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VAPOR GROWTH OF ZnO NEEDLE CRYSTALS

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Needle crystals of zinc oxide were obtained by the oxidation of zinc vapor produced from the reduction of ZnO powder with carbon. The reduction of ZnO powder was the rate-determining step in the crystal growth. The growth direction of the crystals was along a-axis.

Single crystals of zinc oxide were obtained by vapor phase reactions from mixtures of ZnO and carbon powders. The mixtures of reagent grade ZnO powder and G-108 carbon made by Tokai Electrode Mag. Company were put into a porcelain crucible with a lid. The carbon contents in the mixtures were in the range of 3 to 10 wt.%. The porcelain crucible containing the mixtures was introduced into an electric furnace which was maintained at 1100 to 1200°C. Colorless and transparent crystals having a maximum size of 60 to 100 μ in diameter and 30 mm in length were grown from the mixtures of ZnO with 8 wt.% carbon by heating at 1150°C for 3 hours. In the initial stage of crystal growth, the crystals began to grow on the wall of the crucible, and then they were grew from the upper side toward the bottom of the crucible with increase in the growth durations. Dendrite crystals were formed at the upper side of the crucible. Needle crystals grew under the dendrite crystals.

The needle crystals of zinc oxide were formed by the oxidation of zinc vapor produced from the reduction of ZnO powder with carbon. The reduction of ZnO powder by carbon at 1150°C is as follows,[1)]

$$ZnO + C \longrightarrow Zn + CO \quad (1),$$

$$2ZnO + C \longrightarrow 2Zn + CO_2 \quad (2).$$

The reaction(1) is predominant thermodynamically in comparison with the reaction(2) at 1150°C. The zinc vapor produced by the reaction(1) is oxidized by the oxygen introduced through the space between the crucible and the lid according to the reaction(3), so that the crystals grew up.

$$2Zn + O_2 \longrightarrow 2ZnO \quad (3).$$

Though zinc has vapor pressure over 1 atm at 1500°C, the vapor produced from reaction(1) is controlled by the reduction rate of ZnO powder. Therefore, zinc vapor evolved in the crucible has a relatively low partial pressure. This zinc vapor is suitable for the growth of needle crystals formed with the oxygen introduced through the space between crucible and lid. Temperatures above 1150°C were not suitable for the production of

large crystals, because the zinc vapor produced by the redution of ZnO powder increased with raising up the temperatures. At the temperatures lower than 1150°C, small crystals were formed by instantaneous oxidation of zinc vapor with low partial pressure. In the case of carbon contents over 10 wt.%, crystals were not obtained by producing a large amount of zinc vapor, because the reduction rate of the ZnO powder with carbon was faster than that in the sample with 8 wt.% carbon. Table 1 shows the results obtained under the representative growth conditions.

Table 1 Remarks on the crystals of zinc oxide obtained under the representative growth conditions.

Temperature (°C)	Carbon contents (wt.%)	Duration (hr.)	Remarks on the crystal growth
1150	4	1	Small crystals grew on the surface of the starting mixtures.
1150	6	2	Needle crystals having 20 to 30 mm in length.
1150	8	2	Needle crystals having 30 to 40 mm in length under dendrite crystals.
1200	5	1	Fine crystals on the edge of the crucible.

Needle crystals of zinc oxide obtained by chemical transport and vapor phase reaction method are normally the hexagonal prisms,[2,3] and the growth rate perpendicular to the c-direction is usually quite slow. In the present experiments, it was confirmed that the growth direction of these needle crystals is along a-axis as reported previously.[4] The fact that the growth direction in this study differs from that of the crystals obtained from vapor phase method may be explained by the differences in vapor phase, in which there is carbon monoxide or carbon dioxide produced by the reaction of ZnO powder with carbon. The electrical resistivity of the crystals along the growth direction was also the same as reported previously.[4]

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