# 화학증착법에 의해 제조된 $PbTiO_3$ 박막의 AES 와 XPS 에 의한 조성분석

# The Chemical Composition Analysis by AES and XPS of $PbTiO_3$ Thin Films Fabricated by CVD


윤 순 길°, 김 호 기 한국과학기술원 재료공학과

Soon-Gil Yoon and Ho-Gi Kim KAIST Dept.of Mat.Sci.& Eng.



ABSTRACT

Lead titanate thin films with a perovskite structure were successfully fabricated on titanium substrate by Chemical Vapour Deposition(CVD). Analyses of Auger Electron Spectroscopy(AES) and X-ray Photoelectron Spectroscopy(XPS) have been performed in order to find a chemical composition of lead titanate films. The analysis of chemical composition by AES and XPS was investigated for variations of deposition temperature and Ti $(C_2H_5O)_4$ fractions. The chemical composition of $PbTiO_3$ by XPS analysis was almost constant regardless of deposition parameters and the comparison of chemical composition by AES and XPS was performed.


## I. INTRODUCTION

Much attention has been recently paid on ferroelectric thin films from a viewpoint of its wide applications in electronic(1), optoelectronic devices(2), and optical integrated circuit elements(3). A number of efforts have been undertaken to prepare good ferroelectric thin films with various method such as rf sputtering (4), electron beam evaporation(5), and ion beam sputtering(6).

The present work is concerned with the deposition of $PbTiO_3$ films by CVD. The properties of such films are strongly dependent upon film composition. In the study, the composition of analyzed films was evaluated with respect to a wide range of deposition conditions.

## II. EXPERIMENTAL DETAILS

The reaction chosen to produce the lead titanate films is written in over-all form as:

$$2Pb(g) + 2Ti(C_2H_5O)_4(g) + 25O_2 \longrightarrow 2PbTiO_3(s) \quad 16CO_2 + 20H_2O$$

The growth system used for the lead titanate deposition consists of a mullite tube reactor of 38 mm inner diameter and a gas flow system as shown in Fig.1. An alumina boat filled with Pb powder was placed at the highest temperature position near the gas inlet in a horizontal furnace, and a quartz boat holding a titanium disk substrate 14.9 mm in diameter and 2 mm thick was placed at the lower temperature part behind the Pb boat.

The temperature of the specimens was controlled by a k-type thermocouple in contact with the substrate. In our experiments, the reactor was kept at atmospheric pressure. The flow rate of Pb vapor was held constant at 200 sccm(standard cc/min), and the mole fraction of $Ti(C_2H_5O)_4$ vapor was varied from 0.02 to 0.23. The partial pressure of $O_2$ was varied from 0.06 to 0.32 atm. The temperature required to vaporize the Pb powder was about 1000 °C, and the Pb vapor was transported to the substrate by nitrogen(99.9999 %) as the carrier gas. The ethyl titanate($Ti(C_2H_5O)_4$ ) vapor flowed from a nozzle at the ends of the delivery lines and was directed onto the substrate.

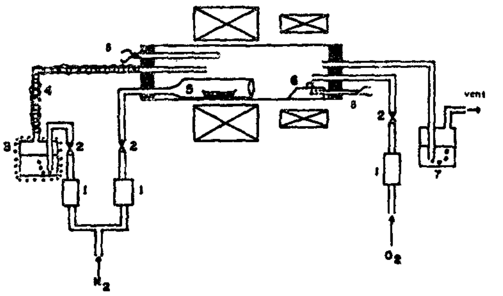


Fig.1 Schematic diagram for $PbTiO_3$ growth in the Pb-$Ti(C_2H_5O)_4$-Oxygen system (1, flow meter; 2, needle valve; 3, $Ti(C_2H_5O)_4$ bath; 4, heating coil, 5, Pb boat; 6, substrate; 7, trap; 8, thermocouple)

## III. RESULTS AND DISCUSSION

### III-1. Composition of $PbTiO_3$ coatings by AES

The elemental composition of coatings is of primary interest and can be obtained by quantification of AES. Quantification of AES depends on sample and instrumental characteristics and above all, on the in-depth distribution of the elements(7). Most frequently, the relative elemental sensitivity approach is used, which is based on elemental standard intensities. Relative sensitivity factors for semiquantitative analyses were calculated from the spectrum on the perovskite $PbTiO_3$ ceramic material which was chosen as a composition standard. The concentration of each element in a $PbTiO_3$ standard sample can be obtained using the Atomic Absorption Spectrophotometer (Perkin-Elmer 5000) and inductively coupled plasma spectrometer(Labtest Plasmascan 710). Fig.2 shows the AES spectrum after sputter cleaning of $PbTiO_3$ standard sample. The calculated values are listed in Table.1. Table.2. shows AES analysis results of the $PbTiO_3$ films obtained for various deposition temperatures. The deposition condition of the $PbTiO_3$ film by CVD is deposition temperature, 600-750°C; total gas flow rate, 800 sccm; $Ti(C_2H_5O)_4$ fraction, 0.152; $O_2$ partial pressure, 0.06 atm. The result of AES analysis shows that the $PbTiO_3$ film deposited at 750°C has the stoichiometric composition. Composition of $PbTiO_3$ film deviates from the stoichiometry till the deposition temperature of 700°C. This result

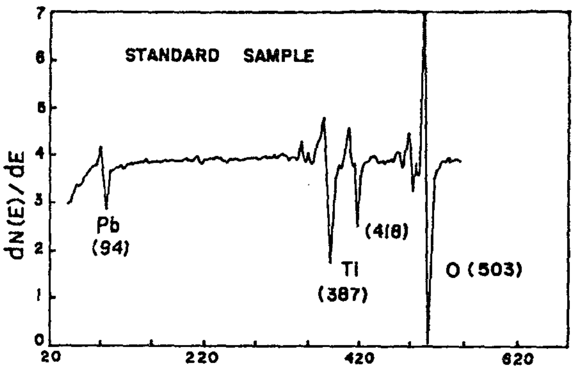


Fig.2 . AES spectrum ($E_p$=3 keV) after sputter cleaning of $PbTiO_3$ standard sample (film made by silk screen using TAM ceramic $PbTiO_3$ powder)

shows that the TiO phase exhists in the deposition layer in the case of $PbTiO_3$ CVD at low deposition temperature. Table.3 shows the atomic composition of the $PbTiO_3$ films for various $Ti(C_2H_5O)_4$ fractions. Deposition conditions are the deposition temperature, 800° C; total gas flow rate, 800 sccm; $Ti(C_2H_5O)_4$ fraction, 0.08-0.27; $O_2$ partial pressure, 0.06 atm. When the $Ti(C_2H_5O)_4$ inlet fraction is 0.08, the $PbTiO_3$ film has the stoichiometric composition. But , as the $Ti(C_2H_5O)_4$ fraction increased, the composition deviates from the stoichiometry. This result suggested that the TiO content in the $PbTiO_3$ film increased with increasing the $Ti(C_2H_5O)_4$ fraction.

Table. 1 Relative Auger Peak heights and Relative Sensitivity Factors for $PbTiO_3$ standard sample

| Peak Energy (eV) | Peak-to-Peak height | Atomic Concentration | Relative Sensitivity Factor |
|---|---|---|---|
| Pb, 94 | 27 | 0.179 | $K_s$(Pb/Ti).0.690 |
| Ti, 418 | 43 | 0.198 | $K_s$(Pb/O ).0.652 |
| O 509 | 144 | 0.623 | $K_s$(Ti/O ).0.537 |

Table. 2 Atomic Compositions of the $PbTiO_3$ films for various deposition temperature.

| | Various Deposition Temperature(℃) | | | |
|---|---|---|---|---|
| | 600 | 650 | 700 | 750 |
| Pb | 0.153 | 0.136 | 0.164 | 0.204 |
| Ti | 0.195 | 0.223 | 0.219 | 0.195 |
| O | 0.652 | 0.641 | 0.617 | 0.601 |

Table. 3 Atomic Composition of the $PbTiO_3$ films for various $Ti(C_2H_5O)_4$ fraction

| | $Ti(C_2H_5O)_4$ fraction | | |
|---|---|---|---|
| | 0.08 | 0.15 | 0.27 |
| Pb | 0.233 | 0.144 | 0.144 |
| Ti | 0.203 | 0.215 | 0.215 |
| O | 0.594 | 0.641 | 0.641 |

III-2. Compositional analysis of the lead titanate films by X-ray photoelectron spectroscopy (XPS)

III-2-1. Quantitative XPS

Core level XPS data give not only results useful for quantification, but also of the chemical bonding as well as on *stoichiometry and defects. Furthermore, the* angular dependence of the effective mean free path can be used for qualitative, and in some cases for quantitative determination of in-depth composition(8). An example of the $Ti_{2P}$ doublet a sputter cleaned(3.5 keV Ar+) sample of $PbTiO_3$ is shown in Fig.3. Data were taken by a Perkin-Elmer PHI 5400 ESCA spectrometer using Mg k$\alpha$ radiation. A quantitative peak fitting procedure for $Ti_{2P}$ in $PbTiO_3$, particularly in the presence of oxides, is rather complicated due to various physical effects including core/valence band interactions. Inspection of the measured $Ti_{2P}$ peak(as shown in Fig.3) shows that it is composed of at least two main doublets. The doublets could be ascribed to $PbTiO_3$ and TiO according to a standard sample measurement and by comparison with data from the literature(9).

Quantative analysis can be performed by using the same formalism as in AES (10) but different sensitivity factors. Standard relative sensitivity factors used in XPS analysis are $Pb_{4f}$ : 8.329, $Ti_{2p}$ : 2.001, $O_{1s}$ : 0.711. A quantitative evaluation of the $PbTiO_3$ sample of Fig.3 with standard sensitivity factors from the respective total peak areas for $Ti_{2p}$ doublets was performed. The atomic composition of the $PbTiO_3$ films for various deposition temperatures and $Ti(C_2H_5O)_4$ fractions were compiled in Table.4 and Table.5, respectively. Comparison with the AES result

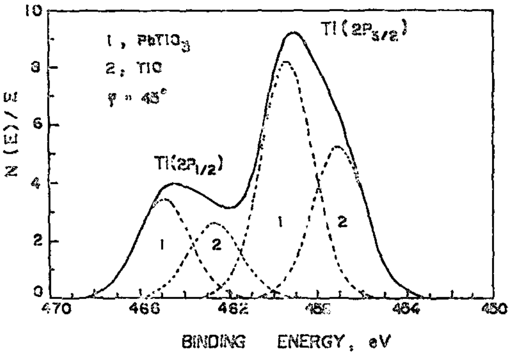


Fig.3 . XPS spectrum of the $Ti2p_{1/2}$, $Ti2p_{3/2}$ peak of a Chemical Vapour Deposited $PbTiO_3$ layer after sputter cleaning with 3.5keV $Ar^+$ bombardment.

(11) additionly conforms that the large analyzed area is *incompletely sputtered in* XPS analysis. Each atomic compositions of the $PbTiO_3$ sample have almost similar values regardless of the variations of deposition temperature and $Ti(C_2H_5O)_4$ fractions. This suggested that the resolution of measurement is too low and sputtering calibration is not sufficiently formed.

Table.4 Atomic compositions of the $PbTiO_3$ films for various deposition temperatures (by XPS)

| | Various deposition temperature(℃) | | | |
|---|---|---|---|---|
| | 600 | 650 | 700 | 750 |
| Pb(a.c) | 0.183 | 0.171 | 0.179 | 0.167 |
| Ti(a.c) | 0.261 | 0.263 | 0.270 | 0.269 |
| O (a.c) | 0.556 | 0.566 | 0.551 | 0.564 |

Table. 5 Atomic compositions of the $PbTiO_3$ films for various $Ti(C_2H_5O)_4$ fractions(by XPS).

| | Various $Ti(C_2H_5O)_4$ fractions | | |
|---|---|---|---|
| | 0.08 | 0.15 | 0.27 |
| Pb(a.c) | 0.115 | 0.103 | 0.112 |
| Ti(a.c) | 0.219 | 0.208 | 0.237 |
| O (a.c) | 0.667 | 0.689 | 0.651 |

## CONCLUSIONS

Chemical vapour deposition seems to be a suitable method for preparing $PbTiO_3$ films with better stoichiometry than those of conventionally prepared films. The analysis of chemical composition of $PbTiO_3$ by AES was well obtained. However The analysis by XPS was almost constant regardless of deposition parameters.

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