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Homogeneous Addition of Small Amount of Bi_2O_3 to ZnO Powder by Plasma Enhanced MOCVD

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Abstracts:

Small amount of Bi_2O_3 was homogeneously added as a sintering aid to ZnO powder using a plasma enhanced MOCVD. The mixture of ZnO and TPB (triphenyl bismuth) was charged into the bottom of the reaction tube. Inductively coupled plasma with 120 W of plate power was generated in the reaction tube. TPB was evaporated by the plasma and reacted with oxygen in the plasma to deposit the product containing bismuth on the surface of ZnO powder grains. The product containing bismuth is converted to Bi_2O_3 at a sintering temperature. Maximum conversion of TPB (90%) was obtained under the following conditions; Net weight of sample (ZnO+TPB): 1.0 g, Content of TPB: 2 wt%, O_2/Ar: 2, Total flow rate: 4 sccm, Duration: 120 min., Total pressure: 142 Pa. This conversion was remarkably large compared to the conventional MOCVD. The product was efficiently deposited on the surfaces of the ZnO grains. Shrinkage of ZnO pellet was measured by dilatometer to evaluate the additive effect of Bi_2O_3. ZnO pellet containing 0.48 wt% of Bi_2O_3 added by plasma showed a large shrinkage at high temperature. Homogeneously added Bi_2O_3 seems to effectively play a role of sintering aid.

Key Words: plasma, MOCVD, ZnO powder, Bi_2O_3, additive

1. INTRODUCTION

In the fabrication of ceramic materials, various kinds of additives were used to improve sinterability, electric resistivity, dielectric and magnetic characteristics, etc[1]. Small amount of additive has been added by mixing a powder or by drying a slurry consisting of an additive and powder of raw material. In the former case, the grain size of additive is comparable to that of the raw material, leading a microstructure of an additive grain in many grains of raw material. Distribution of additive is not homogeneous[2]. In the latter case, it requires a long period of time or a large amount of energy to dry the slurry. In recent years, small grain size is preferred in the raw material to fabricate the down-sized product. It becomes very difficult to add a small amount of additive homogeneously. To solve this problem, we have suggested a chemical vapor deposition (CVD) on the powder grains. However, the CVD has usually been performed at high temperature enough to grow the grains of raw material. The grain growth will be prevented by low temperature CVD using a glow discharged plasma. Therefore, a small amount of additive will be homogeneously added on the powder grains by the plasma enhanced MOCVD method[3),4)].

In the present study, small amount of Bi_2O_3 has been added to ZnO powder by the plasma enhanced MOCVD using triphenyl bismuth (TPB). The efficiency of the decomposition of TPB, the distribution of bismuth and the sintering characteristics of Bi added ZnO powders were investigated.

2. EXPERIMENTAL

2.1 Addition of Bi_2O_3 by plasma enhanced MOCVD

Figure 1 shows the MOCVD apparatus for the addition of Bi_2O_3. In the preliminary experiment, TPB was evaporated in an evaporation vessel and was then carried to the reaction tube in which plasma was generated. However, most of TPB vapor did not react with oxygen in the reaction tube and was carried out from the reaction tube. Therefore, the evaporation vessel was not equipped in the apparatus. TPB was mixed with ZnO powder with 1-4 wt%. The mixed powder (0.25-1.0 g) was charged in the bottom of the reaction tube. The system was evacuated by a rotary pump, flowing into a mixed gas of Ar and O_2 (O_2/Ar = 0.25-0.50, flow rate of the mixed gas: 1.5-10 sccm). After 30 min., plasma was generated with 120 W of plate power under the pressure of 80-240 Pa. The TPB was vaporized and was accelerated to react with oxygen by the plasma to deposit the product containing bismuth on the ZnO grains for 10-240 minutes. During the process, the mixture in the reaction tube was stirred by a

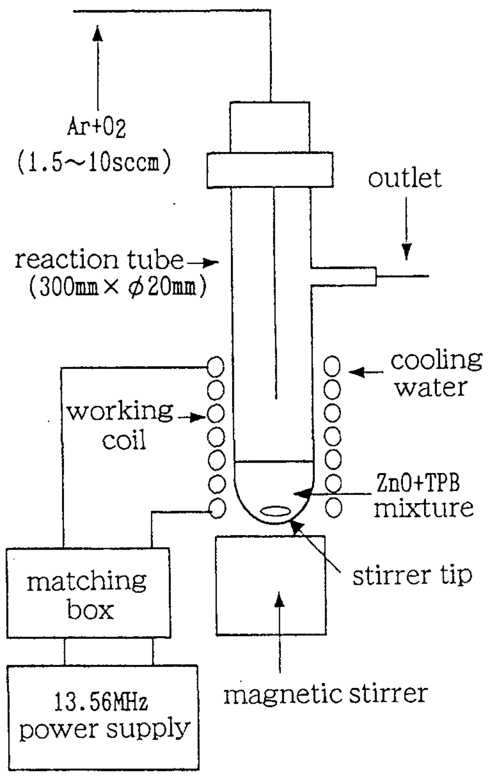

Fig.1 Experimental apparatus for plasma treatment.

Table 1 Deposited conditions.

O_2/Ar	0.25-5.0
Total flow rate / sccm	1.5-10
Duration / min	10-240
Addition of TPB / wt%	1-4

magnetic stirrer. Table 1 summarizes the deposit conditions. After the deposition, the mixture was washed by acetone to remove unreacted TPB. The deposited Bi was analyzed by ICP analysis. Conversion of TPB was calculated from the deposited amount of Bi to evaluate the efficiency of the TPB used.

2.2 Sintering of the plasma treated mixture

The sample treated by plasma was washed by an acetone to remove TPB in the mixture. The sample was then dried and calcined at 450°C for 30 min. The powder obtained was pressed into a pellet (4.5 mm ϕ·2.5 mm) with 100 MPa. Shrinkage of the pellet was measured by a dilatometer with a heating rate of 10°C.

3. RESULTS AND DISCUSSION

3.1 Addition of Bi_2O_3 to ZnO powder

Figure 2 shows the conversion of TPB vs. gas flow ratio (O_2/Ar). In the total gas flow rate of 3 sccm, the maximum conversion of 73.8% was obtained at O_2/Ar = 2. When the O_2/Ar gas flow ratio was larger than 2, the

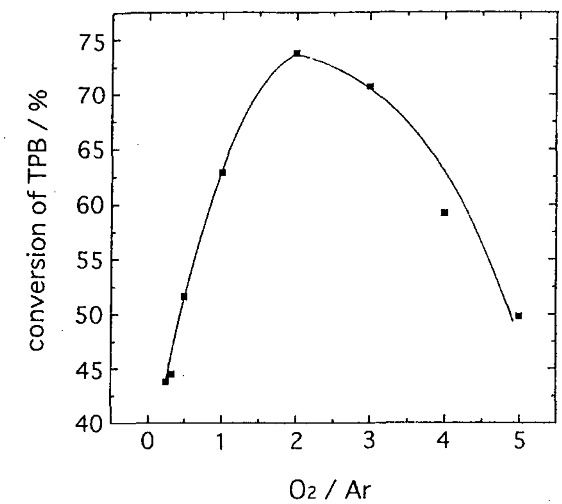

Fig.2 Conversion of TPB vs. O_2/Ar.
(Total flow rate: 3 sccm; Addition of TPB: 2 wt%; Pressure: 133 Pa)

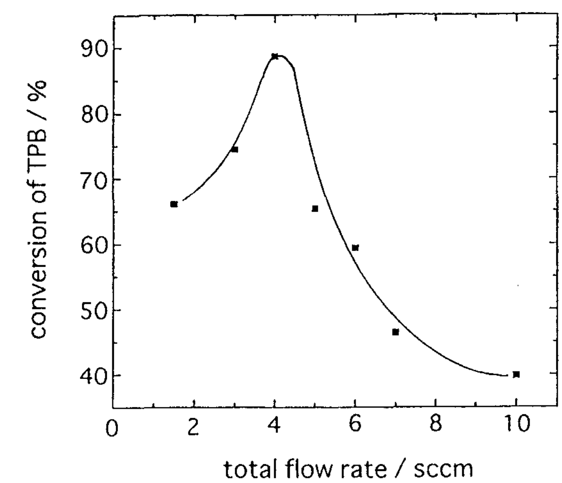

Fig.3 Conversion of TPB vs. total flow rate.
(O_2/Ar: 2; Duration: 120 min, Addition of TPB: 2 wt%; Pressure: 80-240 Pa)

stability of Ar-O_2 glow plasma decreased to lower the Bi content. As the result, the O_2/Ar ratio was determined as 2, under the total gas flow rate of 3 sccm.

Figure 3 shows the conversion of TPB vs. total flow rate under O_2/Ar ratio = 2. The maximum conversion of 88.3% was obtained at 4 sccm of the total flow rate. The conversion of TPB lowered when the amount of total gas flow was more than 4 sccm.

The conversions were also measured for the ZnO powders with 1, 2, and 4 wt% of TPB content under 4 sccm of the total flow rate and O_2/Ar: 2. Figure 4

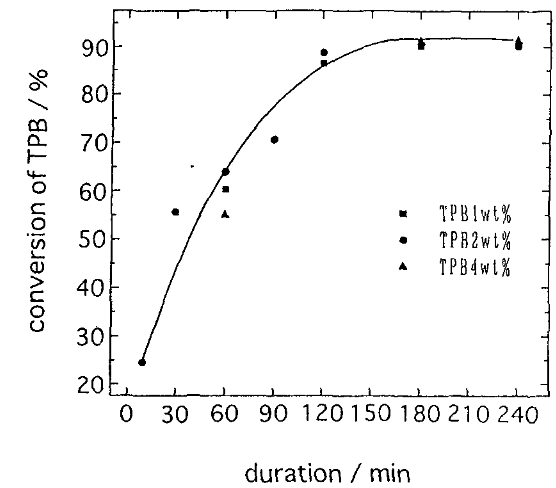

Fig.4 Conversion of TPB vs. duration.
(O_2/Ar: 2; Total flow rate: 4 sccm; Net weight of sample: 1 g; Pressure: 142 Pa)

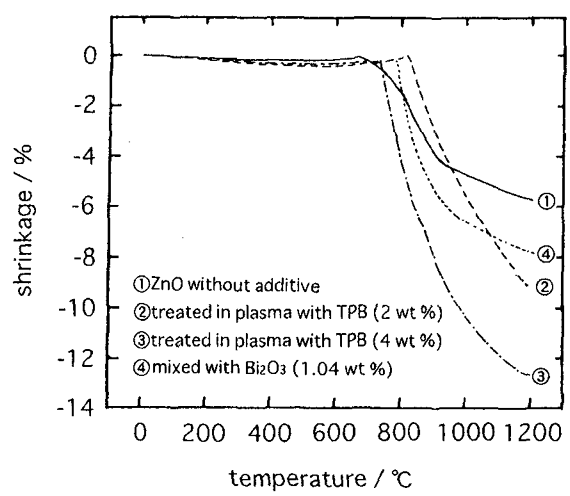

Fig.5 Shrinkage of green compacts.
(Heating rate: 10°C/ min)

shows conversion of TPB as a function of the reaction time. The conversions obtained at different TPB contents were almost equal to each other at same reaction time. Large conversion of TPB (about 90%) was obtained for sufficiently long time (150 minutes). Table 2 shows the most suitable conditions for each TPB content. It was concluded that an expensive MO reagent could be effectively decomposed at a low temperature by a glow plasma.

When the amount of raw materials was lowered to 0.5 g, the conversion of TPB improved to about 96%. However, the amount of raw materials (0.5 g) was too small. Thus, the amount of raw materials was selected as 1 g (90%).

3.2 Sintering of ZnO powder with Bi_2O_3 additive.

Figure 5 shows the shrinkage of the ZnO compacts with a heating rate of 10°C/min. The shrinkage of the green compacts started from about 700-800°C. Shrinkage of the ZnO compact without additive began from 700°C and was 5.8% at 1200°C. In the compact of ZnO powder with TPB treated in plasma, the shrinkage was 13.6% at 1200°C, which was much larger than that of ZnO without additive. The green compacts prepared by the powder treated in the plasma were also remarkably densified compared to the compact of ZnO with Bi_2O_3 prepared by mechanical mixing (shrinkage; 7.9% at 1200°C). In addition, the shrinkage curves of the plasma treated samples were sharply decreased. This may be due to the homogeneous distribution of the bismuth in the plasma treated ZnO powder. The homogeneous distribution of bismuth was also confirmed by EPMA.

Table 2 Suitable conditions for each TPB content.

TPB / wt%	1	2	4
Bi_2O_3 / wt%	0.48	0.96	1.93
Duration / min	150	240	240
Conversion / %	90.2	90.1	91.3

4. CONCLUSION

In the present study, small amount of Bi_2O_3 has been added to ZnO powder by the plasma enhanced MOCVD using triphenyl bismuth (TPB). High conversion (90%) of TPB was obtained under the following conditions; Net weight of sample (ZnO+TPB): 1 g, Content of TPB: 2 wt%, O_2/Ar: 2, Total flow rate: 4 sccm, Duration: 120 min. MO reagent, which is high cost, was efficiently decomposed at low temperature. The conversion 90% is enormously high compared to the conventional CVD process. Bi_2O_3 added by MOCVD efficiently worked to reveal high shrinkage in sintering. This may be due to the homogeneous distribution of the bismuth in ZnO powder.

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