Mem. Fac. Sci. Shimane Univ.,
23, pp. 85–88 Dec. 20, 1989

Characterization of Vapour-phase Growth SnO_2 Single Crystal

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(Received September 6, 1989)

Since crystals of SnO_2 were prepared by vapour-phase reaction method from anhydrous SnI_4 powder. The single crystals were characterized by optical microscope and X-ray Lang camera in order to clear the growth mechanism and internal defects in them. A lot of black dots were observed in the Lang topograph. It seems that the dots are planar defects with the Magnéli structure in the crystal. The single crystals were grown by the Kossel mechanism.

§1. Introduction

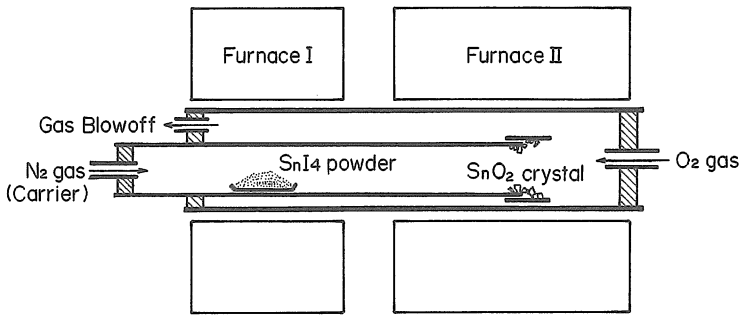
It is well-known that stannic oxide (SnO_2) with the rutile structure is a clear conducting material and has been widely used as clear electrodes. Many investigations have been made on a vapour-phase growth SnO_2 single crystal.[1–5] However most of the investigations have dealt with the growth condition or the morphorogy. There are little investigations on the growth mechanism or the internal defects. So, we have made SnO_2 single crystals from the stannic halides with lower temperature vapour growth, which is preferable for avoiding contamination of the grown crystals. SnO_2 single crystals have been characterized by optical microscope and X-ray diffraction topography technique of Lang. From the results, the growth mechanism and the internal defects will be discussed in this paper.

§2. Experimantal Procedure

SnO_2 single crystals were grown by following vapour-phase reaction,

$$SnI_4 + O_2 \rightarrow SnO_2 + 2I_2.$$

The arrangement used in this experiment is shown schematically in Fig. 1. Anhydrous SnI_4 powder as the starting materials was placed at central part of furnace I, where the temperature was about 200°C. The SnI_4 vapour was transported by N_2 gas through a combustion tube, 20 mm in internal diameter, to the growth region in furnace II, whose temperature was varies between 100°C and 1300°C at each growth run. Dried O_2 gas



$$SnI_4 + O_2 \longrightarrow SnO_2 + 2I_2$$

Fig. 1. Schematic illustration of arrengement used for growth SnO_2 single crystal.

or wet N_2 gas was supplied through the glass pipe as the reaction gas. The flow rates of the dried N_2 gas for carrying the SnI_4 vapour and the dried O_2 or wet N_2 gas were 230 ml/min and 150ml/min, respectively. After growth runs of several hours, many crystals were observed on the tip of the combustion tube. They were identified as SnO_2 crystals by X-ray diffraction. The growth condition and the morphorogies of SnO_2 single crystals have been reported previously.[6)]

A optical microscope was used for the observation of crystal surface. The internal defects in the crystal was observed by X-ray Lang camera. A characteristic X-ray used in this work was $AgK_{\alpha 1}$ radiation. The accelerating voltage and the beam current were 50 kV and 1.5 mA, respectively. The diffraction plane used for the topograph was a crystallographic plane (200) and the exposure time was about 20 hours. $AgK_{\alpha 1}$ radiation was exposed on Illford L-4 nuclear plate with emulsion thickness 50 μm.

§3. Experimental Results and Discussion

The crystallographic property of the SnO_2 single crystal used in the present work is shown schematically in Fig. 2. The microphotograph of (011) plane is shown in Fig. 3. Many dots and lines are observed in this crystal surface. So, the microphotograph with high magnification is shown in Fig. 4. From this microphotograph, most of the dots and the lines are identified as the pits and the growth bands on the surface, respectively. A few dots are hillocks on the surface. Figure 5 shows the reverse plane of the crystal shown in Fig. 3 and many pits and growth bands are also observed.

Figure 6 is X-ray Lang topograph of the single crystal. In this figure, dislcation lines are not observed but a lot of black dots, whose mean diameter is about 20 μm, are obsreved. These black dots don't correspond with the pits or hillocks on the crystal surface observed by the microscope. So they are lattice defects contained in the crystal. They may not be inclusions because the starting meterials and the carrier gas

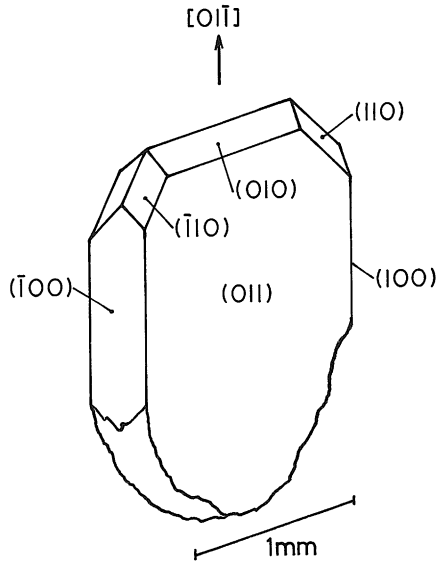


Fig. 2. Crystallographic property of SnO_2 single crystal.

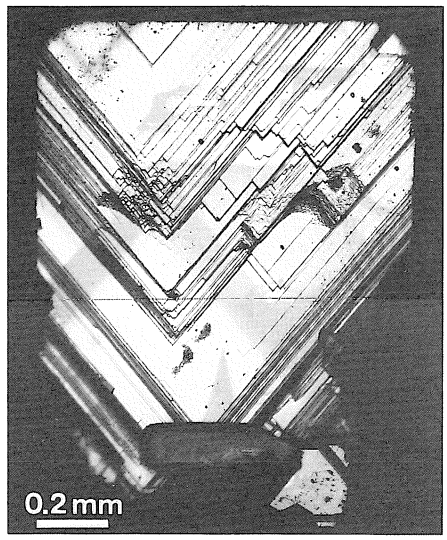


Fig. 3. Optical microphotograph of SnO_2 single crystal. Growth bands and dots on the surface are observed.

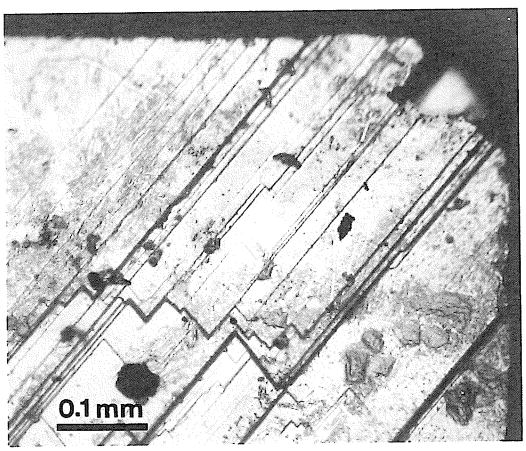


Fig. 4. Optical microphotograph with high magnification of SnO_2. Inclined lines are growth bands or growth stepts. Most of dots are pits on the surface and a few hillocks are also observed.

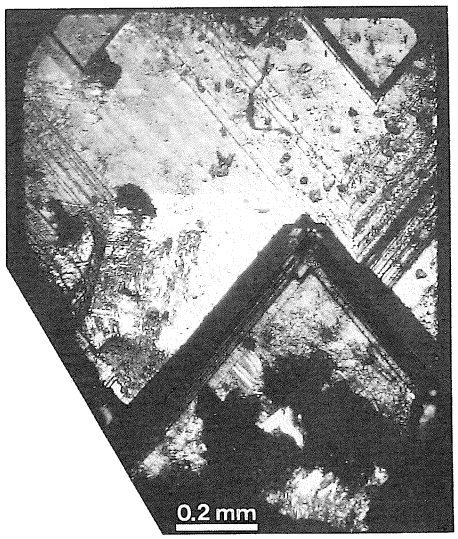


Fig. 5. Optical microphotograph with reverse side of Fig. 3.

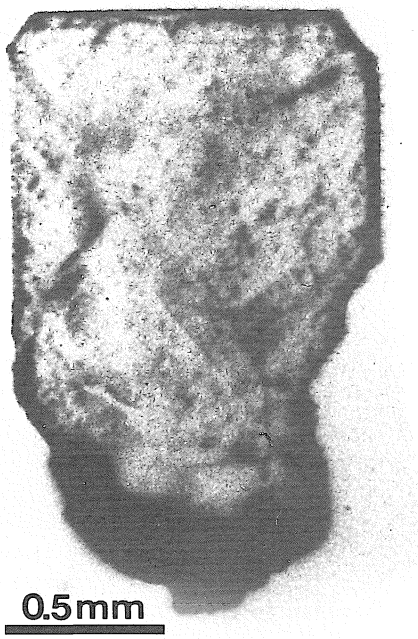


Fig. 6. X-ray topograph ($AgK_{\alpha 1}$) of SnO_2 single crystal. A lot of black dots are observed.

are high purity. Kaito *et al.* suggested that SnO_2 with the rutile sturucture prefers the Magnéri structure under the tin rich condition.[7]. Therefore it seems that the black dot is a planar defect which has the Magnéri sturucture because this single crystal has been made by the vapour growth. The inclined thick lines are also observed at the central part of the crystal in the topograph. These lines correspond with the growth band observed in the microphotograph. The spiral pattern is not observed on the crystal surface and this crystal is dislocation free one. Therefore, SnO_2 single crystal was grown by the Kossel mechanism and the surface steps are growth steps by the two dimensional nucleation mechanism.

In conclusion, the vapour-phase growth SnO_2 single crystal is dislocation free and black dot defects in the crystal may be the planar defects with the Magnéri structure. Furthermore, this single crystal was grown by the Kossel mechanism.

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