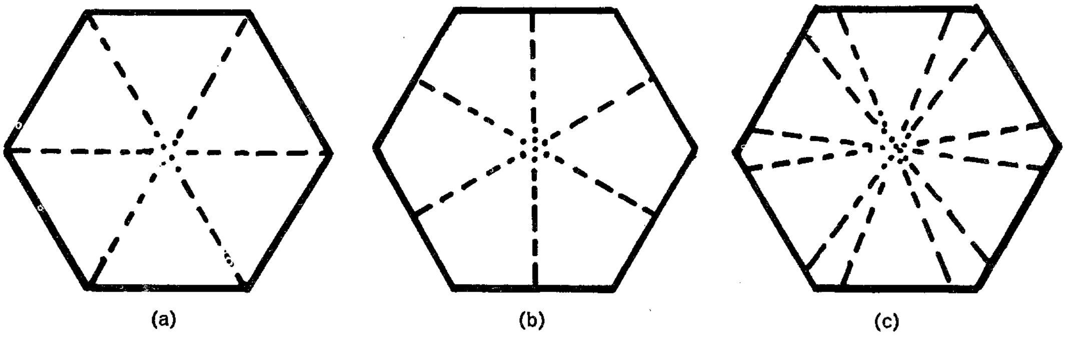
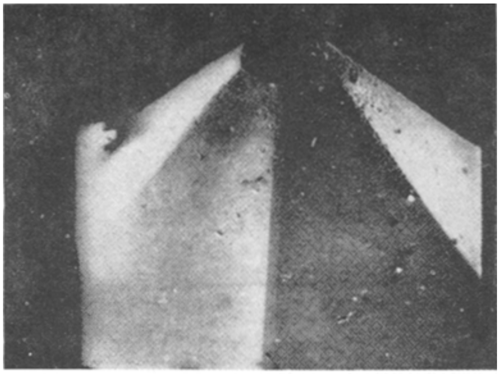
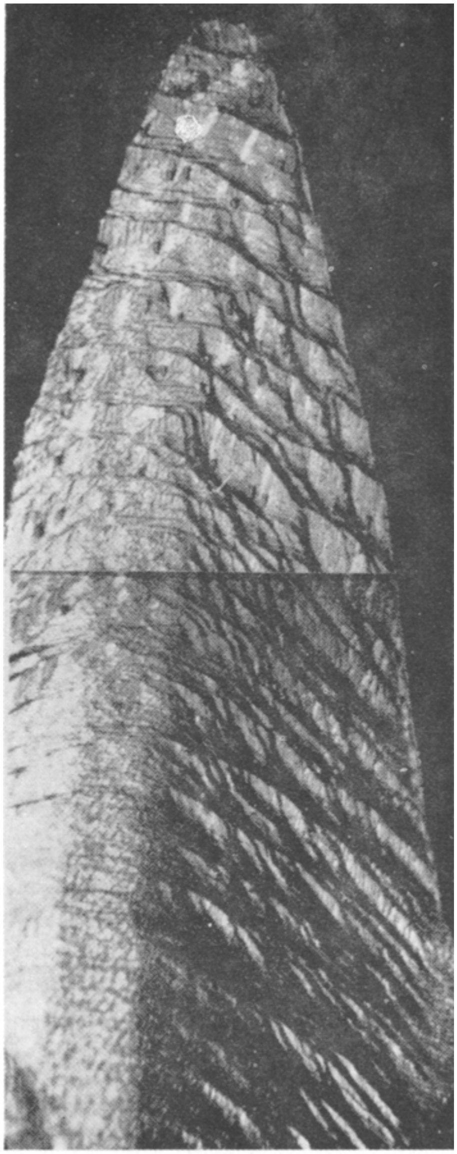

(a) (b) (c)

Figure 3 Terminal planes on the needle tips: (a) $\{10\bar{1}1\}$; (b) $\{11\bar{2}1\}$; (c) $\{10\bar{1}1\}$ and $\{11\bar{2}1\}$.



(a)



(b)

Figure 4 (a) Electron micrograph of a crystal tip showing $\{11\bar{2}1\}$ planes (×26). (b) $\{11\bar{2}1\}$ plane on a crystal tip showing a stepped surface (×92).

direction is shown in fig. 6, where it is seen that no OH absorption is present, indicating that little hydrogen was incorporated in the growing crystals in the form of OH. The 60% level of transmission should not be taken as accurate, because of the loss of signal owing to the use of a small specimen. Crystals tested from all but one of eight growth experiments showed acousto-electric interaction, the resistivity varied in the range 7 to 30 Ω cm, while the drift mobility was of the order of 125 cm^2/V sec. Crystals from the lithium-doping experiments were of increased resistivity up to 128 Ω cm, depending on the lithium concentration employed. But no acousto-electric interaction was observed, possibly owing to non-uniform doping.

The mullite reaction tubes were very impure, containing an estimated (by the manufacturers) iron, plus transition element, content of 1% or more. However, it is possible to grow relatively pure crystals in such tubes if very little of the impurities are present in the vapour phase. The average purity of the sintered ZnO source material and that of some of the early crystals is shown in table II, from which it appears that there has been no major pick-up of impurities from the mullite.

4. Summary

Electrically useful, single-crystal needles of ZnO up to 2 cm long by 2 to 3 mm diameter have been grown in the temperature range 1280 to 1325° C. During normal growth, heterogeneous nucleation occurred on surfaces, leading to single-crystal growth. But homogeneous nucleation occurred in the vapour stream, yielding ZnO powder, when the supersaturation was too high at hydrogen flows greater than 16 cm^3/min, or when the supersaturation was too high owing to too low a vapour temperature resulting from a high carrier gas flow.

This method of random nucleation on ZnO liner tubes is not by any means ideal for the growth of single crystals, especially if crystals up to 1 cm diameter are required. In principle, the

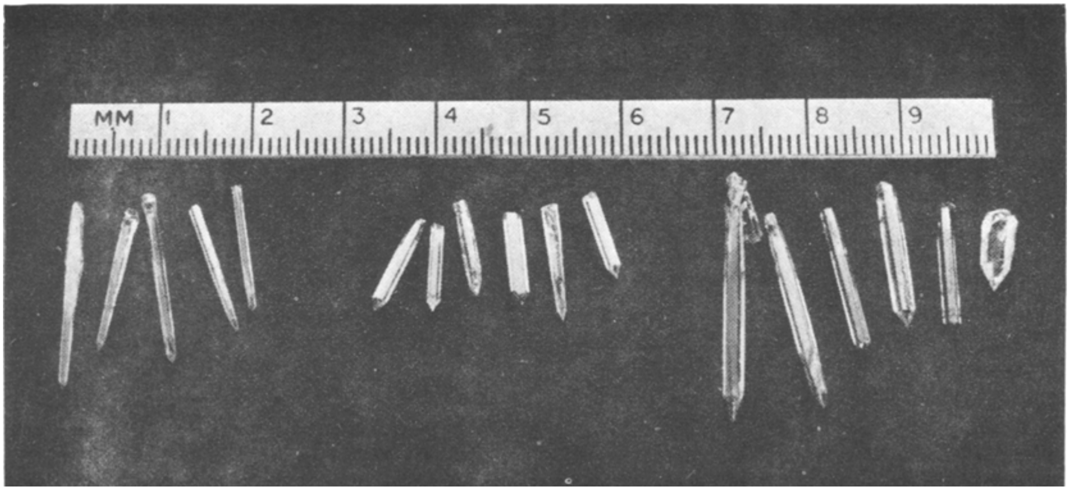


Figure 5 General view of crystals grown at increasing temperatures; from left to right: 1270, 1295, 1325° C.

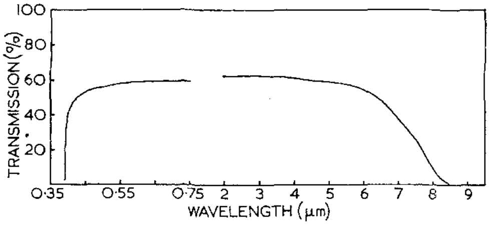


Figure 6 Visible and infrared spectrum of ZnO in the $[10\bar{1}0]$ direction – specimen thickness 0.19 cm.

TABLE II Spectrographic analysis (ppm).

Element	ZnO liner	ZnO crystals
Cu	ND*	1 to 2
Fe	<1	1 to 2
In	ND	Trace
Mg	ND	<1
Si	ND	Trace
Sn	ND	2
Pb	0.1	ND
Cd	1.5	ND
As	<0.2	ND
Cl	20	—
SO_4	60	—

*ND=not detected

growth of ZnO on a seed has been shown to be possible, therefore future work will be directed towards seeded growth and a study of the growth mechanism and crystal defects in relation to purity, electrical properties, and growth parameters.

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