Short Note

Effects of Pretreatment of Source Powder Mixture on Aerosol Gas Deposition Film Synthesis and Luminescence

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ABSTRACT

In this study, we report that the deposition rate of films is indicated to be strongly related to the preheating conditions of source powder mixture of ZrO2 and NiO. A stable luminescence was observed clearly during film fabrication. In an aerosol gas deposition method, the source powder is charged during transport by the mutual friction of particles and their collision against the inner surfaces of the tubing and nozzle. The charged powder contributes to the deposition rate of film synthesis and the generation of static electricity depends on the surface condition of the source powder. In particular, the amounts of gas and moisture adsorbed on the particle surface might be key factors.

KEY WORDS

Aerosol gas deposition, pretreatment, zirconia, luminescence

1. Introduction

The fabrication of thin films has been the focus of attention because it is a key technique for modern applications such as semiconductors and other electronics. The recent development of nanotechnology in electronics is also based on thin film technology. Additionally, thick films are also of interest, whose properties are between those of thin films and bulk layers such as mechanical and thermal properties.

We have been involved in the development of two new film formation techniques: a gas deposition (GD) method[1,2] for film formation from nanoparticles and an aerosol gas deposition (AGD) method[3-5] for film formation from conventional powders. We started to develop the former method from 1970 and the latter method from 1981. The advantage of these two methods is that they can be used to produce thin films at room temperature.

The films produced by these two methods have several promising applications because these methods involve dry and low-temperature processes; hence, substrate degradation does not occur. For example, metal films formed from nanoparticles by the GD method were used as conducting wires for electric fields[6] since the use of this method helps to prevent the degradation of base materials.

The use of the AGD method for the fabrication of various types of ceramics has been investigated. Oxide films, such as alumina, titania, silica, yttria, $(Ba_{0.6}, Sr_{0.4})TiO_3$, lead titanate zirconate (PZT),

and zirconia including yttrium-stabilized zirconia, have been easily obtained by this method[7-10]. The AGD method is also expected to be one of the key technologies in advanced environmental material developments for the realization of a low-carbon-emission society[11-13]. Zirconia films fabricated by this method can be used as thermal barrier coatings and oxygen sensors, as well as solid oxide fuel cells[14-20].

In our previous papers, we reported that luminescence was produced by the AGD process and induced by zirconia particles charged by frictional electrification during friction and collision among particles and fractoelectrons[21,22]. We considered that the luminescence is related to plasma generation and the plasma drives forward the low -temperature synthesis of zirconia[23].

Concerning AGD film research, Akedo et al. have energetically performed such work since 1996 and published many papers, and their AGD equipment was nearly the same as that used in our study. However, they consider that the mechanism of synthesis involves the plastic deformation of ceramic particles caused by the collision of particles with a substrate. Therefore, they recommend the use of submicron particles as source materials as these particles deform easily[7].

The difference in the mechanism of AGD might introduce the difference in particle size suitable for the AGD process. That is, we conclude that the appropriate particles size is several micron meters from the standpoint of ease of the generation of static electricity. We were able to synthesize ceramic films using several micrometer

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particles, but they do not seem to result in films of good quantity.

When we consider the key factors to be the mechanism of generating static electricity for AGD in ceramic fabrication, we point out the importance of the shape and surface condition of particles, along with the frequency of collision and friction between particles and the inner surfaces of the tubing and nozzle. Concerning the pretreatment of source powder, on the basis of our experience we recommend the introduction of degassing at about 573 K for several hours. The pretreatment was also conducted by Akedo et al. However, they did not clearly explain the effect of the pretreatment.

In this paper, we attempt to clarify the effect of the pretreatment of source powder on the fabrication of zirconia films on the basis of the relationship between the degassing temperature and deposition rate of the films.

2. Experimental methods

Fig. 1 shows a schematic diagram of the AGD apparatus, which comprises an aerosol container, a deposition chamber, and a transfer pipe. The chamber is evacuated to a pressure of 10 Pa using a root blower pump (138 L/s) and a rotary pump (2500 L/min). The deposition chamber is equipped with a nozzle and an X-Y moving stage to be used during the fabrication of the films. The nozzle is linked to a container holding the source powder via a transfer pipe.

The chamber is first evacuated, and then, nitrogen gas is introduced into the chamber from the bottom of the aerosol container. Subsequently, the gas is transported to the deposition chamber through the transfer pipe. The rate of gas supply is maintained at 18 L/min. The mixture powder in the aerosol container is entrained by the supply gas and ejected from the nozzle into the deposition chamber, where it is deposited on to a substrate for film formation.

Fig. 2 shows the illustrations of the nozzle and substrate arranged at the deposition site. The nozzle with a width of 30 mm is used; the nozzle has a 0.3-mm-wide slit. Stainless steel plates are used as substrates for the aforementioned deposition. Each substrate is 30 mm in diameter and 1 mm in thickness. The substrate holder can be moved in the X- and Y-directions using a digital programmable
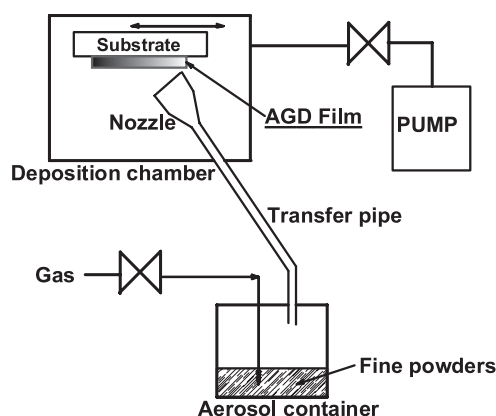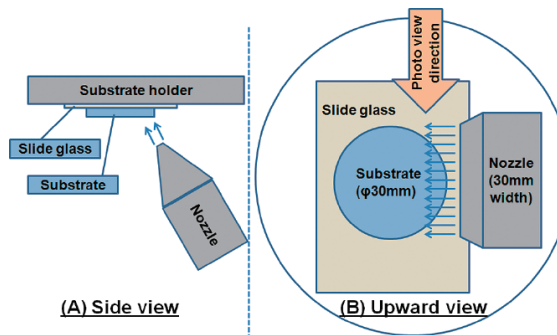

Fig. 2　(Color online) Illustrations of nozzle with width of 30 mm and substrate with diameter of 30 mm arranged at deposition site: (a) side view, (b) upward view.

controller. The scanning speed is maintained at 0.1 mm/s or 1 mm/s for a 30-mm-long film, and scanning is performed 1 to 60 times in the X-direction to obtain the final product.

ZrO_2 (8 mol%Y_2O_3 doped ZrO_2) and NiO powder samples were used as raw powders (Fig. 3 (a) and (b). Powder samples containing 50 wt% each of raw powder were mixed in a planetary ball milling device (Ito Seisakusho, LP-2/4) using 500 cc zirconia vessel and zirconia balls with a diameter of 15 mm. The mixing process was conducted at a milling speed of 180 rpm for 30 min and a ball-to powder weight ratio of 188 to 100. Under these conditions, only mixing was achieved and no obvious pulverization was observed, as shown in Fig. 3 (c). The powder mixture was heat treated at 573 K for 30 min in air and used as the source powder. One hundred grams of the powder mixture was placed in the aerosol container. The amount of source powder consumed in each batch was varied from 3 g to 60 g. Under the main AGD condition, the pressures of the aerosol container and deposition chamber were 50 kPa and 0.8 kPa, respectively. The entire deposition process was carried out at room temperature.

The amount of powder ejected from the nozzle was estimated from the difference between the charged powder amount and the residual amount in the aerosol container. Deposition rate was calculated from the obtained film thickness and deposition time. Film thickness was measured using a micrometer.

3. Results and discussion

3.1 Relationship between the pretreatment of source powder and the deposition rate

Fig. 4 shows the relationship between the deposition rate in the AGD process and the amount of powder ejected from the nozzle. The amount of powder ejected from the nozzle for the powder pretreated at 573 K was twofold higher than that pretreated at 523 K accompanied by the higher deposition rate of the film. In the case of the powder pretreated at 573 K, the experimental data for the amount of powder ejected and the deposition rate of formed films markedly scattered. The experimental results strongly suggest that the characteristics of the initial powder transmute after the
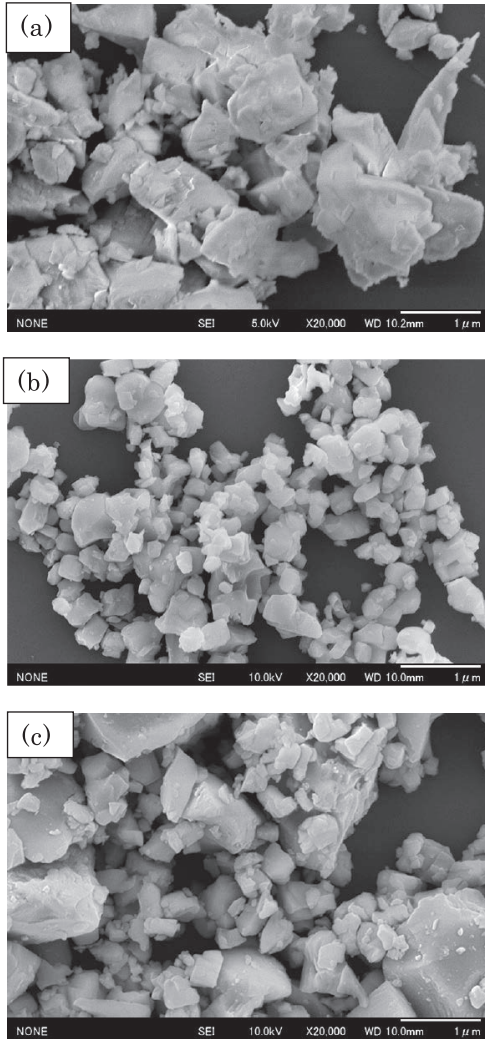

Fig. 1　Schematic diagram of AGD apparatus.

Fig. 3   SEM photos of as received raw powder of 8 mol%Y2O3 doped ZrO2 (a) and NiO(b), and powder mixture used as source powder (c).

pretreatment of raw powder. Indeed, the pretreated powder has a high fluidity such that the amount of powder blown from the aerosol chamber clearly increases.

Generally, the powder surface was covered with the adsorbed moisture. The moisture might be removed by the pretreatment at a temperature higher than 373 K. However, we found that a suitable pretreatment should be carried out at a temperature higher than 573 K. This indicates that the residual powder surface consists of other species. The surface might consist of hydroxyl and adsorbed oxygen on metallic ions. We consider that the desorption of moisture on the powder surface is important for developing a high-performance AGD method.

Fig. 5 shows the effect of the attained discharge pressure of the deposition chamber on the amount of powder ejected from the nozzle when we used the powder pretreated at 573 K. In the case of insufficient discharge pressure of the chamber (e.g. 40 Pa), the amount of powder ejected decreased to be the same as that of 523 K-pretreated powder.

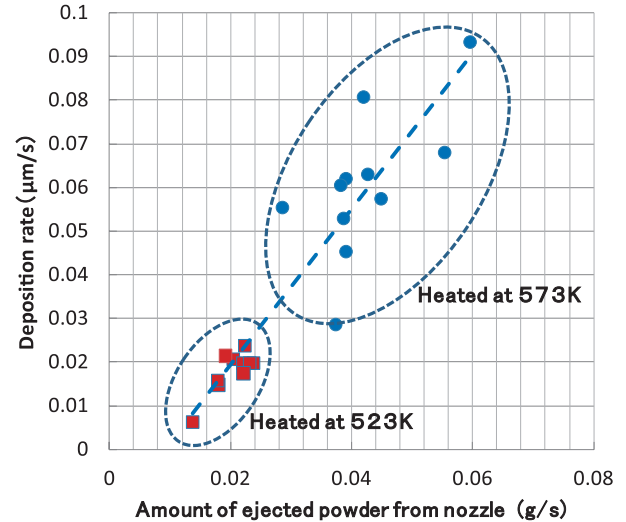The decrease in the amount of powder ejected in the case

Fig. 4   (Color online) Relationship between deposition rate in AGD process and the amount of powder ejected from nozzle. Circles and squares show the heat-treatment data obtained at 573 K and 527 K, respectively.
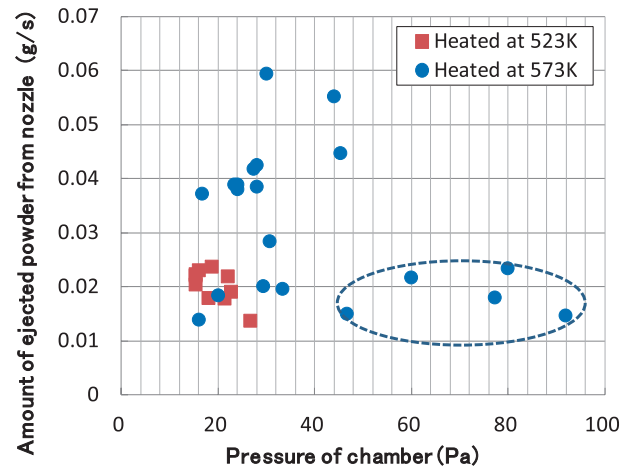

Fig. 5   (Color online) Relationship between pressure of chamber and amount of powder ejected from nozzle. The data marked by a dashed line circle are indicated in the text.

of insufficient evacuation of the deposition chamber might be explained as follows: The insufficient evacuation of the deposition chamber generates moisture from the inner surface of the chamber and/or raw powders such that moisture contamination occurs on the pretreated powder surface in the aerosol chamber. As a result, amount of the powder ejected from the nozzle decreased and the deposition rate of films also decreased. The decrease in deposition rate is also related to the decrease in the amount of powder blown because of the loss of powder fluidity due to the adsorbed moisture.

3.2   Film formation and luminescence in AGD process

The increase in the amount of obtained powder increases the number of collisions among particles such that the number of charged particles increases because the collision and friction among particles induce static electricity. Fig. 6 shows the *in situ* observation of the deposition site for 573 K-treated particles ejected from the nozzle;
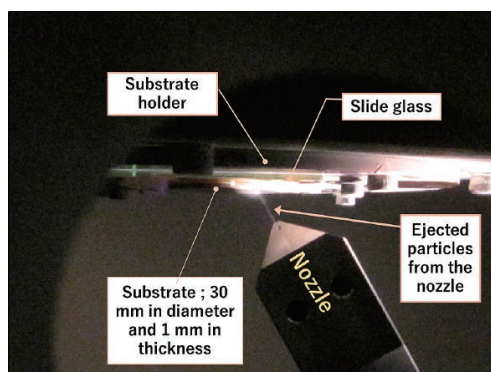
Fig. 6 (a)   (Color online) Deposition site in bright field; the powder ejected from the nozzle are clearly seen as a white line between the nozzle and the substrate.
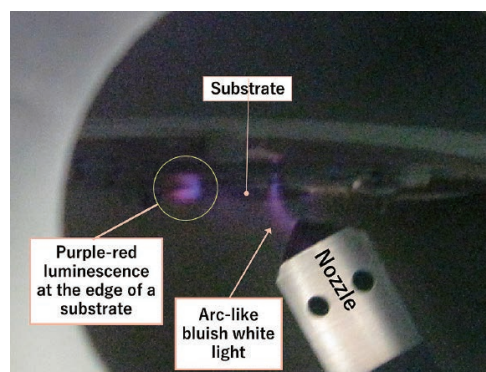

Fig. 6 (b-1)   (Color online) Deposition site in dark field; arc-like bluish white light is observed at the deposition site and purple-red luminescence is also observed at the edge of a substrate 20 mm away from the deposition site.
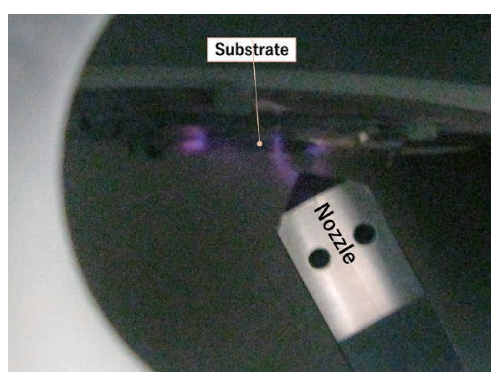

Fig. 6 (b-2)   (Color online) Images taken 6 s after deposition.
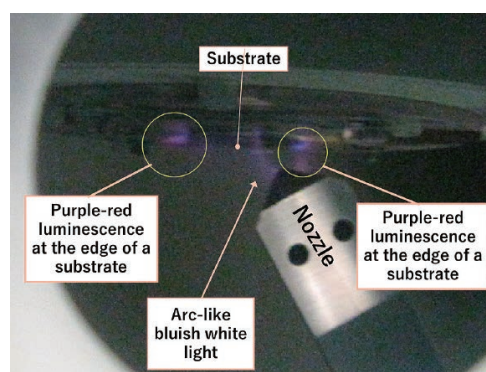

Fig. 6 (b-3)   (Color online) Images taken 14 s after deposition.

here, bright- and dark-field images are taken with and without outdoor light, respectively.

In the bright-field image in Fig. 6 (a), the particles ejected from the nozzle are clearly seen as a white line between the nozzle and the substrate. In the dark-field image in Fig. 6 (b), arc-like bluish white light is observed at the deposition site and purple-red luminescence is also observed at the edge of the substrate 20 mm away from the deposition site. Judging from the color, the luminescence is considered to originate from nitrogen plasma. Fig. 6 (b-2) shows the image taken 6 s after deposition and Fig. 6 (b-3) shows that taken 14 s after. Although the luminescence intensity sometimes fluctuates, the luminescence is generally stable.

The occurrence of apparent luminescence is related to stable plasma generation, which we consider to originate from the generation of nitrogen plasma. When positively charged particles approach the substrate surface, electrons are formed on the substrate surface by polarization. When the discharge condition is satisfied, electrons are released from the substrate and collide with nitrogen gas to generate nitrogen plasma[24,25]. Therefore, the driving force for synthesizing ceramic films at room temperature is considered to be the plasma sputtering itself. However, the state of the powder should be more precisely studied in order to clarify the mechanism of low-temperature film synthesis by the AGD method.

4. Conclusions

The formation of AGD films depends on the pretreatment conditions of raw materials. Such dependence is due to the behavior of moisture and adsorbed gas species caused by powder fluidity and the control of static electricity generation. The moisture disturbs both the powder fluidity and the generation of positive particles. Concerning static elasticity, certain differences in surface adsorbed elements were observed between the particles treated at 523 K and 573 K because they showed different deposition rates and luminescences. As moisture was removed from both powder samples, there might be some other adsorbed as yet unknown species that would disturb the generation of plasma.

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