

# The thermally stimulated discharge of ion-irradiated oxide films

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**Abstract.** The ion irradiation technique is utilized to modify the surface structure of amorphous insulating oxide films. While introducing defects, a number of surface charges are injected into the films and captured in the traps during ion irradiation. The variation of surface morphology and the enhancement of emission spectrum corresponding to vacancy defects are respectively verified by atomic force microscopy and photoluminescence measurements. The surface charges trapped in the shallow traps are easy to release caused by thermal excitation, and discharge is observed during heating. Based on the thermally stimulated discharge measurements, the trap parameters of oxide films, such as activation energy and relaxation time, are calculated from experimental data.

## 1. Introduction

Thermally stimulated discharge (TSD) is a powerful technique to study the motion of molecular and the structures of trap. It also provides useful information on the charge-storage and transport process controlled by the traps [1]. This technique was first proposed by Frei to study the motion of frozen charge during raising temperature [2], and Bucci et al. gave its theoretical basis in 1966 [3]. From then on, TSD is widely used to investigate the basic characteristics of materials, including crystal and amorphous insulators [4], especially polymer community [5, 6]. Through analyzing the space charge distribution in solid, the trap level and charge storage mechanism can be acquired from the measurement of TSD. For space charges, they usually originate from ionization, impurity, electrode emission, physical and chemical adsorption. In this paper, we utilize ion irradiation technology to introduce surface charges into the insulating oxide films, and analyze the variation of surface topography and component caused by ion irradiation. In the process of thermal excitation, the discharge behavior is clearly detected as a result of the release of surface charges during heating, and the trap parameters are obtained from the discharge curves.

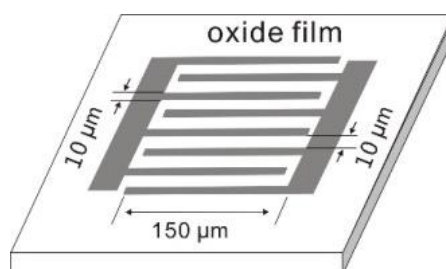
## 2. Experimental

In this experiment, the amorphous Ta<sub>2</sub>O<sub>5</sub> and TiO<sub>2</sub> films, deposited on the silicon substrates with dimensions of 10 × 10 mm<sup>2</sup>, were provided by the 55th Research Institute of China Electronics Technology Group Corporation (CETC55). These insulating samples were irradiated with an Ar<sup>+</sup> plasma with high RF powers in a plasma cleaner (PDC-32G-2). The surface morphology and



roughness of samples were acquired using atomic force microscopy (AFM, SPI3800N) with the non-contact mode. The photoluminescence (PL) spectra of oxide films were measured on a photospectrometer (Hitachi F-7000) at room temperature. The exciting wavelength of an argon ion laser was 486 nm for Ta<sub>2</sub>O<sub>5</sub> and 325 nm for TiO<sub>2</sub>, respectively.

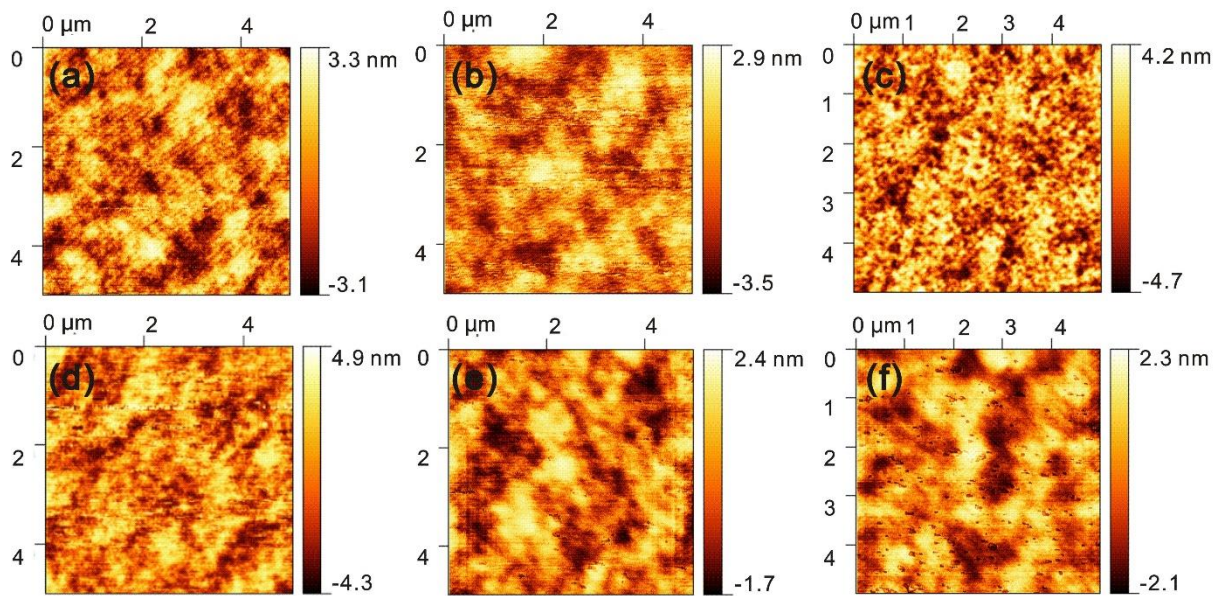
In order to monitor the process of TSD, the patterns of interdigital electrodes were prepared on the surface of samples by lithography. As schematically shown in figure 1, the length, width and distance of each electrode are 150  $\mu\text{m}$ , 10  $\mu\text{m}$  and 10  $\mu\text{m}$ , respectively. The Pt electrodes were sputtered with the thickness of 50 nm. During the measurement, the charges releasing from materials as a result of heating in the vacuum chamber was recorded by an electrometer (Keithley model 6517B), and the temperature was controlled by cryogenic temperature controller (Lake Shore 350) from room temperature to 423 K at a rate of 10 K/min.



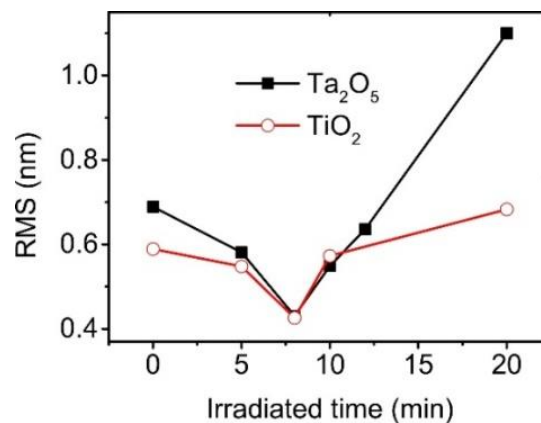
**Figure 1.** Schematic illustration of the interdigital electrodes structure on the oxide film.

### 3. Results and discussion

Ion irradiation is a common tool for cleaning the surface of materials, by which the atoms on the whole surface may get removed. Simultaneously, various types of defects can be generated at the surface because of the different diffusivity for atoms and some new physical performances are introduced into the materials during the process of ion irradiation [7-9]. Nevertheless, the obvious effect of ion irradiation on materials is the variation of surface morphology. By using the AFM, we investigate the topography on the oxide films irradiated by Ar<sup>+</sup> plasma with different time. Before irradiation, the AFM images of virgin films show the relatively smooth surface with the low root mean square (RMS) surface roughness < 0.7 nm (figure 2(a) and (d)). As displayed in figure 2(b) and (e), the irradiation under 8 min originally leads the surface to become smooth. With increasing irradiation time, the surface roughness rises gradually because of the damage induced by Ar<sup>+</sup> irradiation, and even plenty of cavities spread over the film surface are observed as illustrated in figure 2(c) and (f). This consequence is also exhibited obviously in the RMS surface roughness for oxide films with a size of 5 × 5  $\mu\text{m}^2$ . As can be seen in figure 3, the RMS for both amorphous Ta<sub>2</sub>O<sub>5</sub> and TiO<sub>2</sub> films decrease in the initial stage and then increase with the increment of irradiation time. The dynamic process of ion irradiation, like ion-milling, can account for this phenomenon. In the initial stages of irradiation, the intrinsic defects on the film surface, which are demonstrated in the PL measurements, get removed by Ar<sup>+</sup> plasma bombardment, while a number of defects is introduced into the surface in this process. That is the reason for the decrease of the RMS at a short period of irradiation time. However, the defects generated by ion irradiation continually accumulate with increasing treated time, which results in the roughening of film surface.

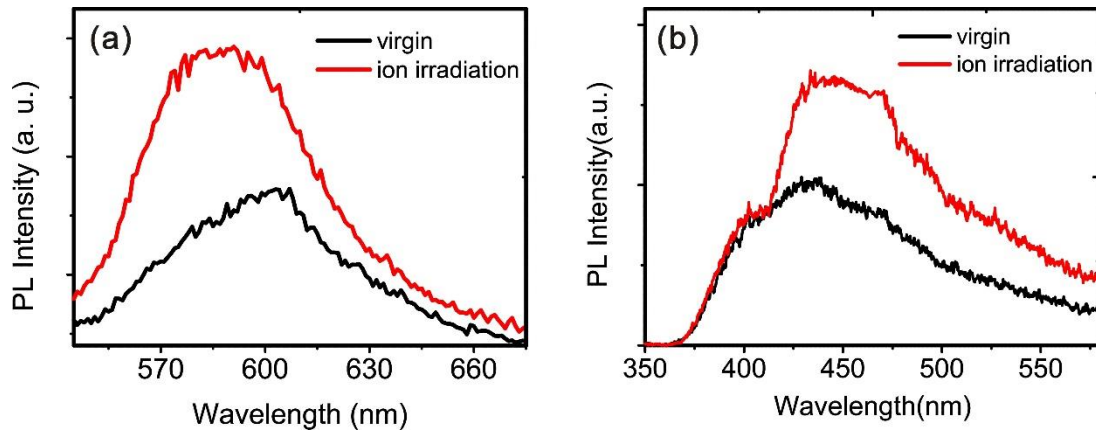


**Figure 2.** AFM images of (a), (b), (c)  $\text{Ta}_2\text{O}_5$  and (d), (e), (f)  $\text{TiO}_2$  films irradiated with 0 min, 8 min and 20 min, respectively.



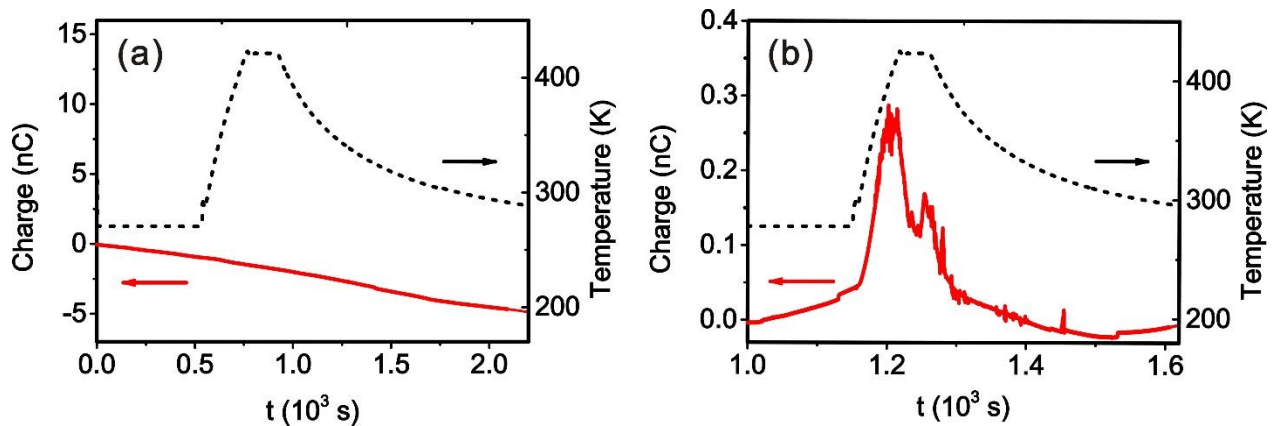
**Figure 3.** The irradiated time dependence of the root mean square surface roughness for oxide films.

PL spectrum is a well-developed optical method for the detection of impurities and defects in materials. As shown in figure 4, both the virgin and ion-irradiated samples were evaluated by PL spectroscopy using an excitation of  $\text{Ar}^+$  laser line at room temperature. Figure 4(a) presents the PL spectra for  $\text{Ta}_2\text{O}_5$  films, and a broad luminescence peak is revealed at around 600 nm for both virgin and ion-irradiated samples, which is attributed to the existence of defects such as oxygen vacancies [10]. The emitted visible light with limited intensity observed in virgin samples indicates the oxide films used in this work have vacancy defects virginally. It is seen that the PL intensity distinctly increases after ion irradiation, which means that more oxygen-vacancy defects are induced at the surface of oxide films through ion irradiation as confirmed in the irradiated  $\text{SrTiO}_3$  single crystal in our previous work [11]. Similarly, this phenomenon also appears in the PL behavior for  $\text{TiO}_2$  films. As can be seen from the figure 4(b), the intensity of emission peaks, correlated with the self-trapped excitons and oxygen vacancies [12, 13], gets enhanced greatly for the samples irradiated in vacuum. In general, the results of PL spectra indicate the increase of the defects via ion irradiation at the surface of amorphous oxide films.



**Figure 4.** Room temperature photoluminescence spectra of (a) Ta<sub>2</sub>O<sub>5</sub> and (b) TiO<sub>2</sub> before and after ion irradiation

During ion irradiation, various types of charge traps may be formed on account of structural damage induced by the generation of defects, and surface charges injected into the film surface through ion bombardment are partly captured by these physical traps. When heating the samples at a linear rate, this part of charges gaining enough energy releases from shallow traps ( $<1.5$  eV), and a current can be detected in the external circuit, which is known as the TSD. Figure 5 shows the variation curves of charge and temperature in the whole process of thermally stimulated measurement. Each sample was heated from room temperature to 423 K at a uniform rate of 10 K/min, and cooled down naturally after kept at 423 K for a few minutes. As plotted in figure 5(a), the discharge caused by thermal excitation does not appear in the virgin films during heating, which implies there is no effective surface charges captured by shallow traps at the film surface before ion irradiation. Nevertheless, the discharge peak is obviously observed in irradiated oxide films at high temperature (figure 5(b)), and the maximum quantity of charge detected in the external circuit is about 0.28 nC. It indicates that a number of surface charges are injected into the surface via irradiated by Ar<sup>+</sup> plasma and the formation of defects during this bombarding process may contribute to the storage of charges.



**Figure 5.** The results of thermally stimulated discharge measurement for (a) virgin and (b) ion-irradiated oxide film.

The results of TSD measurement are very sensitive to the structure of trap, and the trap parameters can be obtained from the current density curve as a function of temperature [3, 14]

$$j(T) = A \exp\left(\frac{-E_a}{kT}\right) \exp\left[-\frac{B}{\beta} \int_{T_0}^T \exp\left(\frac{-E_a}{kT'}\right) dT'\right], \quad (1)$$

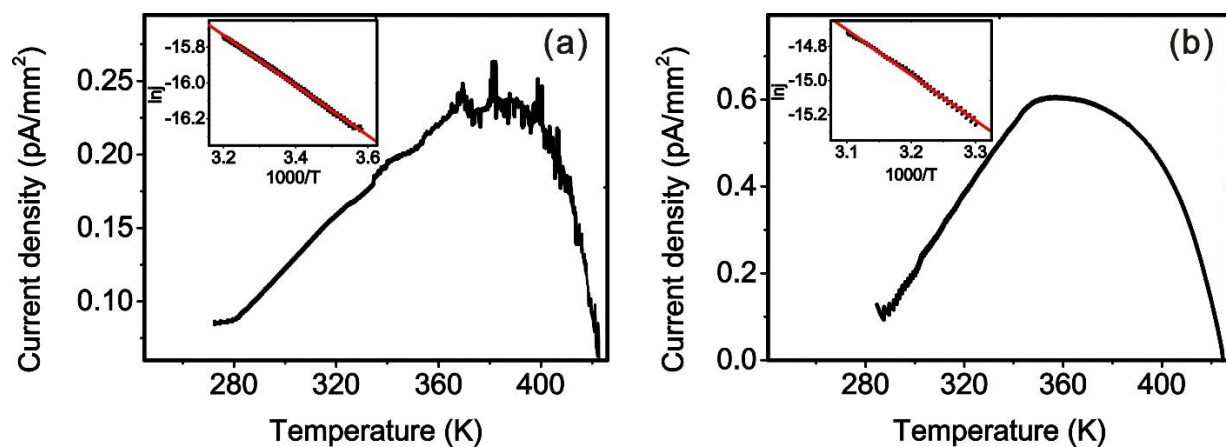
where  $E_a$ ,  $k$  and  $\beta$  denote the activation energy of the process, the Boltzmann's constant and the heating rate, respectively. A and B in this equation are the constants related to the initial polarization and the characteristic relaxation time  $\tau_0$  at infinite temperature. As shown in figure 6, the surface charges release from shallow traps as a result of thermal excitation. However, the activation energy  $E_a$  is linear with  $\ln j(T)$  measured by the following relation for the low temperature part [15, 16]

$$\ln j(T) = \text{const.} - \frac{E_a}{kT}. \quad (2)$$

Based on the fitting of experimental data (the insets of figure 6), the activation energy for  $\text{Ta}_2\text{O}_5$  and  $\text{TiO}_2$  are calculated as 0.121 eV and 0.228 eV, respectively, which implies the surface charges are mainly trapped in these traps with low energy level and are easy to be removed from the film surface. Furthermore, the relationship between the temperature  $T_m$  corresponding to the maximum current and activation energy can be written as [17]

$$T_m = \left[ \beta \tau_0 \frac{E_a}{k} \exp\left(\frac{E_a}{kT_m}\right) \right]^{1/2}. \quad (3)$$

It can be seen that the value of  $T_m$  is fixed for a given heating rate. As displayed in Figure 6(a) and (b), the peaks of current curve are 0.242 pA at 370 K and 0.343 pA at 356 K, respectively. Thus, their characteristic relaxation time  $\tau_0$  obtained from equation (3) are about 13 s for  $\text{Ta}_2\text{O}_5$  and 0.17 s for  $\text{TiO}_2$ . Based on the Arrhenius-type relationship between the relaxation time  $\tau$  and  $\tau_0$  [14], the values of  $\tau$  for irradiated  $\text{Ta}_2\text{O}_5$  and  $\text{TiO}_2$  films at the maximum temperature  $T_m$  can be calculated as 585 s and 287 s, which implies the speedy attenuation of charges due to the low-level traps in our case. In a word, the measurements and analyses of TSD demonstrate that these two kinds of oxide films have certain significance in the research on energy storage, and ion irradiation is an effective method to the injection of surface charges.



**Figure 6.** The temperature dependence of current density for (a)  $\text{Ta}_2\text{O}_5$  and (b)  $\text{TiO}_2$ . The insets show respectively the fit to equation (2) in the initial rise of curves.

#### 4. Conclusions

In summary, defects were introduced into the surface of insulating  $\text{Ta}_2\text{O}_5$  and  $\text{TiO}_2$  films by  $\text{Ar}^+$  ion irradiation, which were characterized by the increase of roughness and the enhancement of PL spectra corresponding to vacancy defects. Simultaneously, space charges were injected into the film surface and captured by the traps during ion irradiation, which were easily removed by heating at a linear rate. According to TSD measurements, the activation energy and relaxation time of the trap in two oxide films were estimated respectively, which provides evidence for the evaluation of trap states. This work demonstrates the combination of ion irradiation and TSD technique is the simple and effective method to help people understand the charge storage characteristics and attenuation process in oxide films.

#### 5. References

- [1] R. Chen and Y. Kirsh, *Analysis of Thermally Stimulated Process* (Pergamon Press, Oxford,

- 1981).
- [2] H. Frei and G. Groetzing 1936 *Phy. Z* **37** 720-724
  - [3] C. Bucci, R. Fieschi and G. Guidi 1966 *Phys. Rev.* **148** 816-823
  - [4] H. Amjadi 1999 *IEEE. Trans. Electr. Insul.* **6** 236-241
  - [5] N. V. Malm, J. Steiger, T. Finnberg, R. Schmechel and H. V. Seggern 2002 *Proc. SPEI-The Int. Soc. Opt. Eng.* **4800** 164-171
  - [6] E. J. Kim, T. Takeda and Y. Ohki 1996 *IEEE Trans. Electr. Insul.* **3** 386-391
  - [7] M. Chassé and G. G. Ross 2002 *J. Appl. Phys.* **92** 5872-5877
  - [8] D. Kan, R. Kanda, Y. Kanemitsu, Y. Shimakawa and M. Takano 2006 *Appl. Phys. Lett.* **88**, 191916
  - [9] M. Rogala, Z. Klusek, C. Rodenbucher, R. Waser and K. Szot 2013 *Appl. Phys. Lett.* **102** 131604
  - [10] M. Zhu, Z. Zhang, W. Miao, and W. Miao 2006 *Appl. Phys. Lett.* **89** 021915
  - [11] Q. Wang, Wanli Zhang, W. Zhang and H. Zeng 2016 *Appl. Surf. Sci.* **365** 84-87
  - [12] L. V. Saraf, S. I. Patil, S. B. Ogale, S. R. Sainkar and S. T. Kshirsager 1998 *Int. J. Mod. Phys. B* **12** 2635
  - [13] Y. Lei, L. D. Zhang, G. W. Meng, G. H. Li, X. Y. Zhang, C. H. Liang, W. Chen and S. X. Wang 2001 *Appl. Phys. Lett.* **78** 1125
  - [14] E. R. Neagu, J. N. Marat-Mendes, D. K. Das-Gupta, R. M. Neagu and R. Igreja 1997 *J. Appl. Phys.* **82** 2488- 2496
  - [15] T. Hino 1980 *IEEE Trans. Electr. Insul.* **15** 301-311
  - [16] W. Liu and C. A. Randall 2008 *J. Am. Ceram. Soc.* **91** 3245-3250
  - [17] J. Vanderschueren and J. Gasiot, "Field-induced thermally stimulated currents," in *Thermally Stimulated Relaxation in Solids*, edited by P. Bräunlich (Springer-Verlag Berlin Heidelberg, New York, 1979), pp. 135-223

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