

# Application of Electronic Devices for Aerosol Deposition Methods

NAKADA Masafumi, KAWAKAMI Toshihiro, IWANAMI Mizuki, OHASHI Keishi

## Abstract

Oxide materials have superior functional characteristics that are attributed to their versatile structures and chemically stable characteristics. These characteristics are expected to enable their employment as the functional device materials that are required to support the ubiquitous society. The aerosol deposition method is a nanocrystalline film forming method that employs the impact solidification phenomenon of ultra fine particles. This method enables the formation of oxide films onto any type of substrate. NEC and NEC TOKIN are co-developing piezoelectric and optical device products to be used in the aerosol deposition.

## Keywords

aerosol deposition, film forming technology, piezoelectric device, optical modulator, fiber sensor, electric field sensor

## 1. Introduction

Functional oxide materials exhibit a huge number of structures that are capable of providing superior functional properties at the same time as featuring chemical stability. These properties result in a wide variety of device applications including ceramic condensers supporting IT infrastructures, piezoelectric sensors for ultrasonic diagnosis units and YAG crystals for high frequency lasers etc. A high speed modulator employing  $\text{LiNbO}_3$  single crystals and an isolator employing garnet films are adopted for optical communications fields as essential devices for the support of modern optical communications networks. All of these optical devices utilize the superior electro-optical (EO) properties derived from ferroelectricity that can be found in most functional oxide materials as well as the non-reciprocity that is also derived from the ferromagnetic property.

Most functional oxide materials form Perovskite crystalline structures with a basic chemical formula that follows the  $\text{ABO}_3$  pattern and exhibit piezoelectric properties and EO effects. The crystalline structure of Perovskite oxide shown in **Fig. 1** is an A-cation hexahedron structure with the B-cation housed at its center and oxygen ions filling the centers of each edge of the unit cell. With this crystalline structure, the position of the B-cation may be distorted due to electric or magnetic fields that may influence its various functional properties. In order to adopt its piezoelectric property for electronic devices, it is necessary to integrate and form such crystalline structured, oxide

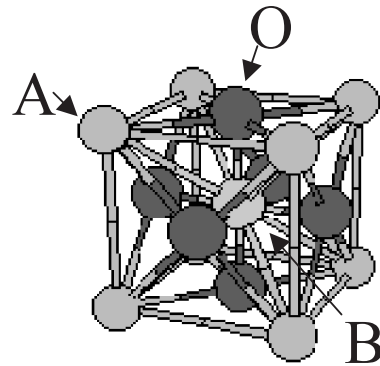


Fig. 1 Crystallization of Perovskite oxide.

films onto substrates.

The thin film forming methods such as sputtering, MBE, CVD and vapor deposition employ a technology that forms thin film onto a substrate by arranging the atoms. When such functional oxide materials are formed at room temperatures onto a substrate such as glass, amorphous structured are the result and piezoelectric properties are not generated. In order to generate useful functions including piezoelectric ones, it is essential to have a Perovskite crystalline structure. For this reason, by utilizing the surface energy of the underlayer, atoms have to be aligned at a temperature high enough for the atoms to be rearranged. Therefore, it has been essential to heat the substrate at a high temperature to form the required oxide materials. Moreover, with this method, crystallization is enabled

by restructuring the particles at the atomic level by the non-equilibrium process so that the films thus fabricated contain many lattice defects that result in the degradation of the EO effects.

The aerosol deposition of the (AD) method is a film fabrication method that solves all of the above issues. This paper introduces the features of the AD, and the electronics device applications in Section 2.

## 2. Features of the Aerosol Deposition

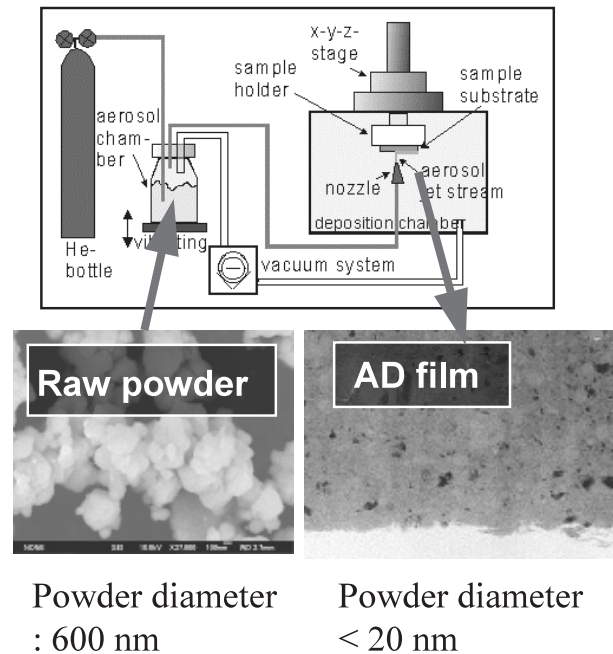
The aerosol deposition (AD) is a film fabrication method<sup>1, 2)</sup> that utilizes an impact solidification phenomenon of ultra fine particles that was invented in 1997 by Dr. Jun Akedo of the National Institute of Advanced Industrial Science and Technology (AIST). Crystalline particles are to a size of approximately 10nm fractured when high speed particles of submicron diameters are impacted onto a substrate. These ultra fine crystalline particles are thus bonded together by mechanochemical reactions. With the AD, a film is formed by restructuring the ultra fine crystalline particles so that the crystalline structure of the raw powder is maintained in the process of the film fabrication. This enables fabrication of film that has the same crystalline structure as the raw powder. This results in a large piezoelectric effect and features the favorable property that the film is not influenced by the underlayers and/or substrates. For example, it enables the formation of films onto silicon or SiO<sub>2</sub> optical devices and combines them with LSIs or circuit boards, a process that has been so far impossible. Raw powder may be manufactured by conventional processing methods for most materials.

**Fig. 2** illustrates the overall configuration of film fabrication by the AD, together with electron micrographs of raw powder and AD film. Raw powders with an average powder diameter of 600nm are mixed and vibrated with a carrier gas in order to form an aerosol. By using the pressure differences between the aerosol and vacuum chambers, aerosol is sprayed from a nozzle to be impacted onto the substrate. Using such a simple process, an AD film which is a combination of ultra fine crystalline particles of several tens of nm can be formed as shown in the cross-sectional image of the AD film.

### 2.1 Applications of the Aerosol Deposition for Piezoelectric Devices

To meet the needs of downsizing and high performance of digital equipment of today, NEC TOKIN has developed and

## AD film fabrication method



**Fig. 2** Overall configuration of the film fabrication process by the AD, and electron micrographs of raw powder particles and AD film.

marketed piezoelectric gyroscopes that incorporate a vibrating element consisting of a piezoelectric ceramic oscillator rod. Thus compensating for hand shake when using digital still cameras and applying piezoelectric actuators to the auto-focus lens drives of camera-equipped cell phones.

A piezoelectric material has superior features with regard to the efficient conversion of electrical energy into mechanical energy compared to those of other materials such as magnetic ones. In conventional materials, bulk type piezoelectric ceramics made of sintered powders have been adopted for the conversion elements between electrical and mechanical energies. However, even more demands are expected of piezoelectric devices for future digital equipment in terms of reductions in their dimensions. **Fig. 3** shows examples of piezoelectric products that can be applied in the future. Film formed piezoelectric devices integrated onto a substrate will be essential for the piezoelectric actuators that are used for sound equipment and for products that require a high-precision positioning motion.

Various technologies used in forming piezoelectric films are examined. However, a film several  $\mu\text{m}$  thick is essential for an actuator to output mechanical energy from an input energy such as electricity. When a thick film of over several  $\mu\text{m}$  is

## Application of Electronic Devices for Aerosol Deposition Methods

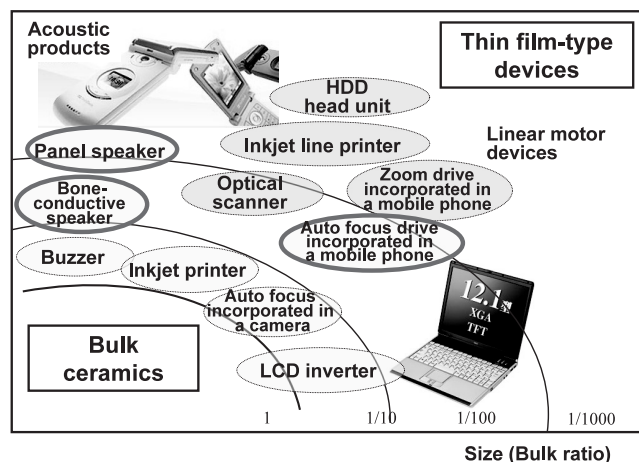


Fig. 3 Piezoelectric applied products.

formed onto a substrate with the conventional thin film forming technologies such as the sputtering or chemical solution methods, various problems might occur: the speed of forming film is not fast enough, composition tends to vary, etc. Due to these concerns the conventional film forming technologies have been used only for limited applications such as for thin film sensors, etc.

The screen printing method that uses a mixture of ceramic powder and binder is one of the thick film forming technologies. However, this technology has been developed based on a conventional technology using ceramic materials, in which the material is heated at the high temperature of 1,000 degrees or more. This technology has the problem that the choice of the substrate material is limited to ceramics.

With the AD, a dense piezoelectric film with a thickness of several  $\mu\text{m}$  can be deposited directly onto a substrate at room temperature. It is also preferable that a breakdown voltage of 600kV/cm or more is obtained. A solid solution of PNN (lead nickel niobate) and PZT (lead zirconate titanate) was examined for possible employment as a piezoelectric material for a properties test of the AD. PNN-PZT has already been used practically for the piezoelectric actuator because of its superior characteristics in withstanding piezoelectric properties. Zirconate ceramics and stainless steel are employed for the substrate materials. Zirconate ceramics have a good resistance to high temperatures and stainless steel features superior characteristics regarding corrosion resistance and processability that leads to low cost manufacturing of practical devices. The film forming process is carried out at room temperature. The film deposition rate achieves 10 $\mu\text{m}/\text{min}$  or higher for an area of 10

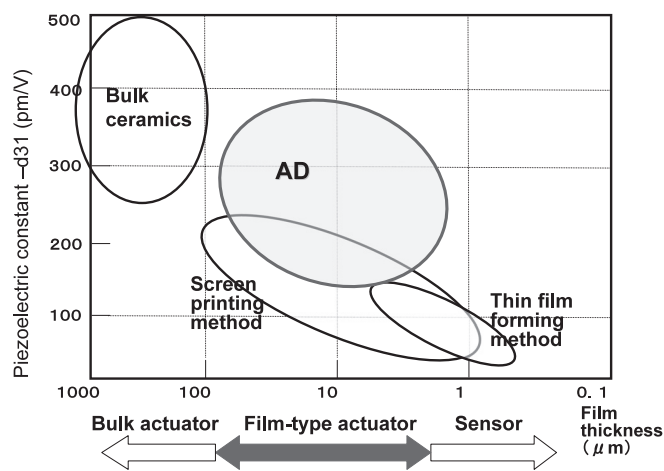


Fig. 4 Piezoelectric film forming technologies and a comparison of piezoelectric properties.

$\times 10\text{mm}^2$ , which confirms favorable characteristics for mass production methods. Fig. 4 shows a comparison of the film properties between the piezoelectric film formed by the AD and the conventional film deposition method.

A piezoelectric film fabricated by the AD showed the piezoelectric constant ( $-d_{31}$ ) of 158mp/V on a stainless substrate, which is almost the same value as that of film fabricated by conventional film forming technology. On a zirconate substrate, 360pm/V was achieved, which is similar to that for bulk ceramics.<sup>3)</sup> We have acquired piezoelectric films fabricated by the AD in which characteristics suitable for practical use can be expected. More detailed applications will be examined in future by using such film type piezoelectric actuators.

## 2.2 Applications of the Aerosol Deposition for Optical Devices

### (1) Ultra Small Optical Modulator

With regard to the advancement of optical communication technologies in the IT markets, the needs of nano-photonics devices are of significant importance in realizing integration of optical and electronic technologies. In particular, it is most essential to reduce the size and the power consumption of the high-speed modulator between the electrical and optical signals in order to realize a practical use of nano-photonics devices.<sup>4)</sup> To this end, it is important to establish a film forming method to deposit thin film material onto silicon or  $\text{SiO}_2$  substrates using a Perovskite structure that features an efficient EO effect. NEC is promoting the development of an ultra small optical modulator by employing the AD.

Oxide thin films fabricated by the AD are composed of particles with diameters of several tens of nm, which is much smaller than the wavelength of light. In consequence, if the oxide material itself does not have the characteristic of optical absorption, it is possible to make the thin film transparent.<sup>5)</sup> Fig. 5 presents a photo of a 3 $\mu\text{m}$  thick film and a graph showing the properties of the optical spectrum of PZT (lead zirconate titanate) film. PZT has high optical anisotropy, so that when it is used for bulk ceramics it is opaque. However, PZT thin film fabricated by the AD is characteristically highly transparent. Also, a tenfold increase in the EO effect has been achieved with such PZT film, which is higher than that of the LiNbO<sub>3</sub> material that is currently adopted for marketed modulators.<sup>6)</sup> This value of the EO effect is greatly superior to those of the thin films fabricated by conventional methods. By employing the AD, it is expected to reduce the size of the electro-optic modulator and the capacity of the drive voltage to one tenth of that of conventional systems.

A Fabry-Perot (FP) modulator is capable of being miniaturized and of carrying out low-voltage driving of an electro-optic modulator. As a result of its simple configuration this modulator is widely employed for optical wiring inside LSI chips. However, with conventional film formation methods, it has been difficult to form an EO thin film made of func-

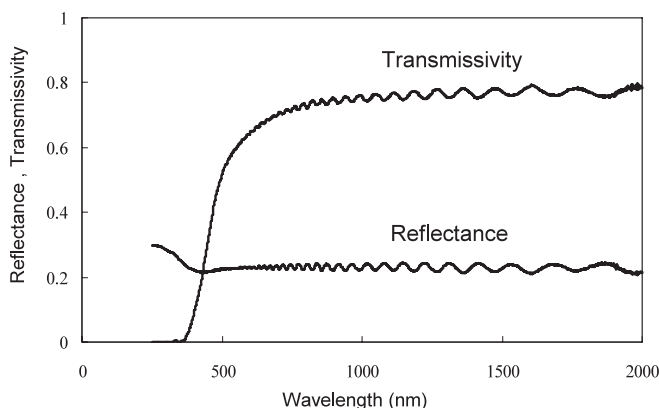
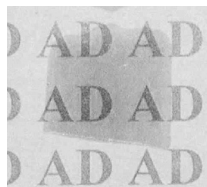


Fig. 5 Photo of 3 $\mu\text{m}$  thick film and a graph showing the properties of the dispersion spectrum of PZT (lead zirconate titanate) film.

tional oxide materials on electrode underlayers incorporated in an FP modulator. Therefore, NEC has employed the AD and have developed the technology for forming an EO film to be mounted in an FP modulator. We have thus acquired an improved value of the transmission spectrum of an FP modulator by applying voltage and have been able to confirm basic operation of the optical modulation.<sup>7)</sup> In future, we plan to promote the study of EO materials capable of higher frequencies and to develop waveguide modulators.

## (2) Optical Fiber Electric Field Sensor<sup>8)</sup>

Miniaturization and high performance capabilities are in demand for electronic products. In support of this environment, there is a need to reduce the generation of unintentional electromagnetic waves and to obtain improvements to both signal and power supply qualities. It is expected that the development of a near-field electromagnetic probe can be applied to the electrical engineering design for high density LSI packages. The fiber edge electro-optic (FEEO) and magneto-optic FEEO and MO probes employing optical technologies have superior characteristics such as being less invasive and featuring high spatial resolution and wide bandwidth. These characteristics are significant advantages in the design of electrical mounting engineering. However, state-of-the-art LSI package manufacturing, for which high density mass production is being rapidly promoted, demands evaluation at ultra small sizes so that in aiming at more effective utilization even more miniaturization of the probes is required.

By manufacturing FEEO probes using the AD, ultra small probes can be manufactured and also high density mounting can be expected because of large EO effects can be formed directly onto a fiber edge. Moreover, the spatial resolution of the probe light direction can be improved due to the reduction of the thickness of the sensor. Even the manufacturing costs may also be reduced. Such advantages, for which conventional probes are not capable, may be confidently anticipated.

We have applied the AD to manufacturing probes and have succeeded in forming PZT film as an EO material onto the edge of an optical fiber.<sup>8)</sup> With this technology, a ultra small EO probe with a sensor size of 125 $\mu\text{m}$ , which is the same diameter as that of a fiber, a thickness of 5 $\mu\text{m}$  has been achieved. It is difficult to form a functional oxide material onto a glass surface like a fiber edge surface by employing other film forming methods. From this point of view, it can be said that the AD offers an effective contribution to optical device engineering.

### 3. Conclusion

The AD, which deposits a film by rearranging ultra small crystalline particles is a unique film forming method that differs from the conventional film forming methods, including the sputtering method that forms a film by rearranging atoms. By using the AD, a crystalline structure of raw material can be maintained during the film formation. This process enables a highly functional film to be formed onto any type of substrate, which is a significant advantage of the AD when it is employed in electronic device manufacture. This paper considers the piezoelectric and optical devices introduced so far, as examples to be applied to EO devices.

The AD is a technology developed in Japan, and its applications introduced in this paper are just some of the examples chosen to demonstrate the significant potential of the AD. There should be many more fields to which the AD method may be applied. We confidently anticipate that this paper will be informative to many readers regarding the AD.

### Authors' Profiles

**NAKADA Masafumi**  
Principal Researcher,  
Fundamental and Environmental Research Laboratories,  
NEC Corporation

**KAWAKAMI Toshihiro**  
Assistant Manager,  
Research and Development Division,  
NEC TOKIN Corporation

**IWANAMI Mizuki**  
Assistant Manager,  
Jisso and Production Technologies Research Laboratories,  
NEC Corporation

**OHASHI Keishi**  
Senior Manager,  
Fundamental and Environmental Research Laboratories,  
NEC Corporation

### References

- 1) Akedo J. and Lebedev, M., "Microstructure and Electrical Properties of Lead Zirconate Titanate ( $\text{Pb}(\text{Zr}_{52}/\text{Ti}_{48})\text{O}_3$ ) Thick Films Deposited by Aerosol Deposition Method," Jpn. J. Appl. Phys. Vol. 38, Part 1, No. 9B, Sep. 1999, 5397.
- 2) Akedo J. and Lebedev, M.; "Piezoelectric properties and poling effect of  $\text{Pb}(\text{Zr}, \text{Ti})\text{O}_3$  thick films prepared for microactuators by aerosol deposition," Appl. Phys. Lett. 77 (2000) 1710.
- 3) Kawakami, Y. et al.; "Annealing Effect on  $0.5\text{Pb}(\text{Ni}_{1/3}\text{Nb}_{2/3})3\text{-}0.5\text{Pb}(\text{Zr}_{0.3}\text{Ti}_{0.7})\text{O}_3$  Thick Film Deposited By Aerosol Deposition Method," Jpn. J. Appl. Phys. Vol. 44, No. 9B, Sep. 2005, 6934.
- 4) Ohashi, K. et al.; "Optical Interconnect Technologies for High-speed VLSI Chips Using Silicon Nano-photonics," International Solid-state Circuits Conference, Solicited Paper, #23.5, Feb. 5-9, 2006.
- 5) Nakada, M. et al.; "Optical and electro-optical properties of  $\text{Pb}(\text{Zr},\text{Ti})\text{O}_3$  and  $(\text{Pb},\text{La})(\text{Zr},\text{Ti})\text{O}_3$  films prepared by aerosol deposition method," J. Cryst. Growth, Vol. 275, e1275, 2005.
- 6) Nakada, M. et al.; "Electro-Optic Properties of  $\text{Pb}(\text{Zr}_{1-x}\text{Ti}_x)\text{O}_3$  (X = 0, 0.3, 0.6) Films Prepared by Aerosol Deposition," Jpn. J. Appl. Phys. 44(2005)L1088.
- 7) Nakada, M. et al.; "Fabry-Perot optical modulator fabricated by aerosol deposition," Proc. of SPIE Vol. 6050 605004-1.
- 8) Iwanami, M. et al.; "Microscopic Fiber-Edge Electro-Optic Probe Fabricated by Aerosol Deposition Method," IEICE ,2006 Spring meeting, C-14-4.