

# Thin Films as Material Engineering

Kiyotaka Wasa

(Grad. School, Yokohama City University)

## 1. Introduction

Thin films are defined as a 2-dimensional material created by condensing, one-by-one, atomic/molecular/ionic species of matter in contrast to a bulk 3-dimensional material. The thin films have been used for more than a half century for making optical coating, electronic devices, instrument hard coatings, and/or decorative parts. However, the thin film technology is still being developed on a daily basis since it is a key technology in the 21<sup>st</sup> century for a development of new functional devices. It is also noted the thin film technology saves materials and energy consumption. Thin film process is environment benign technology [1]. Recently much attentions have been paid for thin film compact MEMS including medical and/or energy harvesting systems. Piezoelectric thin films are commonly used for the compact MEMS. Optimum thin film process condition will possibly make exotic high performance piezoelectric thin films which could not be achieved by bulk ceramic sintering process.

In this paper first fundamentals of thin film materials are described. Then recent exotic piezoelectric thin films created in the optimum thin film process condition are discussed as a possible future piezoelectric MEMS.

## 2. Fundamentals

Atoms evaporated from source materials are deposited on a growing surface of substrates. Adatoms are moving on the growing surface with Brownian motion and some of them are adsorbed on the growing surface. The other adatoms remove from the growing surface. The adsorbed atoms make nuclei resulting in a development of a continuous thin film. Compound thin films are synthesized by the atom to atom collisional chemical reactions on the growing surface. Understanding of the film growth mechanism is important for a controlled film deposition.

The deposition methods comprise thermal deposition, chemical vapor deposition (CVD), and sputtering. The decomposition of source materials in the CVD process can be enhanced by the plasma (PE-CVD). The deposition process using the irradiation of energetic species is known as a sputtering. The cathode electrode material is

disintegrated by the sputtering resulting in the deposition of thin films of cathode materials. The properties of the thin films are governed by the deposition methods. In the PE-CVD the high energetic electrons in the plasma enhance the decomposition of source materials resulting in the deposition at lower substrate temperature. It is known that the disintegration of the cathode material is caused by irradiation of the high energetic ions to the cathode surface. The removed particles, called as sputtered species, comprise high energetic atoms. Their energy ranges are 1 to 10 eV. The sputtering process achieves the deposition of varieties of materials at low temperature. The typical example is diamond growth at room temperature as shown in Fig.1.

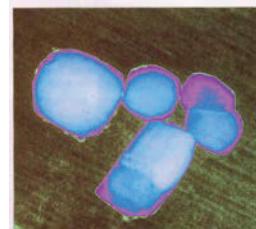


Fig.1. Diamond crystallites grown by sputtering process at room temperature. Size of crystallites, ~0.1 μm. Sputtering, ion beam sputtering [2].

The other example is room emperature growth of PbTiO<sub>3</sub> thin films[3]. If we compare the thin film growth process with bulk ceramic sintering process, in the thin films high rate doping is possible due to a solubility relaxation which will possibly create exotic compound thin films [4].

## 3. Exotic acoustic/piezoelectric thin films

Thin films of piezoelectric materials including ZnO, AlN, and PZT-based thin films were extensively studied for a fabrication of thin film acoustic devices. ZnO and/or AlN thin films were used in practice for SAW devices. PZT-based thin films were used in practice for FRAM and/or MEMS sensors and/or actuators[5]. The acoustic thin films are mostly used in a laminated structure comprising substrates. The acoustic thin films exhibit exotic properties due to the presence of the substrates. Although the development of new bulk acoustic materials are chiefly based on a new chemical composition, the development of new thin film devices are achieved by optimizing laminated structure. It is known the selection of the substrates

materials enhances the coupling of ZnO thin film SAW devices and improves their temperature stability [6]. The PZT-based ferroelectric thin films were used in practice due to their high coupling properties. However, the Curie temperature  $T_c$  of PZT-based materials is below 400°C. New high- $T_c$  materials ( $T_c > 400^\circ\text{C}$ ) will expand their applications. Reentry, Eom enhanced  $T_c$  for heteroepitaxial single crystal thin films of BaTiO<sub>3</sub> (BT) up to 500°C by optimizing substrate materials [7]. The BT thin films show strained structure. In-plane compressive stress initiates higher  $T_c$ . However, the thickness of the BT thin films should be thinner than a critical value  $t_c$ , typically  $t_c \sim 50\text{nm}$ . Contrary to the previous experiments, it is found a sort of relaxed heteroepitaxial PZT-based thin films with thickness  $t_p$ , i.e.,  $t_p > t_c$ ,  $t_p = 1\text{-}3\mu\text{m}$ , shows enhanced  $T_c$  with  $T_c \sim 600^\circ\text{C}$ . The PZT-based thin films show relaxed structure at room temperature. The mechanism of the enhanced  $T_c$  for relaxed PZT based thin films will be induced strain during elevating temperature [8]. Carefully controlled heteroepitaxial process condition creates temperature stable interface on the growing surface of substrates. The PZT-based thin film a-lattices are constrained by the growing surface. Exotic temperature variations of lattice parameters are observed as shown in Fig.2. There are two different lattice parameres at  $T_c$ .

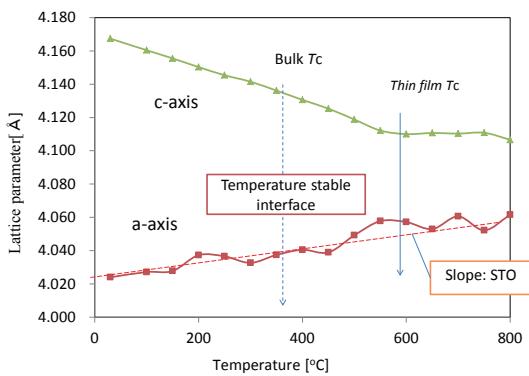


Fig.2. Exotic properties: Temperature vs. lattice parameters. PZT(50/50) thin films, 1μm, epitaxially grown on STO (SrTiO<sub>3</sub>) with quenching after film growth.  $T_c$  (ferro/para transition) at 600°C. The slope of the STO is the same to the slope of PZT a-axis.

The present relaxed PZT-based thin film is one of the ideal thin films beyond PZT. The relaxed PZT-based thin films show low dielectric constants, i.e.,  $\epsilon^* \sim 100$ , due to highly c-axis orientation. The low dielectric constant induces high coupling. The typical example of possible application is

piezoelectric energy harvesting MEMS. The FOM is one order in magnitude higher than conventional PZT's values as shown in Tab. 1.

Tab.1.Dielectric and piezoelectric properties of PZT-based thin films and AlN thin films [9].

| Thin films               | PZT <sup>1</sup>     | PMnN-PZT <sup>2</sup> | AlN      |
|--------------------------|----------------------|-----------------------|----------|
| Substrates               | SiO <sub>2</sub> /Si | MgO                   | Sapphire |
| Structure                | Poly.                | Epi.                  | Epi.     |
| $\epsilon^*$             | 300-1300             | 100                   | 9.5      |
| $e_{31,f}(\text{C/m}^2)$ | -8..-12              | -12                   | -1.37    |
| FOM <sup>3</sup>         | 6.. 18               | 163                   | 22.3     |

1: Conventional, 2: Present, 3:Figure of merit,=  $(e_{31,f})^2/\epsilon(\text{GPa})$

#### 4. Conclusion

Based on sputtering processing thin films create exotic materials and/or devices which could not be achieved by a conventional sintering process.

Thin film technology is old but a key material technology in the 21<sup>st</sup> century.

#### Acknowledgments

The author thanks K.L.Chopra, (Indian Institute of Technol.), R.E. Newnham, L.E. Cross, K. Uchino, and S. Trolier-McKinstry (Penn State Univ.), S. Yoshida, S. Tanaka, and M. Ezashi (Tohoku Univ.), Y. Shigeta (Yokohama City Univ.) and H. Adachi (Panasonic) for their continuous discussion.

#### References

1. K. Wasa: J. Supercond. Nov. Magn., **28** (2015)1665.
2. K. Kusao, K. Wasa, and S. Hayakawa: Jpn. J. Appl. Phys., **7** (1968) 437.
3. M. Kitabatake and K. Wasa: J. Appl. Phys., **58**(1985) 1693.
4. K. Wasa, H. Adachi, and M. Kitabatake: *Thin Film Materials Technology*, (Springer, NY, 2004) p.33.
5. K. Wasa, I. Kanno, and H. Kotera: *Handbook of Sputter Deposition Technology*, 2<sup>nd</sup> edh., ( Elsevier, Amsterdam, 2012) p.573.
6. S. Ono, K. Wasa, and S. Hayakawa: Wave Electronics, **3** (1977)35.
7. S. H. Baek,., and C. B. Eom et al.: Science, **334** (2011)958.
8. K. Wasa, T. Matsushima, H. Adachi, T. Matsunaga, T. Yanagitani, and T. Yamamoto: J. Appl. Phys., **117** (2015)124106.
9. K. Wasa, T. Matsushima, H. Adachi, I. Kanno, and H. Kotera: J. Microelectromechanical systems, **21** (2012)451.