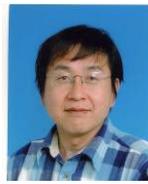


Ceramic coating technology at room temperature using the aerosol deposition method, and the commercialization development for an anti-plasma corrosion coating



Jun Akedo*1
(1959)



Hisato Ogiso*2
(1960)



Masakatsu Kiyohara*3
(1960)



Hironori Hatono*3
(1967)



Junichi Iwasawa*4
(1970)

1. Outline

The aerosol deposition (AD) method is a novel technology for ceramic coatings, blowing solid-state fine particles onto the substrates under room temperature, which resemble to the sand-blast method on the instrumental settings. The distinct feature is that the AD method does not require sintering processes to deposit ceramic films; nevertheless the deposited films have closely packed structure, optical transparency, high strength and strong adhesion with a high-speed deposition rate. We applied the AD method to the fabrication of yttrium oxide films, and attained the high performance of the anti-plasma corrosion and the electric insulating property, which are superior to those of the bulk and the thermal spray coating. We then successfully launched the businesses for the anti-plasma corrosion films used for next-generation semiconductor manufacturing facilities and electrostatic chucks. The development was triggered by the findings that the ceramic particles consolidated at room temperature, named the phenomenon "room temperature consolidation (RTIC)", and was promoted by key researches on various aspects, including the elucidation of RTIC, conditioning of the starting particles, ensuring the homogeneity of the thickness and the flatness in large area as a mass product. The attainment of the researches resulted in achieving a "dream" coating technology, which enabled us to overcome the trade-off relation between the process temperature and the process speed. The AD method, with being the low-environmental load and being applicable to various industries, is filled with promise as a coating technology in a new era.

2. Contents of the technology

Figure 1 shows the schematic diagram of instrumental settings of the AD method. The starting particles whose size were less than $1\ \mu\text{m}$ was mixed with carrier gas in the aerosol generator and made them into the aerosol condition. The aerosol was blown on the substrate through the nozzles in the low pressure chamber, then the particles in the aerosol, with keeping solid states, were collide with the surface of the substrate. In this process, the ceramic films are formed on the substrates. In this research, we found the formation of ceramic films at room temperature, and named the phenomenon "room temperature impact consolidation (RTIC)". **Figure 2** shows the behavior of the RTIC, the particles were fractured and transformed into fine crystals ($10\sim 30\ \text{nm}$ size), then nano-crystal structure was formed, and the process of particles fracture simultaneously gave birth to nascent surface. Therefore, the activity of nascent surface dominantly enhanced the bond among the particles. Controlling and optimizing the RTIC, we achieved to form ceramics films that have dense, strong adhesion, and high transparency, and to coat the films on various substrates with high speed. As for analyzing the mechanism of the RTIC, we developed equipment to undergo a compression test for a single submicron-size particle. Using the equipment, we clarified the fracture conditions and developed technology for particle preparation to cause the RTIC effectively. The findings contributed to the development for the mass production technology.

Figure 3 shows the cross-sectional SEM and TEM images of the yttrium oxide films fabricated by the AD method, and table 1 shows the electrical and mechanical property of the films. Conventionally, to sinter yttrium oxide requires the hot isostatic pressing (HIP) process with more than $1700\ ^\circ\text{C}$. However, the AD method attained not only the dense consolidation at room temperature but also that the AD film has a larger electrical insulating property and mechanical strength than bulk hither. **Figure 4** shows the test result of the anti-plasma corrosion. Even before exposed plasma (**Fig. 3** upper images), the AD yttrium oxide film had certainly better surface smoothness than the bulk yttrium oxide and the film produced by the thermal spray coating. After exposed plasma (**Fig. 3** lower images), the significant difference were found between the AD yttrium oxide films and that produced by the other processes, i.e. the AD yttrium oxide film was free from pores, although noticeable pores were found in the yttrium oxide samples fabricated by the other processes. This result demonstrates that the AD method considerably improved the anti-plasma corrosion and the surface smoothness of yttrium oxide. Owing to the attainment about the AD method, we achieved the anti-plasma corrosion, the wear resistance, and the reduction of the adsorption gas and the particle emission that are required of the next-generation semiconductor manufacturing industries.

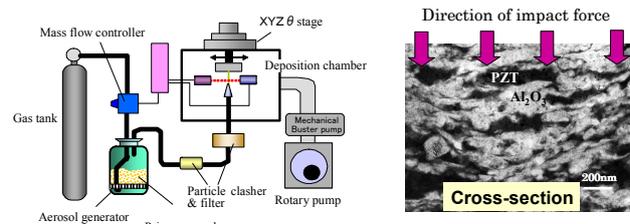


Fig.1 The schematic view of the instrumental setup of the AD method.

Fig.2 The cross-sectional TEM image of the AD film showing the behavior of the fracture and transformation at room temperature.

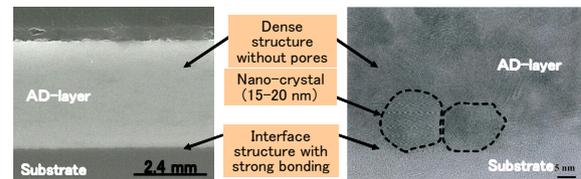


Fig. 3 The fine structure of yttrium oxide films formed by the AD method at room temperature.

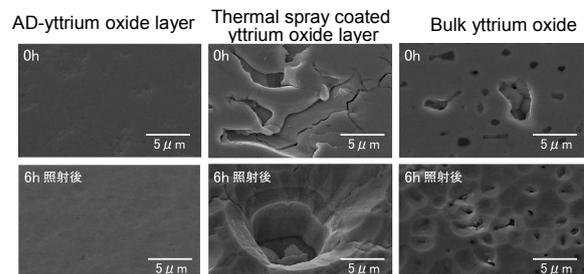


Fig. 4. Before and after exposed to plasma, the surface morphology of yttrium oxide films produced by various methods..

Table 1 The electrical and mechanical properties of AD-yttrium oxide films.

Volume resistance (R.T.)	$>10^{14}\ \Omega\text{cm}$
Breakdown voltage	$150\ \text{V}/\mu\text{m}$
Vickers hardness	9.2 GPa
Adhesion force	80 MPa

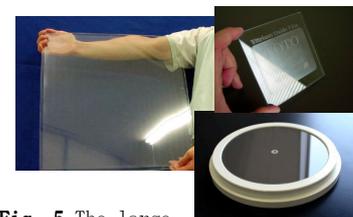


Fig. 5 The large area ($50\ \times\ 50\ \text{cm}^2$) AD yttrium oxide films and the electrostatic chuck produced by the AD method.

3. Summary

The business using the AD method has taken off since 2007 in the fields of the coating technology of anti-plasma corrosion films for next-generation semiconductor manufacturing facilities and the electrostatic chucks. The success of the development is due to the distinct feature of the AD method that can form good-performance ceramic films for the anti-plasma corrosion and the wear resistance at low cost. Furthermore the AD method has basically many advantages, such as it can coat the films not only on a flat surface but also on a complex-shape surface of metallic substrate for example aluminum alloy that has good machinability. These merits of the AD method will allow the AD films to replace conventional ceramics in various products.

*1 Member, National Institute of Advanced Industrial Science & Technology (〒305-8564, 1-2-1 Namiki, Tsukuba, Ibaraki, Japan)

*2 Non-member, National Institute of Advanced Industrial Science & Technology (〒305-8564, 1-2-1 Namiki, Tsukuba, Ibaraki, Japan)

*3 Non-member, TOTO Co. Ltd. (〒253-8577, 2-8-1 Motomura, Chigasaki, Kanagawa, Japan)

*4 Non-member, TOTO Co. Ltd. (〒879-0124, 10 Ohaza Tajirizaki, Nakatsu, Ohita, Japan)