Applied Mechanics and Materials *Online: 2013-09-03*
ISSN: 1662-7482, Vol. 404, pp 127-131
doi:10.4028/www.scientific.net/AMM.404.127

Influence of the Top Metal Electrode on P-V Hysteresis Loops Behavior of 1-μm Thick PZT Films Deposited on a Pt/TiN/Si Substrate Prepared by MOCVD

Masruroh[1, a,], Masaru Umeda*[2,b] and Masayuki TODA [3,c]

[1]Department of Physics, Faculty of Mathematics & Natural Sciences, Brawijaya University, Malang 65145, Indonesia

[2]WACOM R&D CO., LTD, 568 TANAKA, Fukaya shi, Saitama 369-1108

[3] Department of Chemistry and Chemical Engineering, Yamagata University, Yonezawa-Yamagata 992-8510. WACOM R&D CO., LTD, 568 TANAKA, Fukaya shi, Saitama 369-1108

[a]ruroh@ub.ac.id, [b]m-umeda@wacom-mfg.jp, [c]masa-t@ivory.plala.or.jp

Keywords: Top electrode, Hysteresis loop, And electrical conductivity.

Abstract. The effect of various top electrodes (Au, Ag, Cu and Al) on the hysteresis loop behavior of 1-μm thick PZT has been investigated. The PZT films and PT bottom electrode were prepared by MOCVD, and various top electrodes were deposited by evaporation. Using an Ag and Cu top electrode, an improvement in the polarization hysteresis loops of PZT films was observed compared to the other electrodes (Au and Al). A well-saturated P-V hysteresis loop was obtained when Ag and Cu top electrodes were applied. By applying an Au electrode, a decrease in polarization was observed, and the Al top electrode produced P-V hysteresis loops with para-electric behavior. The improvement in the polarization hysteresis loops was affected by the electrical conductivity of the top metal electrode. Namely, a faster supply of compensation charges, which are required to bind polarization charges located near the interface in PZT films, was obtained as the conductivity of the top electrode increased. The electrical conductivity of the metals displayed the following trend: (Ag>Cu>Au>Al).

Introduction

Top and bottom electrodes have a strong effect on the ferroelectric properties of a material. In particular, the bottom electrode plays a critical role in determining the texture and quality of ferroelectric films, which are closely related to the remnant polarization (*Pr*). For ferroelectric materials, perovskite compounds such as lead zirconate titanate (PZT) are widely used. Recently, many studies have been performed to obtain high quality PZT films. For electrode materials based on PZT thin films in ferroelectric random access memory (FeRAMs), various materials such as platinum (Pt) [1], strontium oxide (SrO) [2], ruthenium [Ru] [3, 4], ruthenium oxide (RuO_2) [5], Iridium (Ir) [6], and Iridium oxide (IrO_2) [7] have been studied. Among the aforementioned materials, Pt thin films are widely used as bottom electrodes for PZT capacitors due to the low electrical resistivity, large work function, high melting point, high stability in high temperature oxidizing atmospheres and high catalytic activity of Pt [1].

Pt is also usually used as a top electrode [8]; however, when Pt is employed, the ferroelectric properties of the PZT film may become damaged due to the annealing of hydrogen in ambient air [11]. Therefore, other materials must be investigated for the top electrode. Conducting metal electrodes such as noble metals have been the most popular choice for top electrodes because of their ease of deposition. However, less published data are available on conducting metal top electrode materials. Au [9] and Ag alloys [10] have been used as top electrodes on PZT thin films for ferroelectric capacitors via PLD and dc sputtering, respectively. Gold is used as an electrical contact in top electrodes due to its resistance to corrosion, electrical conductivity, and lack of toxicity. However, the cost of gold is relatively high. Moreover, Ag has several advantages such as no catalytic activity to hydrogen, oxidation resistance, high electrical conductivity and low cost. Moreover,

Lucian et al. [12] reported the effects of both top-contact metals (Cu, Au, Al, Cr, Ni, Pd and Ag) deposited by thermal evaporation and Pt and Ta deposited by radio-frequency magnetron sputtering on the ferroelectric properties of epitaxial PZT/SRO/STO structure. The relationship between the electrical conductivity, work function, electronegativity and current density of PZT films was determined. In the present study, we developed various top metal electrodes including Au, Ag, Cu and Al on PZT thin films with a Pt bottom electrode for ferroelectric capacitors using vacuum evaporation. Hence, the aim of the present study was to deposit various metal electrodes such as Au, Al, Ag and Cu on PZT films and to use the resulting materials as top electrodes. Moreover, vacuum evaporation is a simple and low-cost fabrication method for the production of top electrodes. Furthermore, the influence of the top electrode on the ferroelectric properties of PZT films was investigated.

Experiments

Preparation of films

The substrates used in this work were 8-inch silicon wafers with a platinum bottom electrode layer and an TiN adhesion layer. The generate substrate structure was Pt/TiN/SiO_2/Si(100). The PZT films were grown on the Pt/TiN/SiO2/Si(100) substrate using a liquid delivery metal organic chemical vapor deposition (MOCVD) method system named ″Doctor T″ developed by WACOM R&D Corporation. This MOCVD system features a novel instantaneous vaporizer and has excellent stability for depositing homogeneous films for large wafers. A 1-μm- thick film was deposited on the Pt bottom electrode. In the growth of the PZT films, the source precursors used were $Pb(DMAMP)_2$: 0.025 CCM, $Zr(MMP)_4$: 0.025 CCM, and $T(MMP)_4$: 0.025 CCM, and the total pressure was 1067 Pa. Oxygen (O_2) and argon (Ar) were used as the oxidizing gas and carrier gas, respectively. The sources materials used in this study and typical deposition conditions are summarized in Table 1.

Table 1 Summary of PZT deposition conditions

Sources materials	
Pb sources (ccm)	0.025
Ti sources (ccm)	0.025
Zr sources (ccm)	0.025
Substrate	Pt/TiN/SiO_2
Thickness of Pt (μm)	100
Thickness of TiN (nm)	20
Thickness of SiO_2 (nm)	100
Thickness of PZT (nm)	90
Carrier gas (Ar) flow rate(SLM)	0.3
Oxygen gas flow rate (SLM)	5
Suceptor temperature (C)	525
Total pressure (Pa)	1067
Deposition time (min)	35

Electrical measurements

For electrical characterization of the thin films, various top electrodes including Au, Ag, Cu and Al were applied to the film surfaces using a shadow masking evaporation method. The top electrode structures were patterned with circles using a shadow mask with a diameter of 500μm. The films were annealed by an RTA process at temperatures of 750C for 60 sec in an O_2 atmosphere in order to crystallize the PZT films in the ferroelectric phase. The polarization as a function of voltage (P-V) was measured after performing a rapid thermal annealing (RTA) process. A ferroelectric test system (Precision LC Radiant Technology) was used to measure their electrical properties. A ferroelectric

test system (Precision LC, Radiant Technology) was employed to measure the electrical properties by the drive terminal bottom electrode (Pt) that was connected to the drive of the precision LC. The illustration model for connections between drive terminal and top or bottom electrode have been reported in previous paper [13].

Result and Discussion

Polarization as a function of the electric field (P-V curves) was measured on PZT samples with different top electrodes, and the hysteresis was determined. All of the P-V hysteresis loops were measured at a frequency of 100 Hz for 1-μm thick PZTs with an area of 1.96×10^{-3} cm^2. Figure 1 shows the P-V curves of PZT/Pt samples with different top electrodes, which provided different P-V hysteresis loops. All of the Ag top electrodes (Fig. 1-a) exhibited the best hysteresis P-V loops and the greatest remnant polarizations. The Cu top electrode and Au top electrode provided intermediate results (Fig. 1-b and 1-c), while the poorest hysteresis loops were obtained for the Al top electrode (Fig. 1-d). The observed improvement in the hysteresis loops may be related to the electrical conductivity of the top electrode. For instance, Ag displayed the highest electrical conductivity and provided the best hysteresis loops. Higher conductivity in the top electrode may lead to a faster compensation charges, which are required to bind polarization charges located near the interface. Moreover, the coercive field increased due to strong interactions between dipoles.

On the other hand, the poorest hysteresis loop as obtained for the Al electrode may be due to the tester of precision LC can not supply as many charges to sample as needed to arrive at the equilibrium state. Moreover, the actual voltage can not reach to and be staying at the targeted voltage, therefore the actually applied Vmax of hysteresis can not reach to the expected (planned) Vmax, so the P-V hysteresis seems to be a leaky sample.

The relationship between the electrical conductivity of top metals and remnant polarization ($2Pr$) is shown in Table 2. The values were obtained from the literature [15], and the electrical conductivities displayed the following trend: Ag>Cu>Au>Al. Ag and Cu presented the highest electrical conductivity and provided the best hysteresis loops, while Au and Al, which possess lower electrical conductivity, were comparable. However, the hysteresis loop gap of the Au top electrode was smaller than those of the Cu and Ag top electrodes. The observed gaps in the hysteresis loops in opposite directions are related to the asymmetry of the electrode (different work functions of the bottom and top electrode, as reported in a previous paper [14]. The work function of Au was higher than those of Cu, Ag and Al, as shown in Table 3. The work function increased according to the following trend: $\phi_{Au} < \phi_{Cu} < \phi_{Ag} < \phi_{Al}$. Thus, the work function of Ag is lower than that of Au (for example, ($\phi_{Ag} < \phi_{Pt}$) is lower than ($\phi_{Au} < \phi_{Pt}$)). As a result, an electron from Ag electrode is unlikely to move to the Pt electrode, and it is more difficult for the system to switch from the final negative polarization to the initial positive polarization. Thus, a large gap occurs between the final and initial polarization states. Because the work function of Au is more similar to that of Pt than that of Ag, an electron from Au can easily move to the Pt electrode. As a result, the gap between the initial and final polarizations was small (as shown in Figure 1).

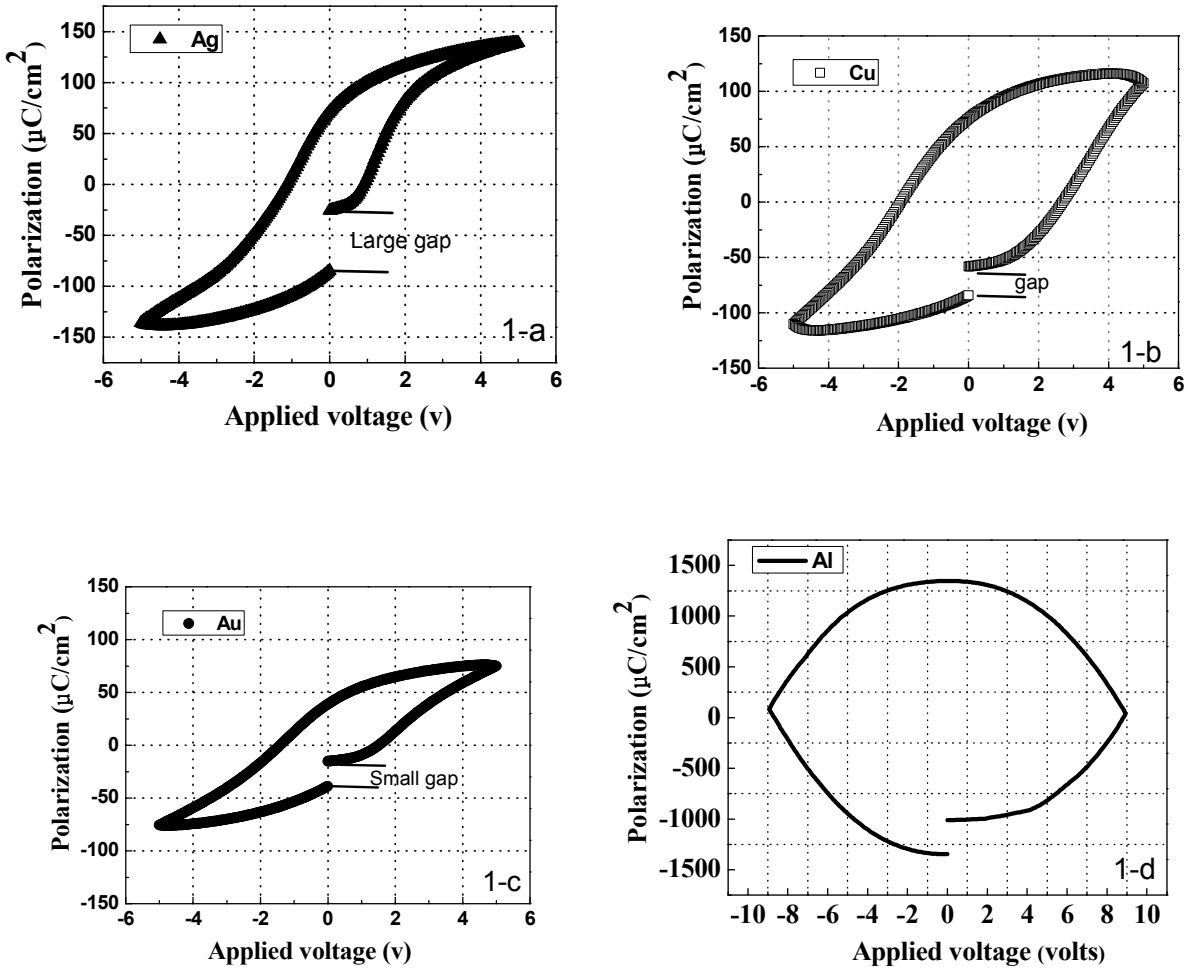

Fig 1. P-V Hysteresis of PZT films at Vmax 5 V using various top electrodes; namely 1-a Ag electrode, 1-b Cu electrode, 1-c Au electrode and 1-d Al electrode.

Table 2 $2Pr$ of each top electrodes used in this study

Top electrode	P_r (μC/cm^2)	$-P_r$ (μC/cm^2)	$2Pr$ (μC/cm^2)
Ag	71.3591	84.8363	156.1956
Cu	72.37119	82,1756	154.5486
Au	38.7598	38.8158	77.5756
Al	-	-	-

Table 3 Conductivity and work function of metal used as top electrodes

Metal	Conductivity(10^{-6} Ohm-cm-1)	Work function (eV)
Ag	0.6410	4.64
Cu	0.5988	5.1
Au	0.4255	5.47
Al	0.3906	4.2

Summary

The effect of various top electrodes (Au, Ag, Cu and Al) deposited by evaporation on the hysteresis loops of 1-μm thick PZT films prepared by MOCVD was investigated. The ability of the metal electrodes to supply compensation charges required by bound polarization charges located near the

interface of PZT films had a significant effect on the ferroelectric behavior. PZT films with an Ag top electrode presented a high value of polarization. Among the four electrodes examined, the hysteresis loops obtained from the Al top electrode exhibited the poorest performance.

Acknowledgment

The authors would like to thank the WACOM R&D Co. Ltd. Japan for providing the materials and technologies for deposition of PZT films using MOCVD named Dr. T. Special thank should go to Mr. Yoshikazu Sasaki for the Deposition of PZT sample using MOCVD, Mr. Yutaka Kojima and Mr. M. Ohata from NFT Co., Ltd, and Mr. Scott. P. Chapman and Mr. Joe T. Evans from Radiant Technologies, Inc. for discussion about Radiant Technologies. The authors also wish to thank Brawijaya University for supporting Masruroh to the ISMSE through the PPKID Unit.

Corresponding Author

Masruroh, Email: ruroh@ub.ac.id or rafizen_02@yahoo.com, +62-81913140970

References

[1] K Bauman, P. Doppelt, K.Frohlich, O. Valet, V. Cambel, D. Machajdik, M. Schumacher, J. Linder, F. Schienie, H. Guillon and C. Jimenez, 15 The International Symposium on Integrated Ferroelectrics (ISIF 2003) p. 392-393.

[2] U. Ellerkmann, P. Schorn, D. Bolten, U. Boettger, and R. Waser: 15 The International Symposium on Integrated Ferroelectrics (ISIF 2003), p. 492-493

[3] Sang Yeol Kang, Ha Ji Lim, Cheol Seong Hwang and Hyeong Joon Kim: 15 The International Symposium on Integrated Ferroelectrics (ISIF 2003)ISIF 2003, p. 404-405

[4] S. D. Berstein, T. Y. Wong, Y. Kisler and R. W. Tustison: J. Mater. Res. 8 (1993) 12

[5] H. N. Al. Shareef, A. I. Kingon, X. Chen, K. R. Bellur and O. Auciello: J. Mater. Res. 9 (1994) 2968

[6] K. Okuwada, K. Yoshida, T. Saitou and A. Sawabe: J. Mater. Res. 15 (2000) 2667

[7] H. S. Lee, W. S. Um, K. T. Hwang, H. G. Shin, Y. B. Kim and K. H. Auh: J. Vac. Sci. & Technol. A 17 (1999) 2939]

[8] Jong Myeong Lee, Suk-Kyoung Hong, Cheol Seong Hwang and Hyeong Joon Kim: J. of the Korean Physical Society, vol 33, pp S148-151 (1998)

[9] Jin-Ping and T.P. Ma: Appl. Phys. Lett. 71 (9) 1997

[10] Hiroshi Masumoto, Atsushi Kojima, Takashi Iijima and Takashi Goto: JJAP vol. 41 (2002) pp. 6882-6885

[11] J. D. Baniecki: J. S. Cross, M. Tsukada and J. Watanabe: Appl. Phys. Lett. 81 (2002) p. 3837

[12] Lucian Pintilie, Ionela Vrejoiu, Dietric Hesse, and Marin Alexe: J. Appl. Phys. 104, (2008) p. 114101-1

[13] Masruroh, Masaru Umeda, and Masayuki Toda: International Journal of Applied Physics and Mathematics, Vol. 2, No. 6, November (2012) p. 454-457.

[14] Masruroh and Masayuki TODA: Applied Mechanics and Materials Vols. 110-116 (2012) pp 294-298

[15] Dr. Lide CRC, Baco Raton: C. R. C. Handbook of Chemistry and Physics, 76th (1995)