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The rate of deposition and the morphology of zinc oxide deposited from Zn(v)/CO/CO_2/Ar gas mixtures

J. A. CLARKE,* D. J. FRAY
Department of Metallurgy and Materials Science, University of Cambridge, UK

Zinc oxide has been deposited onto a silica substrate from a Zn (v)/CO/CO_2/Ar gas mixture and the rates of deposition are presented as a function of temperature and gas composition. The morphology of the oxide deposits is described in detail.

1. Introduction

The deposition of zinc oxide from the vapour phase is of interest in several industrial applications. For example, zinc oxide in the form of both thick and thin epitaxial films is used extensively in the electronics industry. The addition of varying amounts of dopants to zinc oxide can change its semiconductivity, allowing a range of semiconductors to be produced from this low cost material merely by the judicious use of dopants. Another property of zinc oxide which has been successfully exploited by the electronics industry is its remarkably high piezoelectric coupling constant [1, 2], which results in the use of zinc oxide in the production of ultrasonic transducers by the deposition of zinc oxide onto a substrate using the techniques of chemical vapour deposition.

The other major industrial application is the Imperial Smelting Process [3] where zinc oxide is reduced by

$$ZnO + CO = Zn(v) + CO_2 \qquad (1)$$

carbon monoxide giving a gas mixture consisting mainly of Zn(v), CO, CO_2 and N_2. Due to the cooling of the gases, some back reaction occurs with the deposition of zinc oxide on the walls of the cross-overs from the furnace to the condensers. The thermodynamics of the reoxidation reaction is well defined [2, 4] but little is known about the deposition rate or the morphology of the deposit under various conditions.

2. Experimental

The apparatus, which has been described previously [5, 6] consisted of a silica reactor tube inserted into two furnaces, held at different temperatures. In the high temperature region, the tube was packed with zinc oxide pellets over which the carbon monoxide and argon mixtures were passed. The gas mixture containing zinc vapour then passed into the low temperature region of the silica tube where the reaction

$$Zn(v) + CO_2 = ZnO + CO \qquad (2)$$

occurred. At the end of the silica tube, the temperature fell below the dew point of the zinc vapour and droplets of zinc condensed on the wall of the silica tube.

From the weight loss of zinc oxide and the known composition of the input gases, the composition of the gases entering the low temperature region could be calculated. By sectioning the tube and dissolving off the zinc oxide in dilute acid, the weight of zinc oxide could be measured allowing the rate of deposition of the oxide to be determined. In addition, the quantity of zinc deposited at the end of the tube was obtained to allow a mass balance to be calculated. Samples of deposited oxide and zinc were examined using a Cambridge Scanning Electron Microscope.

3. Results and discussion

In the region of 1100 K, it was found that the rate could change dramatically from 1×10^{-7} to $3 \times$

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*Present address: Research Department, Imperial Smelting Processes Ltd., Avonmouth, Bristol.

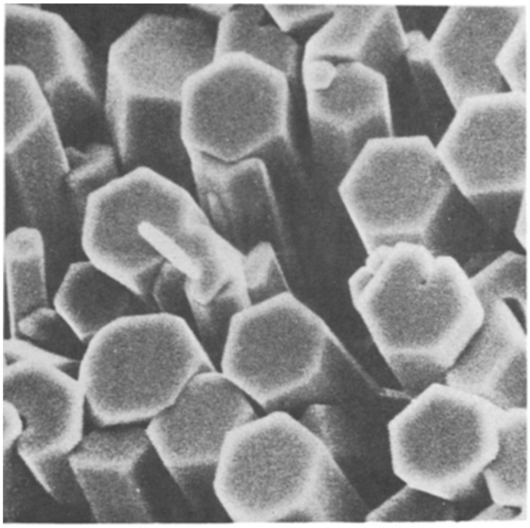

Figure 1 Large-grained deposit formed at 1050 K, $p_{Zn} = p_{CO_2} = 0.0795$ atm. and $p_{CO} = 0.8410$ atm. (× 5800).

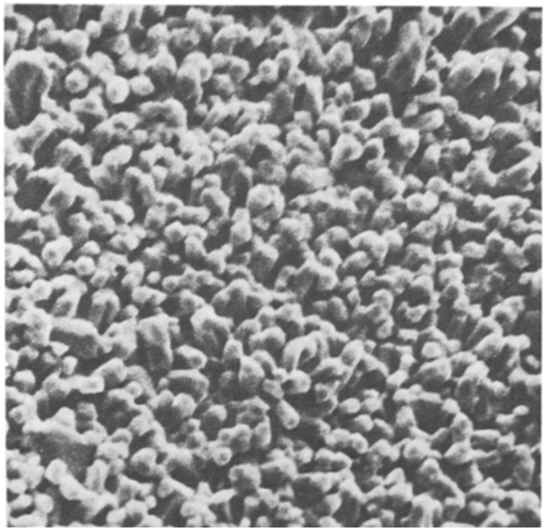

Figure 3 Fine-grained deposit formed at 1094 K, $p_{Zn} = p_{CO_2} = 0.0713$ atm. $p_{Ar} = 0.252$ atm. and $p_{CO} = 0.6054$ atm. (× 3400).

10^{-7} moles ZnO cm^{-2} sec^{-1} to 5×10^{-9} moles ZnO cm^{-2} sec^{-1} in the same experiment. Examination of the deposit showed that the morphology ranged from a very large-grained deposit at the high deposition rates (Fig. 1), through spikes (Fig. 2) and then to a dense fine-grained deposit (Fig. 3), as the temperature was raised above 1100 K. The morphology was not solely a function of temperature but depended, also, on the zinc partial pressure as shown in Fig. 4. By varying the temperature during an experiment it is possible to initially deposit the heavy deposit followed by the fine deposit.

Figure 2 Spiked deposit formed at 1111 K, $p_{Zn} = p_{CO_2} = 0.0243$ atm. $p_{Ar} = 0.0472$ atm. and $p_{CO} = 0.1042$ atm. (× 3560).

Both deposits grew at a much slower rate than calculated assuming diffusion in the gas phase was rate controlling. The rates of deposition could be represented by the following equation:

$$R = -k'\left(p_{Zn}p_{CO_2} - \frac{p_{CO}}{K}\right)(p'_{eCO} - p_{CO}) \tag{3}$$

for the fine deposit and

$$R = -k^* (p_{Zn} - p^{e}_{Zn}) \tag{4}$$

for the heavy deposit. k' and k^* are the rate constants, p_{Zn}, p_{CO_2}, p_{CO} are the partial pressures prevailing in the gas mixture, p^{e}_{Zn} is the equilibrium zinc partial pressure and p'_{eCO} is the equilibrium carbon monoxide partial pressure for a ternary gas mixture of carbon monoxide, carbon dioxide, and zinc vapour. K is the equilibrium constant for Reaction 2. For the intermediate deposits, it was not possible, due to the change in morphology, to represent the deposition rate by a simple equation. From the form of Equation 3, it would appear that the reaction rate could be controlled by the surface desorption of carbon monoxide. The activation energy obtained by plotting the logarithm of the rate constant against the inverse of the temperature is 182 kJ mol^{-1} and is very close to the value of 170 kJ mol^{-1} for the activation energy for the desorption of carbon

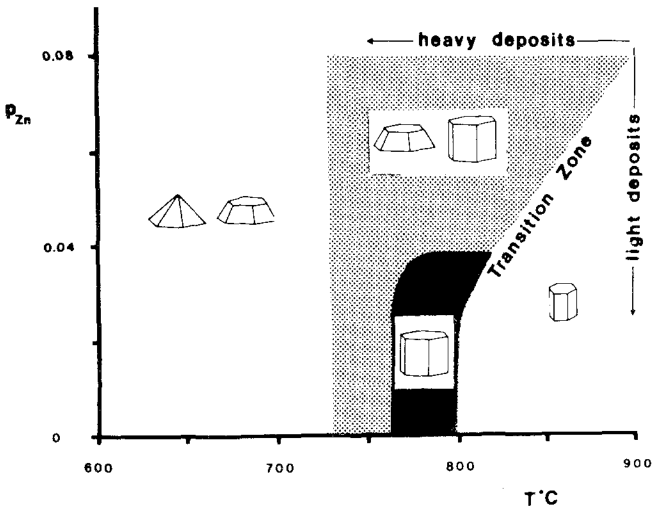

Figure 4 Diagramatic representation of the variation of growth morphology with temperature and zinc partial pressure for the $Zn/CO/CO_2/Ar$ system.

monoxide from zinc oxide observed by Kubokawa [7]. The pronounced retardation by carbon monoxide of the oxidation of zinc vapour by carbon dioxide shows strong similarities to the oxidation of graphite by carbon dioxide as demonstrated by Turkdogan and Vinters [8] who found that the oxidation of graphite, charcoal, and metallurgical coke, by carbon dioxide was retarded by the presence of the reaction product carbon monoxide and suggested that this could be accounted for by the preferential adsorption of carbon monoxide at the reaction surface sites.

For the heavy deposit, it was found that the rate was directly proportional to the excess partial pressure of zinc. At the low surface coverages expected at these elevated temperatures for zinc adsorption from the unsaturated vapour phase, the concentration of surface adsorbed zinc would be proportional to the zinc partial pressure, and since oxidation would only be observed for partial pressures in excess of the equilibrium partial pressure, a linear adsorption isotherm would result in a rate expression similar to that found experimentally.

A linear rate dependence on the excess zinc partial pressure may also be accounted for by zinc adsorption into the oxide lattice, as it has been shown that the concentration of interstitial zinc ions is proportional to the square root of the prevailing zinc partial pressure for zinc–zinc oxide equilibria. The electrons produced by the zinc ionization results in an increase in available surface sites proportional to the zinc ion concentration. Thus, the population of surface adsorbed species such as CO_2^- may also depend on the zinc ion concentration. Reaction between CO_2^- and interstitial zinc would then result in a reaction rate dependent on the product

$$\text{Rate} \propto (N_{Zn_i^+})(N_{CO_2^-}) = (p_{Zn}^{1/2})(p_{Zn})^{1/2} = p_{Zn} \qquad (5)$$

When allowance is made for equilibrium concentrations of these species, the observed linear rate dependence would be predicted. From the experimental results, it is not possible to differentiate between these two mechanisms.

Powder samples of both forms of deposit were obtained by scratching the surface of the deposited oxide with the tip of a 0.3 mm file. The powder was placed in a capillary and mounted in a Debye X-ray powder camera. The spacings calculated from the powder film were found to be the same for both forms of deposit, as were the c/a ratios of the unit cells. This showed that the change in deposition mode was not due to a

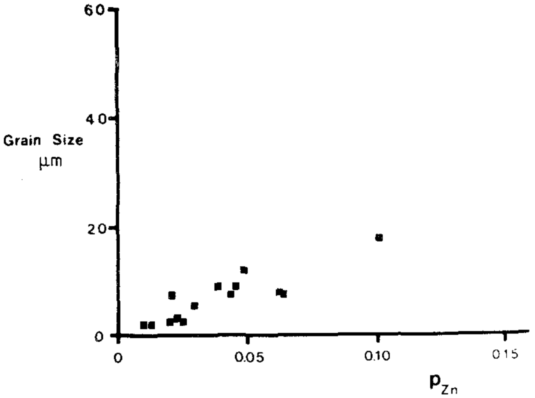

Figure 5 Variation of grain size of deposits with zinc partial pressure.

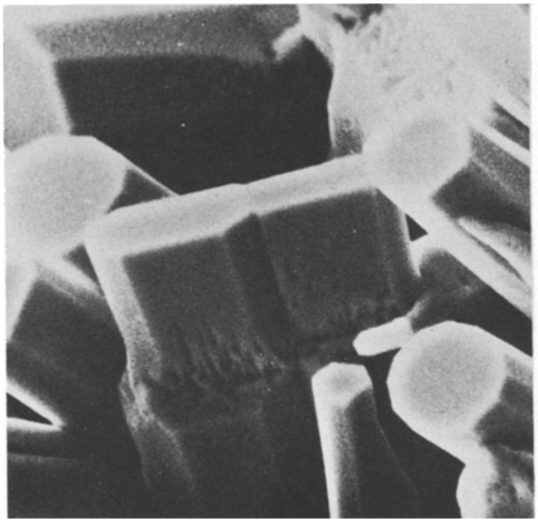

Figure 6 Etch pits. Deposition conditions $p_{\text{Zn}} = p_{\text{CO}_2} = 0.0445$ atm., $p_{\text{Ar}} = 0.5770$ atm., $p_{\text{CO}} = 0.3340$ atm. (× 7440).

Figure 7 Zinc droplet on column of zinc oxide. Deposition temperature 920 K (× 540).

change in the crystal structure but more likely a change in adsorption as is hypothesized above.

In order to investigate further the morphology of the deposits, oxide was deposited on polished silica discs which were inserted into the constant temperature section of the reactor tube for several of the experimental runs. In this way oxide deposits were obtained on a flat substrate which were amenable to investigations for preferred orientation using a scanning diffractometer. It was found that there was a preferred alignment of the basal planes of the individual crystallites of the deposits of zinc oxide parallel to the growth substrate. To investigate whether the crystallites were aligned parallel to each other in any of the basal plane directions, back reflection Laue photographs were taken which showed that the distribution of intensity around each Debye ring was very even, indicating that no preferred orientation exists between the individual crystallites along any specific crystal direction parallel to the substrate.

Another observation of the physical appearance of the heavy form of deposit was that oxide grain size was a function of the prevailing zinc partial pressure at the time of deposition, as shown in Fig. 5.

With the zinc oxide samples, which had grown in the columnar mode, it was found that there were etch pits on their prismatic surfaces as is shown in Fig. 6. These prismatic etch pits bear a strong resemblance to those obtained by Heiland and Kunstmann [9] and by Klein [10], who used aqueous halogen acids to etch columnar needle single crystals of zinc oxide as a method of indexing the direction of their *c*-axis. They found that the apex of the triangular etch pits pointed in the direction of the positive *c*-axis. From this comparison it would appear that in the vapour etched samples, the crystallites are oriented with the positive *c*-axis direction as their growth direction. This was confirmed by etching mounted samples of the deposit for 5 to 10 seconds in 5 vol% hydrochloric acid in water. Etching was found to produce pits similar to those of Heiland and Kunstmann, as well as outlining the grain boundaries between adjacent crystallites. In all of the etched samples, the apex of each pit pointed along the growth direction of the crystallites. This is an important observation as it indicates that the reactions being studied will have taken place, at least for the columnar growth mode, on the (0 0 0 1) zinc basal plane of the oxide crystals. This type of growth appears to be very common with zinc oxide film. McK. Nobbs and Gillespie [11] have produced zinc oxide films on fused quartz and alumina substrates by spraying aqueous zinc acetate solution onto substrates held at 773 K and, again, the preferred growth direction was observed to be parallel to the crystallites *c*-axis. Rabadanov *et al.* [12] also deposited zinc oxide on alumina and obtained the same preferred growth, but they used the reaction of zinc vapour with water vapour as their deposition reaction. The sputtering of zinc

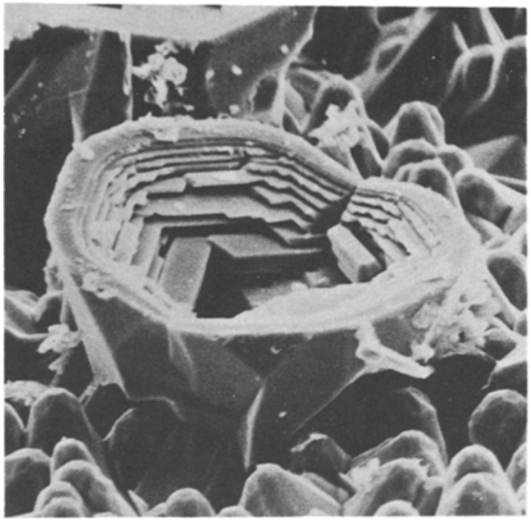

Figure 8 View inside a column of zinc oxide (X 4000).

oxide on pyrex glass [13], single crystal sapphire [14], and on cadmium sulphide [14] has also shown to produce crystals oriented with their *c*-axes perpendicular to the substrate. Reviewing other hexagonal materials, Bauer [15] has stated that the above-mentioned growth mode is the typical growth expected with a hexagonal lattice when the incident flux of material is randomly oriented to the growth substrate.

Towards the end of the oxide deposition region of the reactor tube a situation was often encountered in which the zinc partial pressure exceeded its saturation limit, and that zinc condensation occurred concurrent with zinc oxide growth with the zinc sitting on top of columns of zinc oxide (Fig. 7). To investigate this phenomenon further, the deposits were reheated in argon at 1223 K (Fig. 8). The zinc evaporated showing that the oxide columns were hollow prisms and that plates of ZnO had grown inside the columns inwards from the column walls.

4. Conclusions

In this system two regimes of oxidation were found to occur. The regime characterized by the heavy form of deposit has been associated with zinc adsorption, whereas the regime found to occur only at temperatures in excess of 1073 K has been attributed to the onset of carbon monoxide adsorption. The greater the carbon monoxide partial pressure the more likely was the occurrence of the lighter deposit at the elevated temperatures, and the greater the zinc partial pressure the more likely was the occurrence of the heavier form of the deposit.

Acknowledgments

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