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PREPARATION OF AMORPHOUS TiO_2 FILMS BY THERMOPHORESIS-AIDED CHEMICAL VAPOR DEPOSITION

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TiO_2 films of 50-100 μm in thickness were formed on a cooled substrate from a stream containing titanium-tetraisopropoxide ($Ti(OC_3H_7)_4$, TTIP) at 623 K and atmospheric pressure. The films were amorphous and microporous with a specific surface area of 30-50 m^2/g. The growth rate of these films, around 30 nm/s, was much higher than conventional deposition techniques.

Chemical vapor deposition (CVD) method plays an important role in producing solid state materials because of its potentialities in applications to varieties of ceramics and metals and controllabilities of the properties of produced materials. More rapid growth technique, however, needs be developed for wider industrial applications of this method. Komiyama et al.[1)] and Kanai et al.[2)] reported that porous and amorphous TiO_2 ultra fine particles were prepared by thermal decomposition of TTIP. In this work, we have succeeded in very rapid preparation of porous and amorphous TiO_2 film which can be used as semiconducting materials, gas sensors, antireflection coating in solar cells, and so on. Different from the conditions in conventional CVD methods, the substrate on which films were grown was colder than the reactive gas stream. Thermophoresis is directional Brownian movement of particles in gas with temperature gradient.[3)] Hotter gas molecules have higher kinetic energy, and therefore, particles are forced to move from hotter to colder side. Thermophoretic precipitation of ultrafine particles formed in the gas stream contributed to the rapid growth of TiO_2 films.

Figure 1 schematically shows the reactor, composed of the coaxial Pyrex glass tubes of 48 mm^{Φ}(OD), and 30 mm^{Φ}(OD). Fifteen glass rings of 38.8 mm^{Φ}(ID) and 40 mm in length were inserted as substrates between the outer tube and the inner tube. A TTIP-containing helium stream flowed through the narrow space between the inner tube and the glass rings. The main heater was placed in the inner tube. The outer tube was covered by asbestos ribbons to be cooled moderately. The thermophoretic movement of the fine TiO_2 particles occurred from the hot inner tube toward the cold rings. The reaction rate of TTIP was determined by a gas chromatograph from the concentration of C_3H_6 produced simultaneously with TiO_2.[1)] The TiO_2 deposition on the glass rings along the reactor

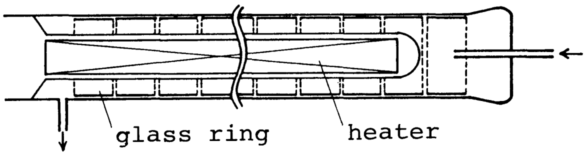

Fig.1. The experimental apparatus.

length was determined by the weight increase of each glass ring, and the morphorogy of deposited TiO_2 was observed by a scanning electron microscope (SEM).

Two runs were made under the condition of feed flow rate : 1.0 l/min, TTIP concentration : 0.65%, the inner tube temperature : 623 K, and the outer surface temperature was 462 K (run 1) and 542 K (run 2). In both cases, TiO_2 films were formed on the cold glass rings near the inlet side of the reactor. On the downstream, particle layers were formed. These films and particles were amorphous, as determined by X-ray diffraction analysis. Figure 2 shows the fracture surface of the TiO_2 films observed by SEM. Clustered particles were observed in run 1. The size was about 2 μm near the substrate and decreased from the substrate side to newly deposited side, down to 0.2-0.5 μm. The formation mechanism of this film is believed to be as follows. Very fine TiO_2 particles are formed in the gas phase, and then deposit on the cold glass ring due to thermophoresis. The deposited particles grow by surface reaction with TTIP to partially fill the interstices between the particles. In run 2, a dense film as shown in the SEM photograph was formed due to higher substrate temperature than run 1, which allowed a higher growth rate of TiO_2 particles to fill interparticle void space more completely. The film formation rate was 30 nm/s, which was much greater than that achieved with conventional techniques. Interesting to note is that the film formation occurred not on the hot side wall but on the cold side wall. The thermophoretic force effectively worked. Judging from the large suface area of more than 30 m^2/g, these films seemed to be porous, containing very fine pores which were invisible in the SEM photographs. The results obtained in this study are consistent with the former results[2] that porous and amorphous fine particles were prepared in the gas phase under the similar reaction conditions.

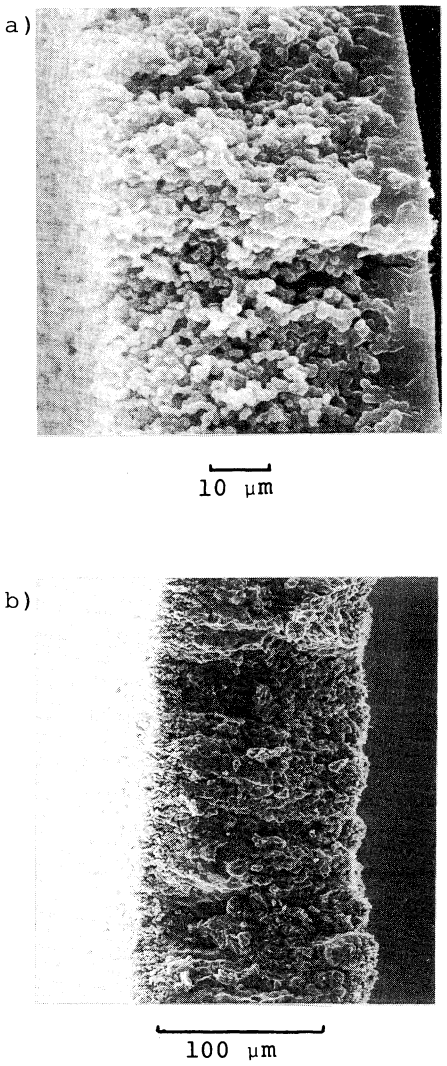

Fig.2. The SEM photographs of the TiO_2 films obtained in a) run 1 and b) run 2. (In both photographs, the right hand is the substrate side.)

In conclusion, porous and amorphous TiO_2 films were successfully prepared at a high growth rate by thermophoresis-aided chemical vapor deposition.

References

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