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Analysis on interface layer between Pt electrode and ferroelectric layer of solution-processed PZT capacitor

Thanh V Pham [1], Trinh N Q Bui [2], Tue T Phan[1], Takaaki Miyasako[2], Eisuke Tokumitsu[2,3], Tatsuya Shimoda[1,2]

[1]Japan Advanced Institute of Science and Technology, 1-1 Asahidai, Nomi, Ishikawa 923-1292, Japan.
[2]Japan Science and Technology Agency, ERATO, Shimoda Nano-Liquid Process Project, 2-5-3 Asahidai, Nomi, Ishikawa 923-1211, Japan.
[3]Precision and Intelligence Laboratory, Tokyo Institute of Technology, 4259-R2-19 Nagatsuta, Midori-ku, Yokohama 226-8503, Japan.

ABSTRACT

Pt/Pb($Zr_{0.4}Ti_{0.6}$)O_3 (PZT)/Pt capacitors were prepared by the sol-gel technique and their electric properties were analyzed. The asymmetry of polarization-electric field (*P-E*) and capacitor-voltage (*C-V*) curves exhibits existence of an interface layer (dead-layer) between top Pt electrode and PZT thin film. By conducting temperature dependant measurement, the Pt/PZT/Pt capacitor was confirmed to be Schottky emission conduction. In addition, the Schottky barrier height of Pt/PZT contact was calculated to be 0.67eV. On the basic of a series capacitors model and Schottky contact of Pt/PZT interface, the thickness and the dielectric constant of this dead-layer were estimated to be 6.4 nm and 170, respectively. Moreover, the dielectric constant of 900 was obtained for the real PZT ferroelectric layer. The existence of the dead-layer was also confirmed by the high resolution transmission electron microscopy (HR-TEM) observation and the energy dispersive X-ray (EDX) analysis on PZT ferroelectric layer in the Pt/PZT/Pt structure. Based on EDX analysis result, a 10-nm layer at Pt/PZT contact was suggested to be the dead-layer.

INTRODUCTION

Ferroelectric thin films (PZT, BST …) have been of great interest for their applications in electronic devices, such as FeRAMs, infrared sensors, etc [1,2]. Some reports showed that an interface layer (dead-layer) exists between electrodes (Pt and $SrRuO_3$) and ferroelectric (PZT, BST…) layers and this dead-layer influences much on electric properties of the ferroelectric capacitors [3-5]. Therefore, this dead-layer forms a parasitic capacitor in series with the real ferroelectric layer. Chen *et al* estimated thickness and dielectric constant of dead-layer to be 2.8 nm and 42.6 on the Pt/BST/YBa_2CuO_7 capacitor [3], respectively, based on a series capacitors model, current-voltage (*I-V*) measurement behavior as the Schottky model and the modified space-charge-limited current model. Larsen *et al* reported that the ratio of thickness to dielectric constant of dead-layer was from 0.036 to 0.05 nm in the Pt/PZT/Pt capacitors [4]. Moreover, Nguyen *et al* reported that the thickness of dead-layer was 6.5 nm in the SRO/PZT/SRO capacitor [5]. However, the value of thickness and dielectric constant of dead-layer of a Pt/PZT/Pt capacitor has not been reported yet, although the existence of the dead-layer has been widely suggested.

In this work, PZT thin films were deposited on Pt(111)/Ti/SiO_2/Si substrates by the sol-gel method. The electric properties of Pt/PZT/Pt capacitors were analyzed. The result shows that *P-E* loop and *C-V* characteristics were asymmetric. By conducting temperature dependant measurement, the Pt/PZT/Pt capacitor was confirmed to be Schottky emission conduction. On the basic of the series capacitors model and the Schottky contact of the Pt/PZT interface [3,6], thickness and dielectric constant of the dead-layer were identified, and simultaneously, dielectric constant of the real PZT ferroelectric layer was estimated. The existence of this dead-layer was further confirmed by the high-resolution transmission electron microscope (HR-TEM) observation and the energy dispersive X-ray (EDX) profile.

EXPERIMENTAL DETAIL

The PZT thin films were prepared on Pt(111)/Ti/SiO_2/Si substrates by the sol-gel technique. Raw solution of $Pb_{1.2}(Zr_{0.4}Ti_{0.6})O_3$ was spin coated at a speed of 2500 rpm for 25 s, then dried at 240 ^oC for 5 min, and finally crystallized at 600 ^oC for 30 min in ambient air by rapid thermal annealing. The excess of the lead was added to compensate for evaporation loss and to assist the crystallization [6]. In this work, thicknesses of PZT thin film were changed from 118 nm to 437 nm. After that, the $100\mu m \times 100\mu m$-Pt electrodes were deposited by RF-sputtering at room temperature and patterned using a lift-off process. Finally, all samples were annealed at 450^oC for 30 min in ambient air in order to improve contact of the Pt electrode and the PZT thin film.

Thicknesses of the PZT thin film were measured by Alpha-step 500 surface profiler. The crystalline structure of the PZT thin films was identified by X-ray diffraction (M18XHF-SRA) using Cu Kα radiation. The *P-E* curves were measured at 1 kHz using the Sawyer-Tower circuit. The *C-V* measurements were performed using a Wayne Kerr precision component analyzer 6440B with a 0.1 V amplitude. The *I-V* characteristics were measured by an Agilent 4155C-semiconductor parameter analyzer and the measured temperature changes from 300 K to 400 K. The cross sectional image of Pt/PZT/Pt structure was observed by high-resolution transmission electron microscope HR-TEM (Hitachi H-9000NAR). The PZT layer of Pt/PZT/Pt structure was analyzed by the energy dispersive X-ray (EDX) measurement (STEM-JEOL Ltd. JEM-ARM200F).

RESULT AND DISCUSSION

The X-ray diffraction spectrum of the PZT thin film presents a preferential orientation in the (111) direction due to the highly (111)-oriented bottom Pt electrode [7,8] (see Fig. 1(a)).

Fig. 1(b) shows the *C-V* characteristics of the Pt/PZT(250 nm)/Pt capacitor measured at an ac frequency signal of 1kHz. As expected for ferroelectric properties, the *C-V* curve is the “butterfly” shape with two maxima which should correspond to the coercive field values[9], and its average value was about 78.5 kV/cm. *P-E* loop of same capacitor is shown in Fig. 1(c). The average remnant polarization P_r and the average coercive field E_c were about 28 $\mu C/cm^2$ and 91 kV/cm, respectively. Furthermore, the *P-E* loop and *C-V* characteristics were asymmetric. This asymmetry behavior was also observed at the capacitors with different PZT layer thicknesses (from 118 nm to 437 nm), which indicates that a space charge region or a depletion layer could exist between the top Pt electrode and the PZT layer [4, 10].

Therefore, the film thickness acting as a real ferroelectric might be reduced [6]. If thickness of the deposited PZT layer is d, it is expressed as

$$d = d_f + d_i \qquad (1)$$

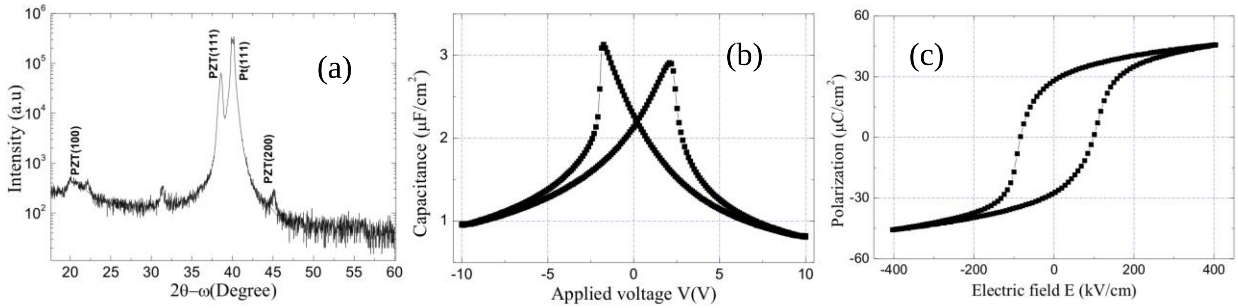

Fig. 1.(a) XRD pattern of the PZT thin film, (b) *C-V* characteristic and (c) *P-E* loop of the Pt/PZT(250 nm)/Pt capacitor.

On the basic of the series capacitors model which include a dead-layer capacitor in series with a real ferroelectric PZT capacitor, the effective dielectric constant (ε_{eff}) of the Pt/PZT/Pt capacitor can be presented as[3,4]

$$\frac{d}{\varepsilon_{eff}} = \frac{d_f}{\varepsilon_f} + \frac{d_i}{\varepsilon_i} = \frac{d}{\varepsilon_f} + d_i\left(\frac{1}{\varepsilon_i} - \frac{1}{\varepsilon_f}\right) \qquad (2)$$

where d and ε are the thickness and the dielectric constant, the sub-index f and i are labeled for the ferroelectric layer and the interface layer, respectively. In this model, it is assumed that d_i is constant for all Pt/PZT/Pt capacitors.

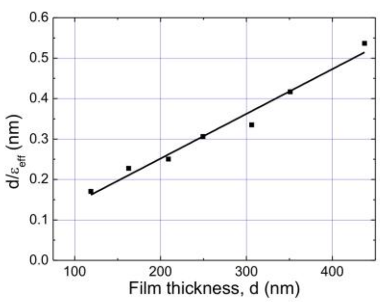

Fig. 2. The d/ε_{eff} as a function of PZT thickness d

Equation (2) gives a linear relation between d/ε_{eff} versus d with a slope of $1/\varepsilon_f$ and a y-axis intercept of $d_i(1/\varepsilon_i - 1/\varepsilon_f)$ as shown in Fig. 2. Values of ε_f and $d_i(1/\varepsilon_i - 1/\varepsilon_f)$ were estimated to be 900 and 0.031 nm, respectively. However, base on the value of $d_i(1/\varepsilon_i - 1/\varepsilon_f)$ and the series capacitors model, the value of d_i and ε_i could not be estimated. Therefore, *I-V* characteristics of the Pt/PZT/Pt capacitors were analyzed to obtain other information of the dead-layer.

I-V characteristics of the Pt/PZT/Pt capacitors were measured. In order to minimize the influence of current polarization, a relative long delay time of 5s was used during *I-V* measurements. The results show that the current density-voltage (*J-V*) characteristics did not depend very much on thickness of PZT thin films in the range of 118 nm to 437 nm [10]. In the Pt/PZT/Pt system, it is assumed that most of the applied voltage drops across the dead-layer [11] and the Pt/PZT is the Schottky contact. Therefore, using the Schottky model, the interface conduction of the Pt/PZT can be expressed as [10,11]

$$J = A^{**}T^2 \exp\left(-\frac{q\Phi_b}{kT}\right)\exp\left(\frac{q}{kT}\sqrt{\frac{qV}{4\pi\varepsilon_0\varepsilon_i d_i}}\right) \quad (3)$$

where J is the current density, A^{**} is the Richardson constant, T is the temperature, $q\Phi_b$ is the Schottky barrier height, k is the Boltzmann constant, V is applied voltage and ε_0 is the permittivity of free space.

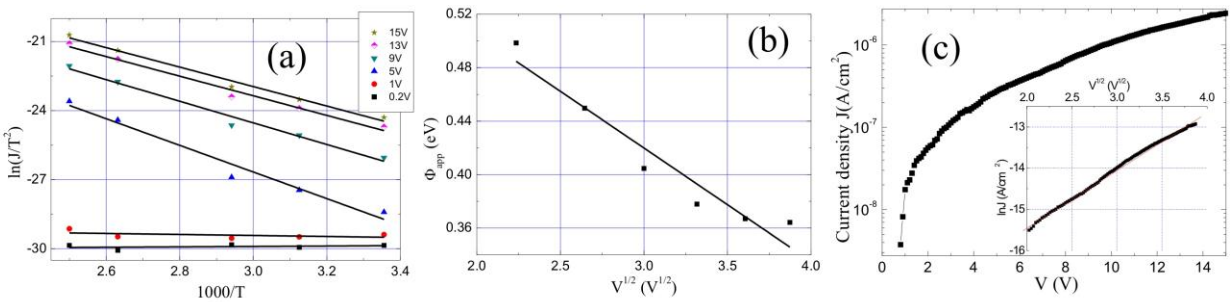

Fig. 3. (a) Schottky representation of the Pt/PZT conduction for different positive voltages, (b) voltage dependence of the apparent potential barrier, and (c) *J-V* characteristic of the Pt/PZT(250 nm)/Pt at T=300K.

In the objective of data analysis, equation (3) can be written in a different way

$$\ln\left(\frac{J}{T^2}\right) = \ln\left(A^{**}\right) - \frac{q}{kT}\Phi_{app} \quad (4)$$

where Φ_{app} is the apparent potential barrier, and

$$\Phi_{app} = \Phi_b + \sqrt{\frac{q}{4\pi\varepsilon_0\varepsilon_i d_i}}V^{1/2} \quad (5)$$

Therefore, the dependence of ln(J/T^2) on $1/T$ should be a straight line and its slope can be used to estimate the apparent potential barrier [10]. Fig. 3(a) shows these dependences for several applied voltages. The results show that the straight lines were obtained when the applied voltages were higher than 5V.

Additionally, the equation (5) exhibits that the dependence of Φ_{app} on $V^{1/2}$ should be a straight line and its intercept should give the value of Φ_b (see Fig.3(b)). We observe that the linear fitting is good, confirming the $V^{1/2}$ dependence. The intercept value of 0.67 eV gives a potential barrier at zero voltage. This value of Φ_b is closed to other estimates of 0.64, 0.80, 0.85, and 0.93 eV [12-15] obtained from the temperature dependence of the *I-V* characteristics. Thus, the interface conduction of the Pt/PZT described by the Schottky emission was well confirmed.

Otherwise, equation (3) can be also expressed as

$$\ln(J) = \ln\left(A^{**}T^2\right) - \frac{q\Phi_b}{kT} + \frac{q}{kT}\sqrt{\frac{q}{4\pi\varepsilon_0\varepsilon_i d_i}}V^{1/2} \quad (6)$$

The equation (6) shows the dependence of ln(J) on $V^{1/2}$ as a straight line. Fig. 3(c) shows the *J-V* characteristics of the Pt/PZT/Pt capacitor with the PZT thickness of 250 nm. The linear relation of $\ln(J)$ vs. $V^{1/2}$ is obtained when the applied voltage is larger than 4 V as shown in the inset of Fig.3(c). The straight line gives the slope of $\left(q/kT\sqrt{q/4\pi\varepsilon_0\varepsilon_i d_i}\right)$= 1.395, then $\varepsilon_i \times d_i$ =1103 nm. Otherwise, combining this result with $d_i(1/\varepsilon_i - 1/\varepsilon_f)$= 0.031 nm, the d_i and the ε_i were estimated to be 6.4 nm and 170, respectively. This estimated dead-layer thickness is in comparison with the thickness of 6.5 nm in the SRO/PZT/SRO capacitor [5].

To further investigate the dead-layer of Pt/PZT, a cross-sectional image of one of these samples was observed by HR-TEM. Fig. 4(a) shows the cross-sectional image of the Pt/PZT/Pt structure, thickness of PZT layer was 174 nm. Fig. 4(b) shows images of the top Pt/PZT contact and the bottom PZT/Pt one. We recognize that the bottom PZT/Pt contact is very sharp due to epitaxial growth of the PZT layer on Pt(111) substrate, nevertheless, the top Pt/PZT contact is slightly blurred. Hence, it seems that there is a nonferroelectric layer existing at the top Pt/PZT contact rather than the bottom PZT/Pt one [4], which corresponds to the above mentioned dead-layer of the top Pt/PZT contact.

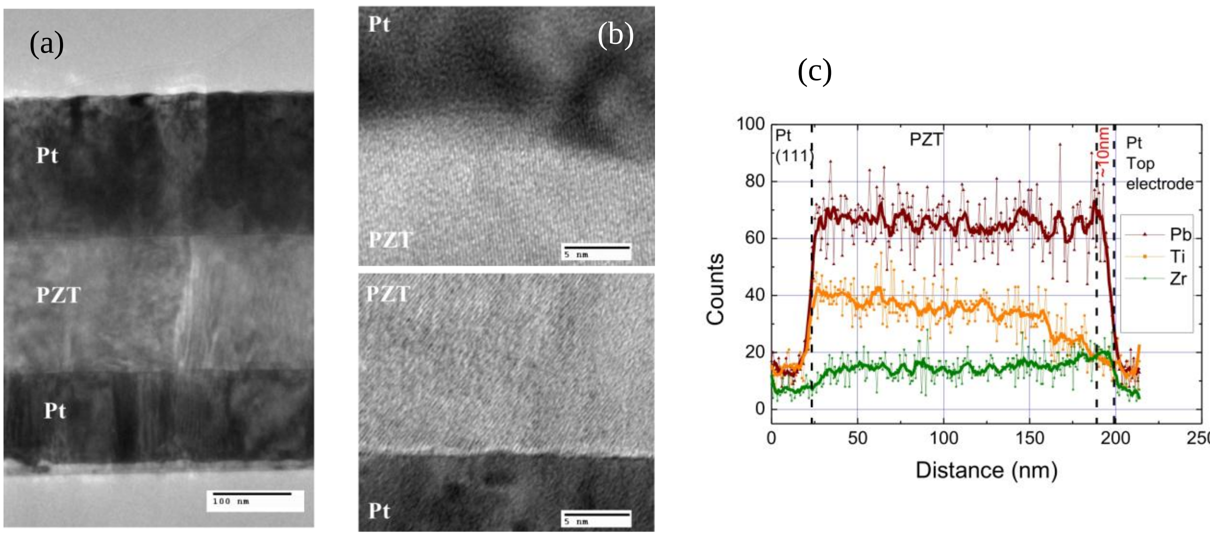

Fig. 4. (a) Cross-sectional image, (b) top Pt/PZT contact and bottom PZT/Pt contact, and (c) EDX profile of PZT layer of the Pt/PZT/Pt structure.

Simultaneously, EDX profile of this PZT layer was analyzed and shown in Fig.4(c). The sharpness of the bottom PZT/Pt contact was reconfirmed because of uniform concentrations of Pb, Ti and Zr near the bottom contact. However, at around 10 nm depth from the top Pt/PZT contact, the Pb and Ti concentrations were decreased very much, while Zr concentration was increased because of high temperature of crystalline process [16]. We suggest that this 10-nm layer is the nonferroelectric layer [4]; therefore, this layer has electric properties which are different from the properties of bulk PZT ferroelectric and it seems to be the dead-layer of the top Pt/PZT contact. The value of 10 nm of thickness of the nonferroelectric layer is comparable with 6.4 nm thickness of the dead-layer obtained from the series capacitors model and the leakage current behavior as Schottky emission. This result is a good experimental evidence to prove the existence of the dead-layer of the top Pt/PZT contact in the Pt/PZT/Pt capacitor.

CONCLUSIONS

PZT thin films were successfully prepared on Pt/Ti/SiO_2/Si substrates by the sol-gel technique. *C-V*, *P-E* and *I-V* characteristics of the Pt/PZT/Pt capacitors were analyzed. The asymmetry of *C-V* curve and *P-E* loop of all the PZT capacitors indicates the existence of the dead-layer at the top Pt/PZT interface.

On the basic of the leakage current behavior as Schottky emission, the top Pt/PZT contact was confirmed to be the Schottky contact and the Schottky barrier height of this contact was estimated to be 0.67 eV. Combining with the series capacitors model, the thickness and the dielectric constant of the dead-layer were estimated to be 6.4 nm and 170, respectively. Simultaneously, the dielectric constant of the real PZT ferroelectric layer of 900 was obtained.

The existence of the dead-layer between the top Pt electrode and the PZT ferroelectric layer was further confirmed by HR-TEM observation. The blurry image of the top Pt/PZT contact was suggested that a nonferroelectric layer exists at this contact, which corresponds to the dead-layer of the top Pt/PZT contact. Based on the EDX profile of the PZT layer of the Pt/PZT/Pt structure, a 10-nm layer at the top Pt/PZT contact was suggested to be the nonferroelectric layer. This 10 nm thickness of the nonferroelectric layer is comparable with previous 6.4 nm thickness of the dead-layer. These results are the experimental evidences to prove the existence of the dead-layer of the top Pt/PZT contact of the Pt/PZT/Pt structure.

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