BaTiO₃ 박막 커패시터의 유전특성

논 문 8-5-6

The Dielectric Characteristics of BaTiO₃ Thin Capacitor

홍경진 '김태성', 김준학', 菱田俊一''' (Kyung-Jin Hong', Tae-Sung Kim', Jun-Hak Kim'', Shunichi Hishita''')

요 약

최근 컨페시터의 전략은 Pt. Au등으로 이용되고 있다. 이리한 전략의 전기적 특성은 우수하나 고가이다. 본 연구에서는 전략의 저가격화 측면에서 알루미늄 전략 위에 BaTiO등을 증착하고 기관의 온도를 실온에서 600[**C]까지 변화시키 RF 스파터링법으로 제작하였다.

BaTiO. 세라막의 유전특성은 구성하고 있는 업자의 창유전 분역 발도와 업자의 크기에 의존하므로 업자가 성상되는 온도영역에서 업자의 크기와 유전율간의 관계를 연구하였다. 또한 BaTiO; 박박 커쾌시터의 유전상수는 BaTiO; 세라막과 알루미뉴기관의 계면에서 산화특성이 일어나기 때문에 기관온도의 변화에 의해조사되었다.

기관의 온도를 증가시킬에 따라 실정면의 피크와 강도는 증가하였으며, 유전투성은 결정입자의 크기가 0.81/m에일 때 가상 양호하였다. 유전율값은 기관 온도가 400[**[인 때 가장 크게 나타났다.

결과적으로, 알루미늄 전략에 BaTiOs 세라믹을 증확하여 저가의 적충용 세라믹 콘텐서를 제조할 수 있음을 알았다.

Key Word(중요용어): BaTiO₃ thin capacitor (BaTiO₃ 박막 커패시터), Ferroelectric domain density (강유전체 분역밀도), Substrate temperature (기판온도), Dielectric factor(유전율)

1. Introduction

Recently the inorganic material has been widely used like electronic elements, sensors, coatings, etc. Many of the several applications of this material have been reported, including radiation insulation, capacitor condenser, and pyroelectric element.

Among various methods for the preparation of the thin capacitor, RF sputtering is one of the simple and convenient methods. The thin capacitor, for improved properties such as increased domain density, enhanced crystallization, and controlled morphology has been produced. For the capacitor of the preparation of the

Also it is well known that the thin capacitor is

strongly influenced by the properties of substrate temperature. Barium titanate is a very promising material for optical coating and dielectric capacitor because of its high refractive index, low absorption, high adhesion to glass surface, chemical stability, high dielectric characteristics, and high hardness which make it resistant to mechanical demage. (1) 80

At this time, the capacitor electrode is being used by Pt, Au, and so on. These material have a good conductivity, but it is very high cost.

The study of BaTiO₃ ceramics has shown that dielectric properties of BaTiO₃ thin capacitor strongly depend on the size and ferroelectric domain density of the constituting grains.

The dielectric constant, ε_{r} , reaches a maximum value of 5000×6000 at the grain size 0.7×1[μ m] at which the domain density is also the highest. 902×100

The purpose of the present study is the dielectric properties analysis of BaTiO₃ thin capacitor because the grain size and dielectric

^{* :} 전남대학교 전기공학과

^{** :} 공업기술원

^{***:} 科學技術廳 無機才質研究所(日本)

접수일자: 1995년 2월 28일 심사완료: 1995년 8월 7일

characteristics is very important on the growing temperature of grain.

In this study, the BaTiO₃ thin capacitor for the low cost was prepared on the Aluminum electrode by RF sputtering. The dielectric characteristics was measured by grain size and the substrate temperature changing, from room temperature to 600 [C]. And, we tried to investigate the oxidation between the substrate and the BaTiO₃ ceramic.

2. Experimental methods.

The thin capacitor using a target of BaTiO₃ ceramics was prepared on Al plate to change the substrate temperature from room temperature to 6001 C1.

The sputtering conditions are listed in Table I.

Table 1. Sputtering condition of BaTiO₃ by RF sputtering

Target	BaTiO ₃ Ceramic
Substrate	Aluminum
Target substrate distance	30[mm]
Substrate Temperature	from 25 to 600 [*C]
RF power	150[W]
Sputtering gas	Ar
Sputtering gas pressure	1[Pa]
Deposition rate	3.2[Å 'S]

The residual gas pressure before sputtering was about $3\times10^{-3}[Pa]$. The thickness of the sputtered capacitor was fixed at $\mathbb{E}[\mu m]$ by the thickness monitor(model TM 200R) which was calibrated by a Dektak 3030(Auto II Programmable Stage Profiler) from measuring the height of a step produced by masking a region of the substrate during deposition. The microstructure and crystallographic properties of the thin capacitors deposited on Al electrode were analyzed by X ray

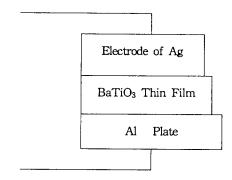


Fig. 1 Capacitor model of BaTiO₃ thin film.

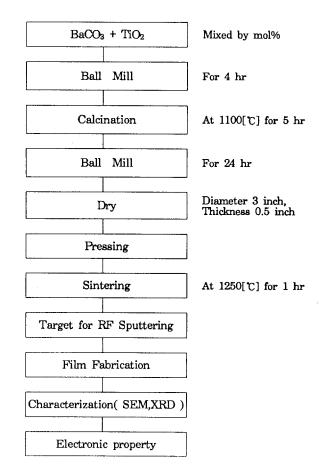


Fig. 2. The flow chart of experiment.

diffraction (XRD) and scanning electron micros copy(SEM).

The dielectric characteristics of BaTiO₃ thin capacitor were measured by the impedance analyzer(model HP 4192A, JAPAN).

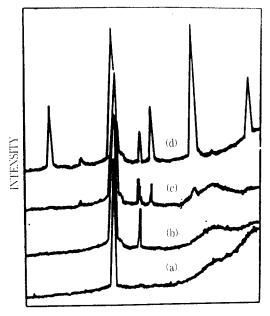
The thin capacitor was fabricated by the Al electrode. Aluminum is used as bottom electrode

and silver is painted as upper electrode.

Fig. 1 shows the capacitor structure and Fig. 2 represents the flow chart of experiment.

3. Result and discussion

The microstructure changing were investigated by the X-ray diffraction, Fig.3(d) shows the X-ray diffraction patterns of the deposited film at 600[C].



±2θ/DEGREE Cu K_c

Fig. 3. The result of X ray diffraction pattern.

- (a) at substrate temperature 25[°C].
- (b) at substrate temperature 300[C].
- (c) at substrate temperature 400 [C].
- (d) at substrate temperature 600[C].

Materials such as BaTiO₃ having a perovskite structure seem to exhibit a similar tendency.

This tendency may be caused by the fact that the (110) crystal plane has the highest occupation density of the component atoms among crystal planes refer. ^{10,(1)}

Al plate can be easily oxidized at atmosphere. Therefore, it is proved that BaTiO₃ thin capacitor was occupied by oxidation at interface between Al electrode and BaTiO₃ ceramics.

According to rising substrate temperature from room temperature to 600[°C], the peak intensity of crystal plane are increased.

As shown in Fig.3(a), the diffraction pattern of the deposited sample at $25 [\,\mathrm{C}\,]$ is basically featureless, indicating that the sample is still amorphous phase. There is no feature to show the X-Ray diffraction pattern the same as substrate temperature $300 [\,\mathrm{C}\,]$ in Fig.3(b). But it shows that the grain is started to crystallize at this temperature. It means that the peak is (111) plane of BaTiO₃. However, the deposited sample at 400 $[\,\mathrm{C}\,]$ shows the weak peak at 30.9° .

This peak corresponds to (110)plane of BaTiO₃ crystall.

The X-ray diffraction revealed that the grain of amorphous BaTiO: ceramic started to crystallize from depositing temperature at 400[°C].

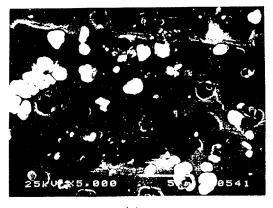
The peak intensity of substrate temperature at 500[°C] was stronger (110) plane than the observed (100) plane in Fig.3(c).

The peak of (214) in Fig.3(d) was shown by XRD analysis. It shows the same peak as 500[°C] substrate temperature. As the result of the same peak, the crystallization of grain starts at depositing temperature 400 [°C] and the grain size can recognize to grow both 500[°C] and 600[°C].

Fig. 4 shows the Scanning Electron Microscopic photo.

The random grain of BaTiO₃ was small size. It is thought that it relates to the dielectric factor.

In Fig.4(a), the BaTiO₃ is only coated on Al electrode. According to rising the substrate



(a)

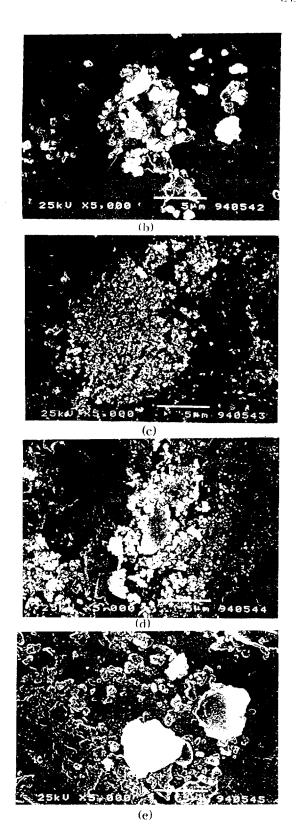


Fig. 4. SEM of BaTiOn thin film

- (a) at substrate temperature 25[C].
- (b) at substrate temperature 300[C].
- (c) at substrate temperature 400 [C].
- (d) at substrate temperature 500[C].
- (e) at substrate temperature 600[(1].

temperature, the grain of BaTiO₃ thin capacitor was more condensed and the grain size was shown 0.8[p/m] at substrate temperature 400[-C].

When the film was deposited at substrate temperature 500[°C], the substrate was oxidized by chemical action and occupied by crack.

According to SEM photo, the sputtering of BaTiO₃ thin capacitor could be to deposit on Al electrode.

As shown in Fig.4, the average grain size of the capacitor was $0.6 \cdot 1.21 \,\mu$ ml.

To measure the dielectric characteristics of BaTiO₃ thin capacitor, the electrode of Ag was painted on the capacitor. The dielectric constant, $\varepsilon_{\rm r}$, and the dissipation factor, $\tan\delta$, were measured from 1[KHz] to 10[MHz] with the Impedance Analyzer.

Not only the dielectric constant but also the dissipation factor increased when the substrate temperature increased.

The dissipation factor at room temperature shows in Fig. 5. In this figure the dielectric constant dependent on the substrate temperature

As shown in Fig.5, the dielectric factor of the deposited sample at 25[°C] is low value because the sample is still amorphous phase such as SEM analysis.

According to rising substrate temperature, the dielectric factor was high value because the grain is started to crystallize by temperature.

However, the deposited sample at 500[C] and 600[C] shows decreasing value because the crack was made of oxidation in grain boundary.

It was found that the substrate temperature of 400 [C] was the best condition of dielectric properties. It is thought that the grain of amorphous BaTiO₃ started to crystallize at depositing temperature from 400 [C].

Fig.6 is the dielectric characteristics according

to grain size. The high dielectric characteristics was substrate temperature at 400|C| and the grain size was $0.8[\mu\,\text{m}]$.

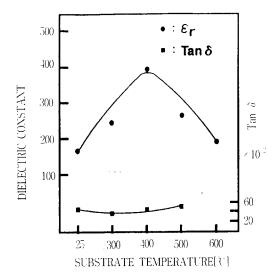


Fig. 5. Dielectric constant and $\tan \delta$ according to rising substrate temperature at 1[KHz].

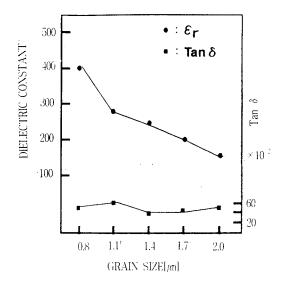


Fig. 6. Dielectric constant and tan δ according to grain size.

Arlt reported that the increasing of the dielectric factor is possibly cause by a summation of the domain size and the stress effect. Higher internal stress near the grain boundary and more domain walls present in a grain may ultimately be the

reason for the dielectric constant value of the BaTiO: ceramics.

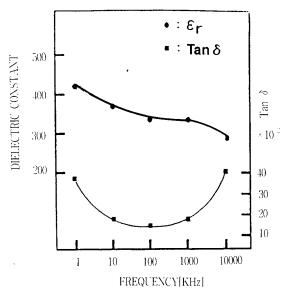


Fig. 7. Dielectric constant and tan∂ according to frequency at 400 [C].

Fig.7 shows the relation between dielectric constant and frequency of the film grown at substrate temperature $400[\,^{\circ}\mathrm{C}\,]$.

The dielectric characteristics of BaTiO₃ as ferrodielectric were shown by polarization effect.

The polarization required the time when the electric field applied, the electric field banished, and the polarization completed or consumed. If the frequency is high, the polarization doesn't appear because the relaxation time is long.

The higher frequency became, the lower dielectric constant did. But the dielectric constant increased 1[MHz] over.

Therefore, it is thought that the ion polarization of BaTiO₃ thin capacitor according to frequency is higher than 1[MHz].

It agreed with the results from SEM and X-ray diffraction. The crystallization of grain to BaTiO₃ thin capacitor started at substrate temperature 400[°C], and the capacitor had the maximum value of dielectric constant at this temperature. It is better than that at substrate temperature 500[°C].

4. Conclusion

As the result of the dielectric properties on BaTiO₃ thin capacitor using RF sputtering, the crystallization of grain started at substrate temperature 400[°C].

The dielectric constant increased as the crystallization of grain grew. The dielectric characteristics increased over 1[MHz].

It was found that the substrate temperature of 400[C] was the best condition of dielectric properties. This is caused by the fact that the (110) crystal plane has the highest occupation density to the component atoms among crystal planes in X-ray diffraction pattern of BaTiO₃ thin capacitor. And at this temperature, the capacitor has the maximum value of dielectric constant.

The grain size of the BaTiO₃ thin capacitor was 0.6-1.2[μ m].

It appeared that the dielectric constant was very high value when the grain size had $0.8[\mu m]$.

It is thought that the sputtering of BaTiO₃ thin capacitor could be to deposit on Al electrode according to measurement dielectric factor, SEM and XRD.

In this study, the BaTiO₃ thin capacitor deposited on the aluminum electrode can be used by multilayer ceramic capacitor of low cost.

5. Reference

- P. Li, J. F. Mc Donald and T. M. Lu, J. Appl. phs. 71, 5596(1992).
- Yamanashi, Tanaka, Nagatomo and Omoto, Jpn. J. Appl. phs. 32, 4179(1993).

- Kyokane and Yoshino, Jpn. J. Appl. phys. 32, 1303(1993).
- Hsing-I Hsing and Fu Su Yen, Jpn. J. Appl. phys. 32, 5029 (1993).
- 5. 小笠原 正、"チタン酸ストロンチウムペ スの高誘電率セラミックコンデンサ"、エレクトロニク セラミクス 1987年 7月號 pp.9-15
- 6. 南木 召更, "水熱法チタン酸バリウム", エンクトロニク セラミクス 1991年104號 pp.9 15
- 7. 幅田 晃士, "BaO TiO」 希上類酸化物系セラミクス のマイクロ波誘電特性",DEI 92~34, pp.27/32
- 8. 景山 惠介, "ヘロブスカイト型セラミクスのマイクロ波誘電特性", DEI-92 33,pp.17-25
- 9. 安倍 一允, "低温藍結性チタン酸パリウム", エレク トロニク セラミクス 1987年 7月魔 pp.54-59
- 10. 野中一洋、"宣霧熱分解法によるBaTiO:系農榜末の 合成とその蟯結性に及ばすBa/Ti比とCuO添加の效 果",日本セラミクス協會學術論文誌 98[8]794-800 (1990)
- 11. KISHIMOTO, "Analogy between Mechanical and Dielectric Strength Distribution in BaTiO: Thick Films Prepared under the Different Processing Conditions", 日本セラミクス協介學海論文誌 96[9] 954-957 (1988)
- 12. TOCHI, "Far Infrared Reflection and Raman Spectra of Complex Perovskite Type Compounds, Ba(Mn_{1:3}Ta_{2(1/3):3}Nb₂₍₃₎O₃", 日本セラミクス協會場确論文誌 97[8] 875-878 (1989)
- 13. 大西一正, "微粒子チタン酸バリウムのHIP蟯結" 日本セラミクス協會學術論文誌 97[4] 473 477 (1989)

저자소개



홍경진

1989년 전달대학교 전기공학과 졸업. 1991년 등 대학원 석자. 1995년 현재 등 대학원 박사과장 수요. 1992년 10월 1995년 3월 일본 탁타대학 연구생. 1994 년 3월 1995년 2월 전달대학교 전기공 학과 소교.



김태성

1935년 11월 29일생. 1959년 2월 전남대학교 전기공학과 졸업. 1981년 2월 조선대학교 대학원 전기공학과 졸업(공박). 1983년 7월 일본 청산대학원대학 전기공학과 연구교수. 1989년 7월 일본 동성공업대학 전기공학과 연구교수. 1995년 현재 전남대학교 전기공학과 교수.



김준학

1958년 9월 19일생. 1983년 8월 연세대학교 요업공학과 졸업. 1985년 8월 연세대학교 대학원 요업공학과 졸업(석사). 1991년 4월 School of Materials Science and Engineering, Univ. of New South Wales, Australia 박사학위.

1993년3월 94년 3월 일본 科技廳 무기재질연구소 연수, 1995년 3월 현재 연세대학교 세라믹공학과 대학원 시간강사(고체통계열력학), 1993년-현재 일본 요업협회 정회원, 한국 요업협회 정회원.



菱田俊 一

1955년 4월 1일생, Ph.D. in Industrial Chemistry, 1983 일본 東京 Univ. of Tokyo, MS of Univ. of Tokyo, 1980. Researcher, 1986-1989 National Institute for Research in Inorganic Materials Tsukuba, Japan. Visiting

Researcher, 1988–1989 Ecole Nationale Superieur de Ceramique Industrialle Limoges, France. Assistant Professor, 1983–1986 Department of Chemistry, Univ. of Tokyo, Tokyo, Japan.