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Polyol mediated synthesis of sub-micrometer Bi_2O_3 particles

H.-O. JUNGK, C. FELDMANN*
PHILIPS Research Laboratories, Weisshausstrasse 2, D-52066 Aachen, Germany
E-mail: claus.feldmann@philips.com

Bi_2O_3 particles 70 to 90 nm in size were prepared with the polyol method. According to this method a suitable metal precursor (e.g. halogenide, acetate, alcoholate) and a defined amount of water were heated in a high boiling alcohol (e.g. diethylene glycol). Based on temperatures up to 180°C crystalline α-Bi_2O_3 particles were formed. The material was isolated by centrifugation and characterized by XRD and SEM. The size of Bi_2O_3 particles in colloidally stable diethylene glycol suspension as well as in diethylene glycol/water mixtures was determined with laser diffraction methods. These suspensions were used to prepare homogeneous thin Bi_2O_3 particle layers on planar glass substrates.

1. Introduction

Several times the polyol method has been reported to be suitable for the synthesis of sub-micrometer metal particles. Here, examples like the noble metals Ru, Pt, Au as well as less noble metals like Fe, Ni or even alloys as Fe-Co-Ni, Fe-Pt are worth mentioning [1–3]. Special features of the method concerning this type of materials are on one hand the high reaction temperatures allowing a decomposition of the metal precursor and on the other hand the reductive properties of the alcohol.

These special features of the polyol medium should also be advantageous for a preparation of oxide particles. However, up to now only the preparation of ZnO, Fe_2O_3 and $CoAl_2O_4$ has been described [4–6]. Said investigations prove that on one hand the high temperature allows a direct synthesis of oxides instead of hydroxides. Moreover, the surface of oxide nuclei is complexed by the polyol medium right after formation what limits the growth of particles and stabilizes them also against agglomeration [6]. Both items make the polyol process interesting in view of other types of oxide particles.

This investigation aims at the polyol mediated synthesis of sub-micrometer Bi_2O_3 particles. This material has some technical relevance for sensors, photocatalysts and high-temperature superconductors because of its unusual magnetic and electrical properties [7–11]. For all of these applications thin homogeneous layers of Bi_2O_3 would be desired. Based on stable suspensions of Bi_2O_3 in the polyol medium such particle layers can easily be realized.

2. Experimental

Bi_2O_3 particles were prepared by suspending 1.66 g bismuth(III)-acetate (Aldrich, 99.99%) in 50 ml diethylene glycol (Merck, 99.00%). After intensive stirring 1.0 ml 0.1 M NaOH were added and the mixture heated in a silicon oil bath to 140°C. When the mixture had become clear, the temperature was continued another hour. Then the temperature was increased to 180°C and continued 2 h. The mixture became turbid again. Finally, after cooling to room temperature 50 ml ethanol were added. The resulting suspension contained 0.50 g Bi_2O_3. It was colloidally stable for weeks while lying on a roller bench. All liquid components as well as the resulting Bi_2O_3 suspension were filtered through 1.0 μm sieves to remove any type of agglomerates.

X-ray powder diffraction (XRD) was performed with a PHILIPS vertical goniometer PW1050 with Bragg-Brentano-geometry. The diffractometer was equipped with a fixed divergence slit and a proportional counter. Cu-K_α radiation was used and monochromatized by a secondary graphite monochromator.

For scanning electron microscopy (SEM) a PHILIPS SEM 525R equipped with a LaB_6 cathode was used. The samples were sputtered with gold. The investigations were carried out at a voltage of 15 to 25 kV, a spot size of 20 nm and a free working distance (FWD) of 9 to 12 mm.

Measurements of particle size were performed based on laser diffraction combined with polarization intensity differential scattering. For this purpose a Coulter LS230 equipped with a laser (750 nm, 5 mW) and a PIDS lamp (tungsten-halogen, 150 lumens at 2900 K) as well as 126 photodiode detectors were used.

Investigations with atomic force microscopy (AFM) were performed with a TOPOMETRIX EXPLORER equipped with a pyramidal Si_3N_4 tip. The vertical scanner span was <2 μm, the lateral scanner span <150 μm and the aspect ratio 1 : 1.

* Author to whom all correspondence should be addressed.

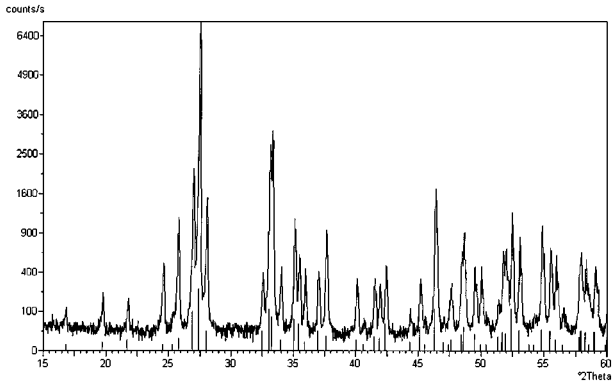

Figure 1 Powder diffraction pattern of Bi_2O_3; ICDD reference diffractogram (bismite, syn, 41-1449) added.

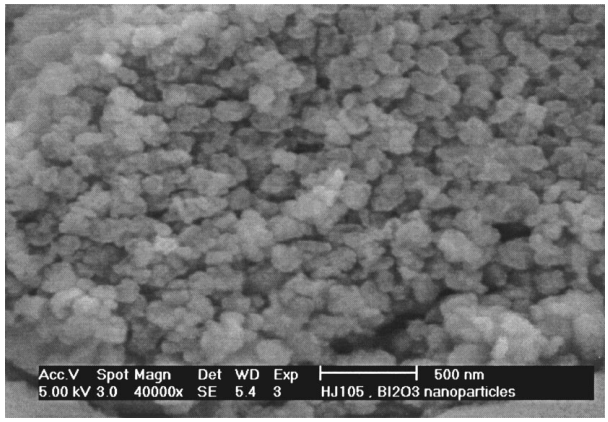

Figure 2 SEM photo of Bi_2O_3 powder.

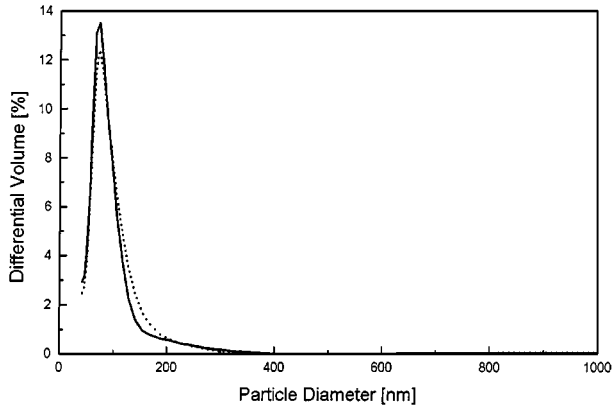

Figure 3 Size of Bi_2O_3 particles in diethylene glycol suspension (line) as well as after mixing with water (dotted, DEG:$H_2O = 1:10$).

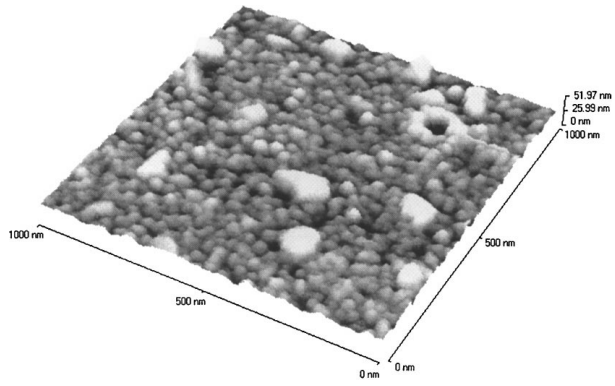

Figure 4 AFM micrograph of a Bi_2O_3 particle layer on a glass substrate (lighter areas are due to leaps of the measuring tip).

3. Results and discussion

In order to characterize the powder material, the Bi_2O_3 particles were isolated from the diethylene glycol suspension by centrifugation and washed with ethanol. X-ray powder diffraction pattern indicate that the pale yellow powder is pure α-Bi_2O_3 (Fig. 1). Obviously, a temperature of 180°C as applied during the synthesis is sufficient to yield well-crystallized material. SEM photos (Fig. 2) confirm the presence of Bi_2O_3 particles 70 to 90 nm in size. However, although the individual particles are definitively in the sub-micrometer region, SEM analysis also gives evidence for the fact that the particles are heavily agglomerated in the powder material. The large surface of particles can be assumed to be highly reactive due to e.g. hydroxyl groups [12], so that after any removal of the liquid phase and additional drying an aggregation is to be expected. In order to come to thin homogeneous Bi_2O_3 particle layers such aggregates are disadvantageous. In fact, they can be quite hard and would need intense milling to be reagglomerated.

A special merit of the polyol method is the stabilization of individual oxide particles by the polyol medium. As shown before in case of $CoAl_2O_4$ [6], the Bi_2O_3 particles represent primary particles in diethylene glycol as confirmed by laser diffraction methods (Fig. 3). The measured d_{50} (75 nm) in suspension corresponds well with the average size of powder particles visible in SEM photos. However, for technical issues water is the preferred suspending medium. Isolating the Bi_2O_3 powder material and resuspending in water on the other hand would ruin, as stated above, all advantages of the polyol method. Therefore, a direct mixing of diethylene glycol suspension and water was tested. With mixing ratios of 1 : 10 still relatively concentrated suspensions can be realized based on diethylene glycol suspensions containing 10 wt.-% Bi_2O_3. The water suspension turned out to be colloidally stable for a limited time too (Fig. 3). The d_{50} (79 nm) remains almost constant right after mixing. However, a slight broadening of the size distribution curve indicates that agglomeration starts, so that colloidal stability is only given in a period of time up to about 30 min.

Particle layers of Bi_2O_3 on planar substrates can be realized based on pure polyol suspensions as well as polyol/water mixtures. As example, a Bi_2O_3 layer on a glass substrate (50 × 50 mm) was prepared via spin-coating based on a suspension with 0.5 wt.-% Bi_2O_3 in diethylene glycol. An AFM image of such a type of layer is pictured in Fig. 4. Again, the averaged particle size is very similar to the findings in the suspension as well as in the powder material. The resulting layer is quite homogeneous and dense. Lighter areas in the image are artifacts due the use of a contact mode AFM. Here, local charging effects lead to leaps of the measuring tip.

4. Conclusions

Present investigations prove that the polyol method is suited for the preparation of Bi_2O_3 particles 70 to 90 nm in size. Here, the particles were yielded by heating of bismuth acetate and a defined amount of water in diethylene glycol to 180°C. The isolated powder

material was investigated by XRD and turned out to be pure bismutite. SEM photos confirm the presence of nanosized but agglomerated particles. However, laser diffraction confirms that the diethylene glycol suspension as well as mixtures with water contain non-agglomerated primary particles. Based on such suspensions planar (e.g. glass substrate) substrates can be homogeneously coated with thin dense Bi_2O_3 layers. Further investigations will concentrate on the preparation of e.g. Y, Zr or Pr doped material in order to yield stabilized δ-Bi_2O_3.

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