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Influence of Light Irradiation on Electrical Properties of Lead Zirconate Titanate Film Capacitors

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$Pb(Zr,Ti)O_3$ (PZT) thin film capacitors have been widely investigated, due to their various applications, including ferroelectric memories and micro-electromechanical systems. However, degradation of electrical properties of the films is caused by crystal defects, and the exact mechanism for this has not been fully elucidated. We have attempted to investigate defects in the films by thermally stimulated current (TSC) measurements, and the identification of the observed TSC peaks and the relationships between the degradation and TSC signal. However, the behavior of carriers in the films, such as recombination, has not been fully elucidated, and quantitative evaluation of carrier movement and defect density has been difficult. We have therefore investigated the influence of UV-light irradiation on electrical properties of PZT film capacitors.

The leakage current and capacitance measurements under UV light (λ = 250 nm) irradiation were carried out. The current and capacitance were gradually changed by the irradiation, revealing that the relaxation time and lifetime of carriers in the films were sufficiently high, above 100 s, and the decrease in the observed current in TSC by recombination seems to be small. The relaxation time slightly decreased with increasing temperature and applied voltage because of carrier drift. The drift properties were also discussed.
Key words: PZT, crystal defects, UV, life time, TSC, thermally stimulated current, degradation

1. INTRODUCTION

Lead zirconate titanate (PZT) films are expected to be applied in various next-generation devices, such as ferroelectric nonvolatile memory devices and micro-electromechanical systems (MEMS). Thus, the preparation and evaluation of PZT films on semiconductors and other substrate materials have been widely investigated. However, there are a high density of crystal defects in the films, causing degradation of electrical properties. Since this degradation adversely affects device properties, the crystal defects and degradation mechanisms have also been investigated.[1] The evaluation of defects in ceramics has been difficult, however, and several evaluation methods used for semiconductors and organic materials such as deep level transition spectrometry (DLTS) and thermally stimulated current (TSC) measurement have been attempted.[2-4] We have also investigated improvements in TSC measurements for PZT films, and analysis of TSC results and a part of the degradation model could be revealed.[5,6] Defects and trap sites of carriers at the interface between PZT and an electrode can be analyzed qualitatively by TSC. However, quantitative analysis, such as trap density and evaluation of the inner part of a PZT film, has been difficult because a portion of carriers in PZT is eliminated by recombination, and the detected TSC signal decreases. Recombination in these films has not been revealed in detail.

In this study, the influence of UV light irradiation on permittivity and leakage current was evaluated. When the films are exposed to a UV light pulse, the excited carriers modulate the capacitance and current of the film capacitors. From the time dependence, the lifetime and recombination of the carriers were examined.

Table I. Sputtering conditions for PZT

Temperature	350 °C
rf power	
$Pb(Zr_{0.5}Ti_{0.5})O_3$	500 W
PbO	90 W
TiO_2	400 W
Gas Ar:O_2(SCCM)	4.5:1.0
Gas Pressure	1.5 Pa
Time	60 min
Thickness	170 nm

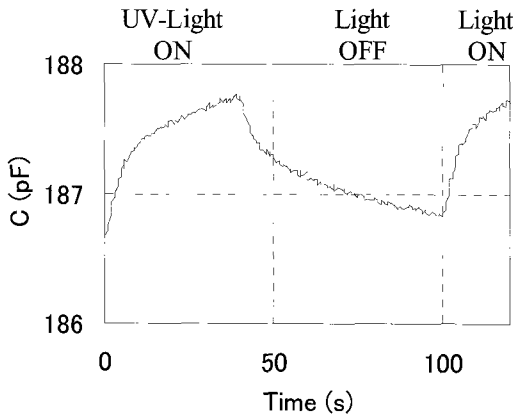
2. EXPERIMENTAL

$Pb(Zr_{0.4}Ti_{0.6})O_3$ films were prepared on Pt/SiO2/Si substrates by rf magnetron sputtering. The conditions used for the sputtering are summarized in Table I. The films were sputtered at a substrate temperature of 350°C and were annealed at 600°C in air to crystallize them, and perovskite films were obtained. Platinum top electrodes with 0.12 mm diameter were formed with a metal mask method. The fundamental evaluation of crystallographic

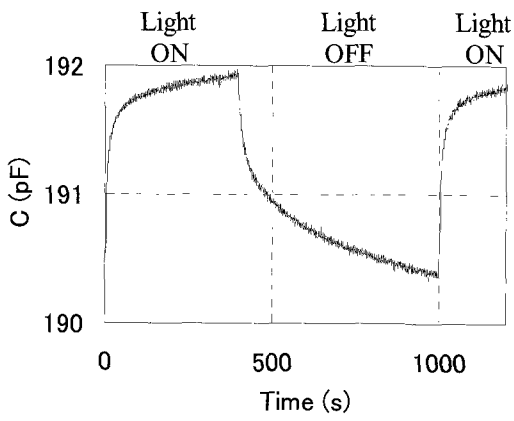
and electrical properties of the films by XRD and a ferroelectic tester have been described in previous reports.[6]

The specimens were placed on a probing stage with a heater into a vacuum chamber. The permittivity and leakage current properties of the specimen were measured with an impedance analyzer (ZM2353, NF Corp.) and an electrometer (K6517, Keithley Co.).

A UV cold cathode fluorescent lamp was used as the light source. The lamp emits UV light with a wavelength of 250 nm, which is irradiated onto a specimen placed in the vacuum chamber through a fused quartz window. The intensity of the light was measured to be 0.5 mW/cm^2 on the surface of the specimens. When the top Pt electrodes were deposited with metal mask patterning, a very thin Pt layer, with thickness under 50 nm, was also formed at the fringe of the electrodes by diffusion during sputtering. The fringe length was about 0.1 mm. The UV light could penetrate through to this fringe, and reached the PZT layer. The UV light source was controlled by an oscillator (33220A, Agilent Co.), and a light pulse was obtained.



(a) 100 s period

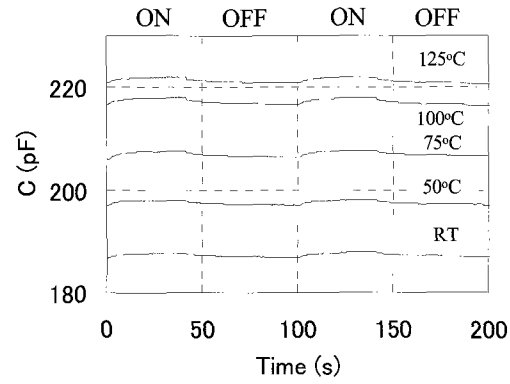


(b) 1000 s period

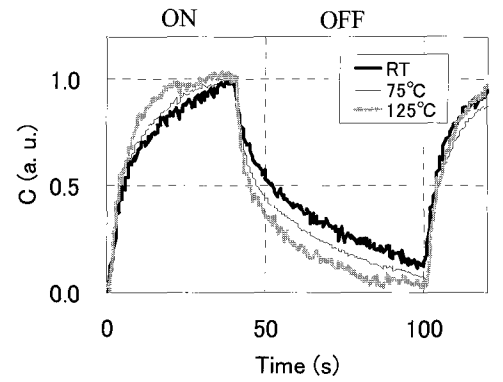
Fig. 1 The dependence of capacitance on the UV light irradiation.

3. RESULTS AND DISCUSSION

The dependence of the capacitance of a film on the UV light irradiation was measured, as shown in Fig. 1(a). The capacitance C increased with light irradiation due to excitation of carriers. After the UV light was switched off, the capacitance decreased, however, this change was slow. Thus, measurement at a 1000 s period was also carried out, as shown in Fig. 1(b). However, obvious saturation was not observed because the change was extremely slow. Assuming that the initial and saturated capacitances were at 400 and 1000 s, respectively, the time constant at which the capacitance was decreased to 36.8% (=1/e) of the initial value was 100 s, revealing that the lifetime of carriers in the PZT film capacitor at room temperature was above 100 s. Since the irradiated UV light is attenuated by the PZT layer, and the capacitance and carriers are also modulated by conditions of a Schottky barrier formed at electrode, there is need to further investigate the change in the band structure with light irradiation.



(a) Measurement result



(b) Normalized data

Fig. 2 The dependence of capacitance on UV light irradiation at various temperatures.

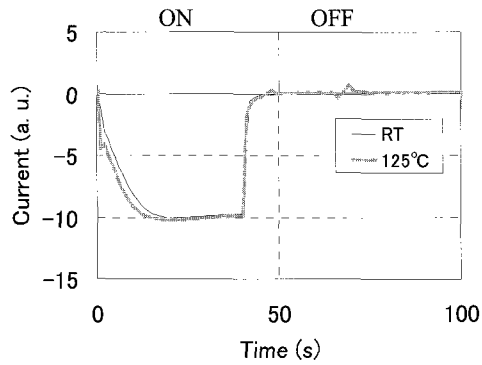
In order to investigate the temperature dependence of the lifetime, similar measurements were carried out at various temperatures. The measurement results are shown in Fig. 2(a). Since the capacitance depends on temperature rather than light irradiation, the normalized capacitance was calculated in such a way that the measured values were subtracted by the capacitance before irradiation at 0 s, and the results were divided by a maximum value at 40 s just before the switching off of the UV light. The normalized results are shown in Fig. 2(b). The time constants at 25°C and 125°C were 25 and 10 s, respectively, revealing that the lifetime decreased

with increasing temperature. The decrease seems to be caused by acceleration of recombination at high temperatures. From the results, the lifetime decreased to about 40% with an increase in the temperature of +100°C. Because the lifetime was above 100 s at 25°C, as shown in Fig. 1(b), the lifetime at a higher temperature, such as at 290°C, which was the maximum temperature of the TSC measurement, is also expected to be sufficiently long, and reduction in the TSC current and the measured defect density by recombination seems to be caused slightly.

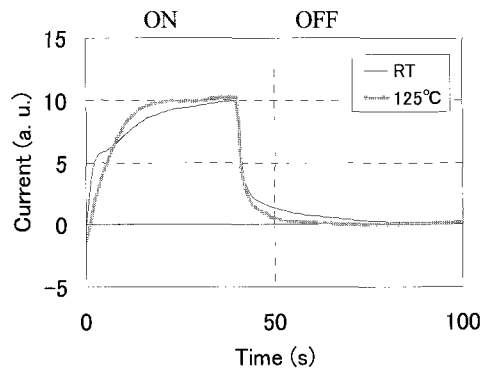
The defect density measured by TSC in the previous report was 2.1×10^{20} cm^{-3}. [7] This value was obtained without consideration of recombination. The density compensated for recombination, *Nt*, is determined from the measured value *Nc*, mobility μ and the lifetime τ,

$$Nt = Nc\, d^2 / (\tau \mu V).$$

Here, *d* is the thickness, and *V* is the applied voltage. Using the values of μ of 0.1 cm^2/Vs and τ of 1×10^{-8} s obtained for bulk $BaTiO_3$ ceramics, [3] the trap density *Nt* was 1.0×10^{23} cm^{-3}, considerably larger than the typical value ($\sim10^{21}$ cm^{-3}). [1] Thus, the reduction with recombination was slight because the lifetime in the PZT films was higher than in the ceramics, and the drift distance of the carrier was extremely short due to interfacial defects.



(a) bias voltage -1 V



(b) bias voltage +1 V

Fig. 3 The dependence of leakage current on UV light irradiation at various temperatures.

From the discussion and measurement results for the lifetime with UV light irradiation, the TSC obtained in the PZT thin film seems to be barely influenced by recombination.

The leakage current under light irradiation was also measured. The measurements were performed at various temperatures, and the normalized currents for reductions in the offset and intensity were calculated, as shown in Fig. 3. Applied voltages of -1 V and +1 V were used for the evaluation, as shown in Fig. 3(a) and (b), respectively. However, an obvious voltage dependence was not obtained. The current increased under the UV light irradiation. The decay time of the current after the light was switched off decreased with increasing temperature similar to the results shown in Fig. 2(b). However, the decay time of the current was much lower than that of the capacitance, and the time of the current at 25°C was 3 s. The carriers in the leakage current measurement flew away swiftly since the carrier was subject to drift due to the applied bias voltage. Therefore, the decay time measured seems to be low.

The dependence of capacitance on light irradiation with dc bias voltage was also measured, as shown in Fig. 4. The decay time after the light was switched off decreased with increasing voltage, revealing that the carrier drift and decrease in the lifetime were caused by the applied voltage.

However, the time constant at +5 V was 150 s, higher than that of the leakage current obtained at +1 V (3 s). The acceleration of carrier drift was caused by the bias voltage, however carriers related to the leakage current were a part of all carriers excited by light since the current path was restricted in some parts of the film, such as grain boundaries. Thus, a decrease of carriers in the capacitance measurement by bias voltage seems to be limited.

From these results, the properties of the observed current, capacitance and carriers and their lifetimes in light irradiation did not agree exactly with those in the TSC measurement. In order to reveal the differences and the relationships, more detailed evaluations under various conditions, such as varying wavelength, thickness etc. are necessary in future studies.

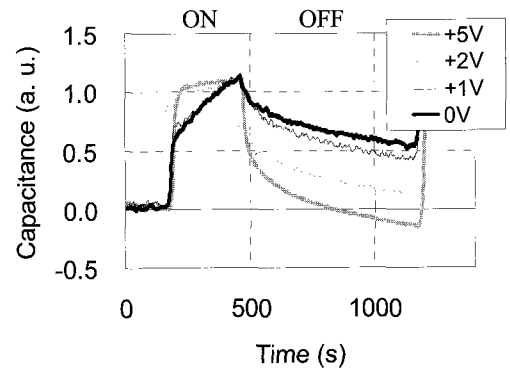


Fig. 4 The dependence of the capacitance on UV light irradiation and dc bias voltage.

4. CONCLUSIONS

Quantitative analysis in TSC measurements such as the calculation of defect density is expected to be influenced by recombination in PZT film capacitors, however, it has

been difficult for such measurements to be performed exactly. Thus, carrier movement in PZT was investigated by UV light irradiation.

Increases in the permittivity and leakage current by light were observed as expected. The lifetime of carriers excited by the light at room temperature was sufficiently high above 100 s from the dependence of permittivity on light irradiation. The lifetime decreased with increasing temperature, however, the rate of reduction was only 40% for a temperature increase of 100°C. Therefore, a reduction in TSC by recombination can be ignored.

The time constant estimated by leakage current measurement under light irradiation was markedly lower than that of the permittivity measurement. From these results and permittivity measurements with applied dc voltage, carriers were collected rapidly by the voltage, and the carriers contributing to the leakage current were a part of the overall carriers excited by light irradiation. Detailed investigation of such a drift mechanism of the carriers in PZT films will be part of future work.

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