Synthesis of Fine Particles of Sn, Ti, and V Oxides by Laser-Induced Vapor-Phase Reaction.

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The vapor-phase reaction induced by dielectric gas breakdown using a pulsed laser has been applied to the syntheses of the fine particles of Sn, Ti and V oxides. The phase characteristics and particle size were investigated using X-ray diffraction and transmission electron microscopy. Stannic oxide with a mean particle size of 8.2 nm was synthesized from a gas mixture of $\text{SnCl}_4 + \text{O}_2$. Titanium oxide (anatase:rutile = 80:20) with a mean particle size of 8.5 nm was synthesized from a gas mixture of $\text{TiCl}_4 + \text{O}_2$. Rutile TiO_2 (rutile:anatase = 91:9) with a mean particle size of 53 nm was synthesized from a gas mixture of $\text{TiCl}_4 + \text{O}_2 + \text{H}_2$. Either VO_2 or V_2O_3 was formed from a gas mixture of $\text{VOCl}_3 + \text{O}_2 + \text{H}_2$ depending on the mixing ratio of the raw materials.

Keywords: fine particle, SnO_2 , TiO_2 , VO_2 , V_2O_3 , vapor-phase reaction, laser.

1. Introduction

A laser is employed in the processing of fine particles as (1) a light source for the photochemical or plasma reaction and (2) a heat source to supply the necessary energy for synthetic reactions or for vaporization. The advantages of utilizing lasers in fine particle synthesis are as follows: (1) lasers excite or heat a reactant gas alone, (2) lasers heat a reactant gas locally in an extremely short period up to a high temperature at almost the same power density as does an electron beam, (3) lasers heat material in various gaseous atmospheres, and (4) the reaction is not affected by the wall of the reactor because it is not heated. Laser processing is classified into three categories: (1) vapor phase reaction, (2) solid phase reaction, and (3) spray method. The vapor-phase reaction is further classified into four categories: (1) photochemical reaction, (2) thermal decomposition, (3) infrared multiple photon decomposition, and (4) dielectric gas breakdown. The laser processing of fine particles by dielectric gas breakdown is of special interest because of its unique method of ceramics synthesis.

When a reactant gas is irradiated with laser pulses which have a high temporary and spatial energy density, the light is absorbed almost completely and plasma accompanied by a sharp noise and strong emission is generated. This occurs even though the reactant gas does not

absorb the light of such a specific wavelength. This phenomenon is known as dielectric gas breakdown. Although the initial stage still remains unclear, the mechanism is postulated to be as follows [1]. First free electrons are generated by a kind of non-linear multiphoton absorption in the gas. They are excited by absorbing energy from the electromagnetic field of the light by the inverse bremsstrahlung process. Next, these electrons simultaneously collide with neutral molecules and generate ions and secondary electrons. Thus the generated secondary electrons are excited by absorbing light energy causing what is called cascade ionization. In this process, repeated ionization and dissociation of the gas generates reactive species. By this method, plasma, which has a much higher density than by other conventional methods, is obtained within a shorter period. The intensity of focused laser beam (laser energy per unit area and unit time) required to induce dielectric gas breakdown depends on the gas used. Generally this value is between 10^6 and 10^9 Wcm^{-2} and it decreases with an increase in gas pressure.

Fine particle synthesis induced by dielectric gas breakdown has the following characteristics. Compared with other reactions utilizing photon energy: (1) it is possible to use a gas which does not absorb light from the light source as a material, and (2) the light absorbancy is high, because practically all the irradiated light is absorbed

(>90 %), the reaction effectively proceeds by the energy absorbed from laser light and the yield is high because the process is a chain reaction. Compared with vapor-phase reactions using a conventional electric furnace: (1) no contamination from the wall of the reactor occurs because it is not heated, (2) the structure of the reactor is very simple, and (3) an unusual reaction is expected to occur because the density of the reactive species is high.

Ronn et al. [23] first reported in 1976 that fine particles of Fe, Mo, and S were formed by the dielectric gas breakdown of $\text{Fe}(\text{C}_2\text{H}_5)_2$, $\text{Mo}(\text{CO})_6$, and OCS. Draper [4] also synthesized fine particles of Cr from $\text{Cr}(\text{CO})_6$. On the other hand, no fine particle syntheses of ceramics by this method have been reported before we synthesized borides and metal oxides by the dielectric gas breakdown using a CO_2 laser pulse [5-8]. We report here the laser breakdown synthesis of fine particles of SnO_2 , TiO_2 , and V_2O_3 , which are useful for practical materials such as electronic devices, catalysts or pigments.

2. Experiments

The gas mixture of raw materials was introduced into a 3-l Pyrex reactor connected to a typical glass vacuum system through a greaseless stopcock. The vessel was baked out before introduction. The pressure of the raw material gas was measured using an MKS Baratron capacitance manometer. A transversely excited atmospheric pressure (TEA) CO_2 laser (Lumonics 103) was used for the irradiation. For all experiments the P (26) line of the $10.6\ \mu\text{m}$ branch at $939\ \text{cm}^{-1}$, one of the most intense radiation lines, was used to induce dielectric gas breakdown and to ignite the explosive reaction. The reactant was irradiated with a laser pulse focused by a BaF_2 lens with a 200 mm focal length through a KBr optical window attached to the vessel. The pulse energy was 3-5 J and the pulse duration was approximately 2 μs . The focused peak power density was, therefore, of the order of GWcm^{-2} . After the reaction, the reactor was evacuated overnight at $150\ ^\circ\text{C}$ to remove any volatile and absorbed species. The produced powders were collected and characterized using an X-ray diffractometer (Rigaku-RAD-IIIR) and transmission electron microscope (JEM-2000EX). The particle size was measured from the particle images in the electron micrographs.

Stannic chloride, TiO_2 and VOCl_3 were purchased from TRI Chemical Laboratory Inc. and their purities were 99.9999% based on metal analyses. The compounds were introduced into the reaction vessel immediately after vacuum distillation. Hydrogen and oxygen (Nippon Sanso Inc., purity 99.9%) were used without further purification.

3. Results and discussion

When a laser pulse was introduced into the reactor filled with the 2.7 kPa SnCl_4 + 53 kPa O_2 gas mixture, gas breakdown was always induced and the reaction started accompanied by a strong emission of light. The resulting greyish white fine particles were deposited on the wall of the reactor. The temperature of the wall, however, was as low as room temperature. After a 180-pulse irradiation, the gas in the reactor was removed and the resulting powders was collected. Figure 1 shows the XRD pattern of the as-grown powders. The d-spacing values, which are obtained from the three strongest peaks, are 0.334832, 0.264214, and 0.176409 nm. They are identical to those published for SnO_2 [9]. The transmission electron micrographs (TEM) of the particles are shown in Fig. 2 and Fig. 3. These observations indicate that the particles of SnO_2 produced by gas breakdown of the gas mixture of 2.7 kPa SnCl_4 + 53 kPa O_2 are spherical and highly crystalline. The particle size, which was obtained by measuring the size of the TEM images, was 2.4-13.4 nm. The spacing of the lattice images shown in Fig. 3 is about 0.33 nm which corresponds to the interplanar spacing value of the (110) plane of a tetragonal crystal [9].

Figure 4 shows the XRD pattern of particles formed by laser irradiation of the 1.3 kPa TiCl_4 + 1.3 kPa O_2 gas mixture. A comparison of the d-spacing values obtained in our method with those already reported [10] indicates that both anatase and rutile TiO_2 s were formed. The d-spacing values for these products are 0.352557, 0.237802, and 0.189232 (anatase), and 0.325235, 0.249001, and 0.168860 nm (rutile). The weight fractions of the anatase and rutile phase in the products are calculated from the relative intensity of the strongest peaks corresponding to anatase and rutile as described by Spurr and Myers [11]. Anatase and rutile TiO_2 s are produced in a ratio of 80:20. The TEM of the particle produced and the high-resolution

Fig. 1. XRD pattern of the powders produced from the 2.7 kPa SnCl_4 + 53 kPa O_2 gas mixture.

Fig. 3. High-resolution TEM of particles produced from the 2.7 kPa SnCl_4 + 53 kPa O_2 gas mixture. Scale bar : 10 nm

Fig. 2. TEM of particles produced from the 2.7 kPa SnCl_4 + 53 kPa O_2 gas mixture. Scale bar : 100 nm

Fig. 4. XRD pattern of the powders produced from the 1.3 kPa TiCl_4 + 1.3 kPa O_2 gas mixture.

TEM of the same product are shown in Fig. 5 and Fig. 6, respectively. The lattice image

Fig. 5. TEM of particles produced from the 1.3 kPa TiCl_4 + 1.3 kPa O_2 gas mixture. Scale bar : 100 nm

Fig. 6. High-resolution TEM of particles produced from the 1.3 kPa TiCl_4 + 1.3 kPa O_2 gas mixture. Scale bar : 10 nm

spacing is about 0.35 nm corresponding to the value of the interplanar spacing of the (101) plane of the anatase crystal [10]. Particle size is between 3.2 and 14.5 nm.

It is found that the irradiation of a reactant gas containing H_2 produces only rutile particles. Figure 7 shows the XRD of the as-grown powders which were formed by the reaction of the 1.3 kPa TiCl_4 + 8.0 kPa H_2 + 2.0 kPa O_2 gas mixture. By comparison of Fig. 7 with Fig. 4, it is found that rutile TiO_2 (91 %), which is highly crystalline, is the main product in the irradiation of a reactant gas containing H_2 . Titanium oxide was probably formed by the hydrolysis of TiCl_4 by H_2O which was formed from H_2 and O_2 . It is shown that a hydrogen atmosphere accelerates the anatase-rutile transformation [12, 13]. The d-spacing values are 0.324770, 0.248734, and 0.168745 nm. Figure 8 shows the TEM of rutile TiO_2 fine particles, the particle size of which is 22-67 nm. The high-resolution TEM of the same particles is shown in Fig. 9. The lattice fringes indicate that this particle is monocrystalline. The lattice image spacing is about 0.31 nm corresponding to the interplanar spacing value of the (110) plane of the rutile crystal [10].

From a 200-pulse laser irradiation of the 1.6 kPa VOCl_3 + 3.2 kPa H_2 + 0.80 kPa O_2 gas mixture, a dark brown powder was obtained. The XRD pattern of the as-grown powder is shown in Fig. 10. The d-spacing values are 0.320646, 0.242505, and 0.165488 nm and the product is identified to be VO_2 based on the reference data [14]. The TEM observation yields some of interesting results: needle-like particles were formed from the vapor phase reaction as shown in Fig. 11. When the 1.6 kPa VOCl_3 + 6.4 kPa H_2 + 1.6 kPa O_2 gas mixture, where the ratios of H_2 and O_2 to VOCl_3 are higher than the previously described run, was used as a reactant gas, the irradiation of the reactant gas with a single laser pulse ignited an explosive reaction accompanied by a bright emission from the entire reactor. A dark brown powder was deposited on the wall of the reactor. The XRD pattern of the as-grown powder is shown in Fig. 12, which indicates the product is highly crystalline. The product is identified to be V_2O_3 by a comparison of the d-spacing values of 0.365682, 0.271051, 0.247408, and 0.169727 nm with those already reported [15]. As is shown by the TEM image

Fig. 7. XRD pattern of the powders produced from the 1.3 kPa TiCl_4 + 8.0 kPa H_2 + 2.0 kPa O_2 gas mixture.

Fig. 9. High-resolution TEM of particles produced from the 1.3 kPa TiCl_4 + 8.0 kPa H_2 + 2.0 kPa O_2 gas mixture. Scale bar : 10 nm

Fig. 8. TEM of particles produced from the 1.3 kPa TiCl_4 + 8.0 kPa H_2 + 2.0 kPa O_2 gas mixture. Scale bar : 200 nm

Fig. 10. XRD pattern of the powders produced from the 1.6 kPa VOCl_3 + 3.2 kPa H_2 + 0.80 kPa O_2

Fig. 11. TEM of particles produced from the 1.6 kPa VOCl_3 + 3.2 kPa H_2 + 0.80 kPa O_2 gas mixture. Scale bar : 1 μm

Fig. 12. XRD pattern of the powders produced from the 1.6 kPa VOCl_3 + 6.4 kPa H_2 + 1.6 kPa O_2 gas mixture.

Fig. 13. TEM of particles produced from the 1.6 kPa VOCl_3 + 6.4 kPa H_2 + 1.6 kPa O_2 gas mixture. Scale bar : 200 nm

in Fig. 13, the resulting V_2O_3 as well as VO_2 particles are found to grow anisotropically.

From these results, it is found to be possible to vary the crystal phase or chemical species of the products by changing the composition of the reactant gases.

4 Conclusion

Crystalline fine particles of SnO_2 , TiO_2 , VO_2 and V_2O_3 were synthesized by a vapor-phase reaction induced by dielectric gas breakdown using a TEA CO_2 laser. The potential utilization of our method is expected to be useful for fine particle syntheses of other metal oxides are to be studied because it is possible to vary the crystal phase or chemical species by changing the composition of reactant gases.

5. References

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