Journal of Engineering, National Chung Hsing University, Vol. 7, No. 2, pp. 33-39 (1996).

RAPID THERMAL PROCESSED THIN FILMS OF Y_2O_3 GROWN BY R. F. MAGNETRON SPUTTERING

C. Y. Kung[1]

Department of Electrical Engineering,
National Chung-Hsing University
Taichung, Taiwan 40227, R.O.C.

R. H. Horng[2], **D. S. Wuu**[2], **and J. W. Yu**[2]

Institute of Electrical Engineering,
Da-Yeh Institute of Technology
Chang-Hwa, Taiwan 515, R.O.C.

Key Words: Y_2O_3, R.F. magnetron sputtering, Rapid thermal processing.

ABSTRACT

Y_2O_3 thin films have been deposited on (100) Si substrates by r.f. magnetron sputtering and subsequently submitted to a rapid thermal processing (RTP). X-ray examinations show that the sputtered Y_2O_3 was dominated by the (111) cubic structure. With increasing the RTP temperature (>700°C), the crystallinity of films was improved, especially for the intensity of (400) diffraction peak. The as-deposited films show good dielectric properties in terms of a relative dielectric constant of 16.67 and leakage current of 440 pA (at 1.8 MV cm^{-1}). After the RTP treatment, both the dielectric constant and leakage current of Y_2O_3 were found to decrease. A typical dielectric constant decreased to 14.77 and its leakage current lowered to 22 pA (at 1.8 MV cm^{-1}) for the film annealed at 850°C. The observed behavior of dielectric constant may be due to the intermediate oxide formation between Y_2O_3 and Si. Capacitance-voltage characteristics confirm that the reduction of leakage current at high electric field comes from the improvement of interface states.

快速熱處理對射頻磁控濺鍍法在矽基板上沈積之氧化釔薄膜之影響

貢中元[1]　洪瑞華[2]　武東星[2]　余建文[2]

關鍵詞：氧化釔、射頻磁控濺鍍、快速加溫製程。

摘　要

本論文主要在探討快速熱處理 (Rapid Thermal Processing; RTP) 對射頻磁控濺鍍法在矽基板上沈積之氧化釔(Y_2O_3)薄膜之影響。X-光繞射量測顯示此濺

[1] 國立中興大學電機系教授
[2] 大葉工學院電機系

鍍之 Y_2O_3 薄膜主要之結晶結構爲 (111) 立方結構。然隨著RTP 溫度升高 (>700°C)，此薄膜之結晶特性明顯地被改進；特別是 (400) 結晶面。對於未經RTP 處理之Y_2O_3 即已呈現良好的介電特性：其相對介電常數爲 16.67，而漏電流在 1.8 MV cm^{-1}之電場作用下爲 440 pA。相對地，經過 RTP 處理之Y_2O_3，其介電常數與漏電流均被發現有減少之趨勢。在850°C 退火之薄膜，其典型之介電常數減少至 14.77，且其漏電流降至 22 pA (在 1.8 MV cm^{-1} 電場作用下)。此觀察之介電常數行爲可能來自於在 Y_2O_3 與矽基板間形成之氧化物之影響。此外，藉由電容一電壓特性之量測，更能確定在高電場作用下漏電流降低之原因主要來自於 Y_2O_3/ Si 介面狀態明顯地被改善。

1. INTRODUCTION

Thin films of high dielectric permittivity and breakdown strength have a potential application in electroluminescent (EL) devices [1-3]. These films in the EL structure can provide the current limiting necessary to prevent device failure. Specifically, they must have a charge storage capacity at breakdown that is at least three times that of the phosphor layer [4]. Among the materials investigated, Y_2O_3 has been regarded as one of the more promising candidates for the dielectric insulator of EL devices [5-7]. Several deposition methods, including r.f. sputtering, electron-beam, and thermal evaporation techniques [8-10] were attempted to study the structural, electrical or mechanical properties of Y_2O_3 films. It has been concluded that the sputtered-Y_2O_3 thin film is superior to the other deposited ones because the former has excellent stoichiometry control. In order to further improve the sputtered material properties, post-growth thermal annealing is usually employed. The annealing effects on the properties of the Y_2O_3 insulator have been less investigated. Moreover, the nonstoichiometry problem would be an important issue for the thermal-annealed EL devices, especially using the traditional furnace process. Such a process is also not desirable for the monolithic integration of EL and Si-based devices, since junction softening may occur for the components of the drive circuitry. Thus decreasing the annealing time and increasing the process temperature are expected to benefit the post-treatment results. In this work, Y_2O_3 thin films were deposited by r.f.-magnetron sputtering, and then subjected to a rapid thermal processing (RTP). The effects of RTP on the material characteristics of Y_2O_3 films will be described.

2. EXPERIMENTAL

Thin films of Y_2O_3 were deposited on p^+-type (100) Si substrates (~0.005 Ω-cm) by r.f.-magnetron sputtering. All the depositions were performed in an in-situ tilted multi-electrode system as shown in Fig.1. The growth chamber consists of three magnetron electrodes oriented so that each cathode is equidistant from the substrate (~10 cm). This system is used primarily for the fabrication of double-insulator EL structures, facilitating the growth of each layer without breaking vacuum to change targets. A base pressure of $\sim 2\times10^{-7}$ Torr can be pumped down by the use of a vacuum load-lock chamber and liquid nitrogen baffle.

The source material for this study was a 1.5" diameter Y_2O_3 target with 99.99% purity, and the films were deposited using only argon as the sputtering gas. During the deposition, the substrate was heated at constant temperature (100-300°C), and rotated to insure uniform film growth over the exposed region. The Y_2O_3 films of thickness 200-300 nm were deposited at a sputtering pressure of 7×10^{-4} Torr with 4.4 W cm^{-2} applied to the target. Postthermal treatment (700-850°C) for the as-deposited Y_2O_3 samples was carried out with a Jetfirst processor (Jipelec Corp., France). The heating rate used was about 100°C/sec, and soaking time was 60 sec. The process temperature

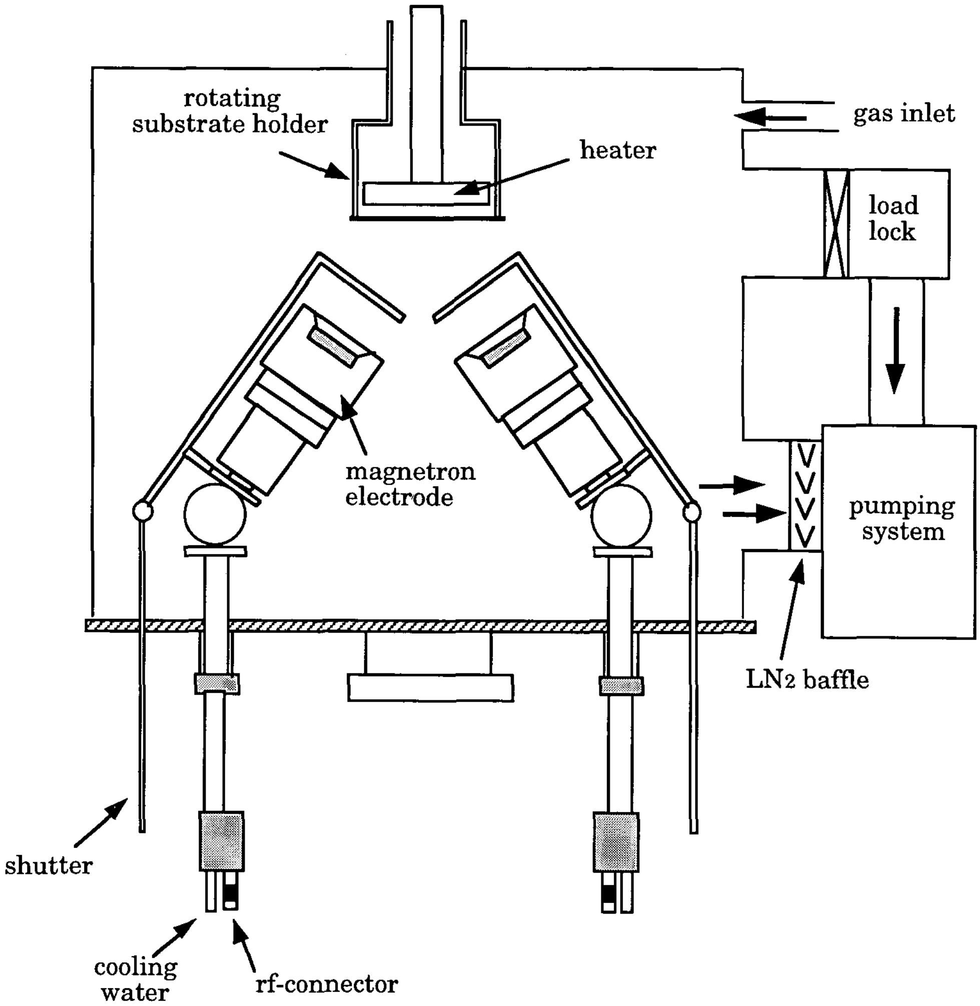

Fig. 1 Schematic diagram of the sputtering system used in this study. The system is equipped with in-situ tilted electrodes and a load-lock chamber.

was monitored by a small K-type thermocouple contacting the backside of the sample wafer. Oxygen was flowed into the RTP chamber to maintain the stoichiometry of the dielectric film, and the samples were then cooled with the chamber door opened. For comparative studies of the RTP effect, samples obtained from a single Y_2O_3 deposition run were used.

Crystallinity of the Y_2O_3 samples was investigated by X-ray diffraction with Cu Kα radiation. Electron probe microanalysis (EPMA, JEOL JXA-8800) was used to determine the stoichiometry of the deposited films. A dry etching process was adopted to define a step in the film down to the Si surface, and the height was then measured using a Dektak 3030 profilometer. The bonding structures of the films were also characterized by a Bio-Rad Fourier transform infrared (FTIR) spectrometer (FTS-40). All dielectric and electrical characteristics were measured in the metal-insulator-semiconductor (MIS) configuration with aluminum as top and bottom electrodes. The top contact (300 nm) was thermally evaporated through a metal mask to produce circular diodes of 0.3 mm diameter. A back ohmic contact to the p^+Si wafer was made by the deposition of a 500-nm-thick Al film. Current-voltage (I-V) and capacitance-voltage (C-V) measurements were performed in a darkened probed station using the HP 4145B semiconductor parameter analyzer and HP 4194A impedance analyzer, respectively. The obtained data was taken from the average value of five measured diodes distributed over each sample.

3. RESULTS AND DISCUSSION

From EPMA examinations, the stoichiometry of the Y_2O_3 samples is determined as 1.49, and has no evident variation with the deposition temperatures used in our experimental range. The value of refractive index measured by He-Ne laser is ~1.91 which agrees well with the value reported for bulk Y_2O_3 [11]. Figure 2 shows the X-ray diffraction patterns of the Y_2O_3 films subjected to different RTP temperatures, as compared with that of the as-deposited sample. It was found that the sputtered-Y_2O_3 thin films strongly oriented their (111) axis of cubic structure. Once the samples were thermal annealed, the crystal quality of the films was improved and the intensity of (400) diffraction peak showed a substantial enhancement with increasing the RTP temperature. The present result suggests that Y_2O_3 films could recrystallize to some extent based on the (100) Si substrate during the annealing process.

For a typical EL device structure, a figure of merit for the insulator is the charge storage capacity ($\varepsilon_r \varepsilon_0 E_{bd}$), where ε_r is the relative dielectric constant, ε_0 the permitivity of vacuum, and E_{bd} the breakdown strength. As concerning the ε_r and E_{bd} behaviors of the RTP-treated Y_2O_3 films, they will be discussed as follows. The MIS diodes for the samples with and without RTP can be swept from depletion to accumulation by applying positive to negative dc bias to the top Al electrode. The dielectric constant of the Y_2O_3 can therefore be determined from the measured value of accumulation capacitance (C_{acc}), using the relation: $C_{acc} = \varepsilon_r \varepsilon_0 A/d$ where A is the area of diode, and d the thickness of dielectric layer. Figure 3 displays the obtained ε_r value as a function of the RTP temperature. The arrow shown in this figure is the corresponding e_r value (16.67) for the as-deposited Y_2O_3 films. It is found that the ε_r value shows a slight decrease to 14.77 as the RTP temperature increases to 850°C. The result is contrary to the theoretical expectation where the higher crystalline property of the dielectric film yields a larger ε_r value. The discrepancy may be due to the fact that Y_2O_3 film is very transparent to oxygen diffusion. Consequently, oxygen coming from the annealing ambient could enable growth of the intermediate thin oxide between Y_2O_3 and Si. The observed FTIR spectra for the above samples can further support this point. The FTIR peak at about 1080 cm^{-1} due to the Si-O asymmetric stretching mode is found to enhance in its integral intensity as the RTP temperature increases. Similar results have also been described by *Rastogi* and *Sharma* in their Y_2O_3/Si report [12]. It is well known that the relative dielectric constants for bulk SiO_2 and Y_2O_3 are 3.9 and 17.1, respectively. The present thin oxide could contribute to decreasing the measured value of ε_r as the RTP temperature increasing from 700 to 850°C.

C-V studies of the films were also performed at a frequency of 1 MHz with a small signal of 10 mV amplitude while the dc voltage was swept from a negative to a positive bias and back again. Figure 4 shows the C-V plots for a 225-nm-thick Y_2O_3 film after RTP at 850 °C as compared with that of the as-deposited film. Since the Si substrate used is heavily doped, the present MIS structure (Al/Y_2O_3/p^+Si) can be regarded as a standard capacitor. That is, the capacitance will approach a constant and is less dependent on bias (Note that the scale in the Fig. 4(b) was expanded). It is observed that there still exists the hysteresis phenomenon for the as-deposited film, while the RTP-treated sample shows a nearly ideal behavior of capacitor. The observed hysteresis behavior could be resulted from the interface states attributed to the difference between the structural properties of polycrystalline Y_2O_3 and Si substrate. The X-ray measured data (as shown in Fig. 2) can confirm the inference because the Y_2O_3 film after RTP has the tendency to recrystallize based on the Si substrate. There exists a transition region-intermediste thin oxide formed during RTP

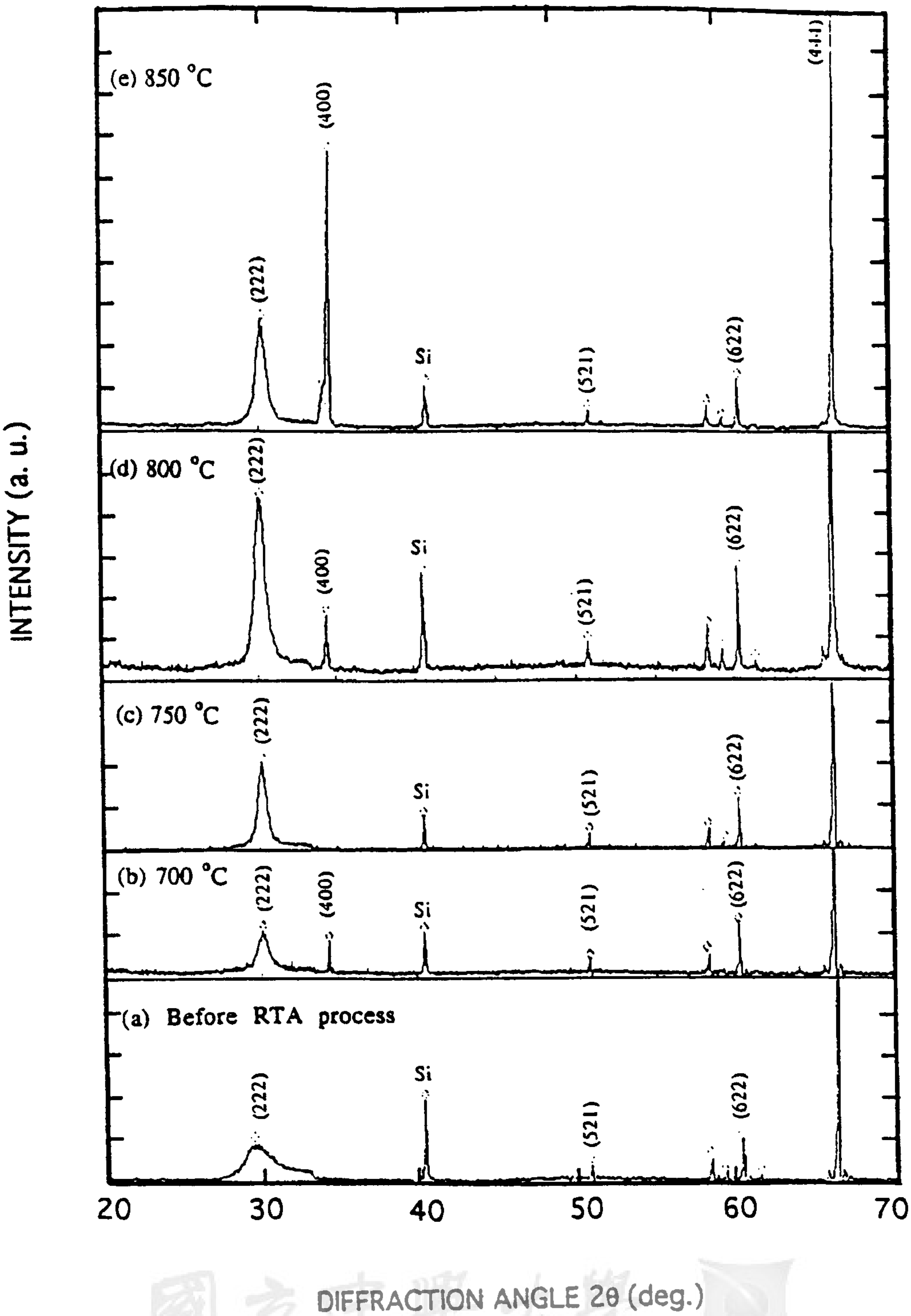

Fig. 2 X-ray diffraction patterns of Y_2O_3 thin films for RTP at different temperatures as compared with that of the as-deposited film.

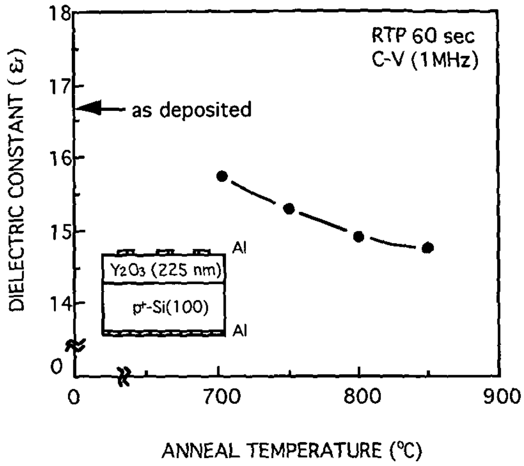

Fig. 3 Dielectric constant ε_r of Y_2O_3 as a function of RTP-treated temperature. Arrow indicates the ε_r value of the as-deposited film.

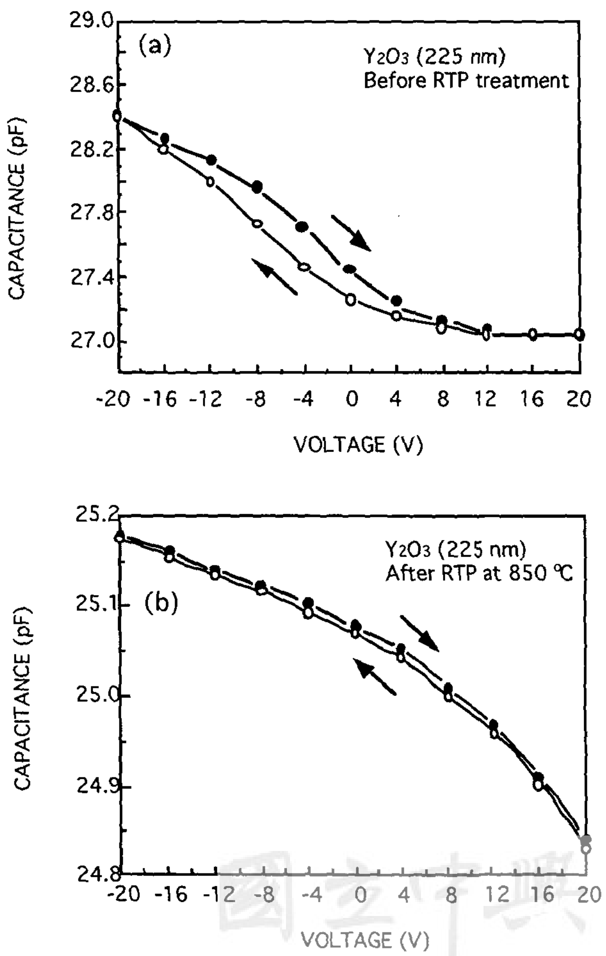

Fig. 4 Typical capacitance-voltage plots for (a) a Y_2O_3 film after RTP at 850 °C for 60 sec and (b) the as-deposited film.

treatment. This indicates that the interface states between Y_2O_3 and Si can be apparently improved by RTP. It can be further proved by transmission electron measurement and is in process.

Another important feature for an insulator to be used in the EL structure is its electrical properties. The effect of RTP on the electric properties of Y_2O_3 films was investigated by measuring the diodes in the accumulation mode with the top Al contact biased negatively. An I-V characteristic for the Y_2O_3 film (the same sample described in Fig. 4) after RTP at 850°C is depicted in Fig. 5. The observed leakage current at an applied electric field of 1.8 MV cm^{-1} was about 22 pA, which corresponded to a leakage current density of 3×10^{-8} A cm^{-2}. It is worthy to mention that the electric breakdown of the film is not observed as the electric field up to 4.4 MV cm^{-1}. These values are superior to those reported for Y_2O_3 films annealed by conventional furnace [12,13]. Figure 6 illustrates the leakage current of Y_2O_3 as a function of the RTP temperature. The measured leakage current decreases considerably with increasing the RTP temperature, and shows one order of magnitude lower than that of the as-deposited sample. Under such high electric field, the effect of the intermediate thin oxide formed by RTP can be ignored since the injected carriers having sufficient energy can tunnel through. The reduction of leakage

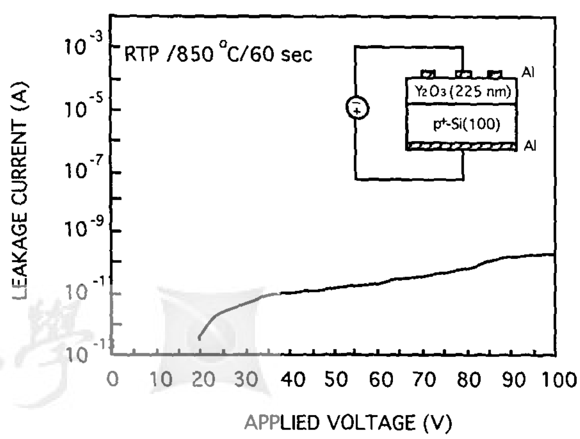

Fig. 5 Current-voltage relationship for a Y_2O_3 film after RTP for 60 sec at 850 °C.

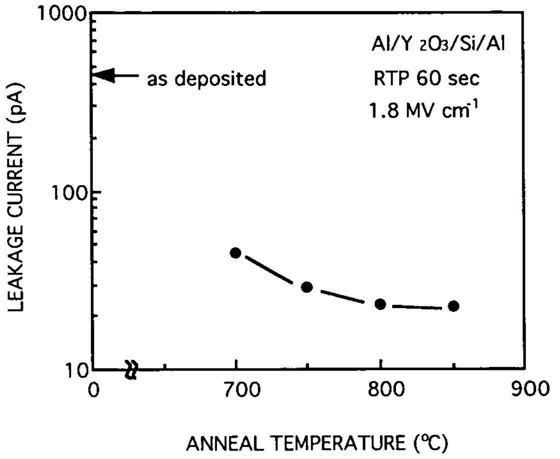

Fig. 6 Leakage current of Y_2O_3 as a function of RTP temperature. Arrow indicates the leakage current of the as-deposited film.

current after RTP could be understood in terms of improvements of crystal quality and interface states, which agrees well with the X-ray and C-V results.

4. CONCLUSIONS

High-quality Y_2O_3 films on Si(100) substrates were obtained by r.f. magnetron sputtering combined with the RTP treatment. The crystallinity of the as-deposited films, strongly oriented their (111) axis of cubic structure, was found to be improved and exhibit the (400) orientation after RTP. The result suggested a recrystallization process occurs based on the (100) Si substrate. The dielectric constant decreases and the leakage current can be reduced to 22 pA, which is lower one order of as-deposited samples. Up to 4.4 MV cm^{-1} electric field, no breakdown behavior was observed. These results suggest that the RTP technology can improve the dielectric and electrical properties of the Y_2O_3 films and is suitable for EL and integrated Si-based devices.

5. ACKNOWLEDGMENTS

This work was supported by the National Science Council of Republic of China and the MRS/ITRI under contract Nos. NSC 84-2215-E-212-001 and 1212067400, respectively. The authors are grateful to S. Y. Lee of National Sun Yat-Sen University, Kaohsiung, Taiwan, for X-ray diffraction measurements.

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論文收稿日期：84 年 11 月 25 日
論文修訂日期：85 年 2 月 27 日
論文接受日期：85 年 5 月 7 日