行政院國家科學委員會專題研究計畫　成果報告

製作高品質焦電薄膜及提升其光感測特性技術之研究

計畫類別：個別型計畫
計畫編號：NSC94-2112-M-164-002-
執行期間：94 年 08 月 01 日至 95 年 07 月 31 日
執行單位：修平技術學院電機工程系

計畫主持人：陳宏仁

計畫參與人員：許進添，藍志學

報告類型：精簡報告
報告附件：出席國際會議研究心得報告及發表論文
處理方式：本計畫可公開查詢

中　華　民　國 95 年 10 月 20 日

行政院國家科學委員會補助專題研究計畫 ■ 成 果 報 告 □期中進度報告

計畫名稱： 製作高品質焦電薄膜及提升其光感測特性技術之研究

計畫類別：■個別型計畫　　□ 整合型計畫
計畫編號：NSC 94－2112－M－164－002－
執行期間：94 年 08 月 01 日至 95 年 07 月 31 日

計畫主持人：陳宏仁教授兼工程學群召集人
共同主持人：
計畫參與人員：許進添，藍志學

成果報告類型(依經費核定清單規定繳交)：■精簡報告　□完整報告

本成果報告包括以下應繳交之附件：
□赴國外出差或研習心得報告一份
□赴大陸地區出差或研習心得報告一份
■出席國際學術會議心得報告及發表之論文各一份
□國際合作研究計畫國外研究報告書一份

處理方式：除產學合作研究計畫、提升產業技術及人才培育研究計畫、列管計畫及下列情形者外，得立即公開查詢
□ 涉及專利或其他智慧財產權，■一年□二年後可公開查詢

執行單位：修平技術學院

中　華　民　國　95　年　10　月　20　日

行政院國家科學委員會專題研究計畫成果報告

製作高品質焦電薄膜及提升其光感測特性技術之研究

Fabricated high-quality pyroelectric thin films and studied promotion its pooperties of optical detection

計畫編號：NSC 94-2112-M-164-002-

執行期限：94 年 8 月 1 日至 95 年 7 月 31 日

主持人：陳宏仁教授兼工程學群召集人　　修平技術學院電機工程系

計畫參與人員：許進添，藍志學

1. Abstract

使用溶膠-凝膠法在 Pt(III)/Ti/SiO_2/Si(100)基板上沉積 $LiTaO_3$ 薄膜，並經由快速熱處理後的高性能焦電紅外線感測器一直被製作。分別經傳統及 RTA 熱處理的 $LiTaO_3$ 薄膜的介電及焦電將性首先被研究。從實驗結果顯示加熱速率會深深影響薄膜介電及焦電性。當加熱速率從 600 增加至 1800 ℃/min 在量測頻率 80 Hz 時，電壓響應度從 5496 增至 8455 V/W；在 300 Hz 時，特定檢測度(D^*)從 1.94 $\times 10^8$ 增至 2.38 $\times 10^8$cm·$Hz^{1/2}/W$ 然而當加熱速率超過 1800 ℃/min，Rv 及 D^* 皆會降低。從此研究中可獲得 $LiTaO_3$ 在加熱速為 1800 ℃/min 時具有最大的電壓響應度及特定檢測度。(本計畫研究成果已接受發表於 **Journal of Electroceramic 及 Eur. Phys. J. Appl. Phys.** 各一篇，現皆正印刷出版中。)

關鍵字：鉭酸鋰，紅外線感測器，快速熱處理，電壓響應，檢測度。

High-performance pyroelectric infrared detectors have been fabricated using Lithium tantalite ($LiTaO_3$) thin films deposited on Pt(111)/Ti/SiO_2/Si(100) substrates by diol-based sol-gel method and rapid thermal annealing (RTA) technique. The dielectric and pyroelectric properties of IR detectors of $LiTaO_3$ thin films crystallized by conventional and RTA processes are investigated. Experimental results reveal that the heating rate will influence strongly on dielectricity and pyroelectricity of $LiTaO_3$ thin films. The voltage responsivities (Rv) measured at 80 Hz increase from 5496 to 8455 V/W and the specific detecivities (D*) measured at 300 Hz increase from 1.94×10^8 to 2.38×10^8 $cmHz^{1/2}/W$ with an increase of heating rate from 600 to 1800 ^oC/min. However, the voltage responsivity and the specific detecivity decrease with heating rate in excess of 1800 ^oC/min. The results show that the $LiTaO_3$ thin film detector with a heating rate of 1800 ^oC/min exists both the maximums of voltage responsivity and specific detecivity

Keywords：$LiTaO_3$, infrared detectors, RTA, voltage responsivity, detecivity.

2. Introduction

Pyroelectirc infrared detectors have been widely used for inrared (IR) detection applications owing to the advantages of wavelength-independent sensitivity and room temperature operation. It employed the

release of surface charge by a pyroelectric material when the temperature is varied. The pyroelectric coefficient . is an important parameter which attributes the rate of variation of spontaneous polarization with respect to temperature. There are commonly used materials for pyroelectric applications include triglycene sulphate (TGS), lithium tantalite ($LiTaO_3$), $Ba_{1-x}Sr_xTiO_3$ (BST), PZT and $PbTiO_3$ [1-5]. In which, $LiTaO_3$ is a suitable material with high figures of merit for pyroelectric detector application. The structure of the ferroelectric phase of $LiTaO_3$ consists of layers of oxygen ions in approximately hexagonal close packing with Li^+ and Ta^{5+} ions occupying two thirds of the octahedral interstices between the layers. Ta and Li ions are displaced from the exact center positions along the ferroelectric *c*-axis, thus giving rise to the ferroelectric polarization. Off-center displacement and distortion of the octahedral cause different bond lengths for the Ta-O and Li-O bonds. It has been found applications in optoelectronic devices, surface acoustic wave devices and pyroelectric detectors due to its unique pyroeletric, piezoelectric, electro-optic and nonlinear optical properties [5-10].

In the past, we have reported the preparations and properties of the diol-based sol-gel derived $LiTaO_3$ thin films crystallized by the rapid thermal annealing (RTA) [11]. The *c*-axis oriented $LiTaO_3$ thin films on $Pt(111)/Ti/SiO_2/Si(100)$ substrates using the sol-gel method and rapid thermal processing have been obtained. The main difference between RTA and CTA (conventional furnace annealing) is that the rise time for heating to the desired temperature is very short for RTA, enabling to reduce the overall annealing period. This leads to reduction in surface damage [12, 13].

In this study, we focused the optical response of the $LiTaO_3$ thin films IR detectors fabricated by the sol-gel method and RTA technology with the various heating rate. The voltage responsivity (R_v), noise voltages (V_n) and specific detectivity (D*) of detectors were measured using a dynamic analysis system. In addition, the effects of various heating rate on the electrical and pyroelectric properties of the $LiTaO_3$ thin films IR detectors are studied.

3. Experimental

The sol-gel process for preparing the precursor solutions of $LiTaO_3$ with a general chemical formula. Lithium 2,4-pentanedionate, $LiC_5H_7O_2$ and tantalum isopropoxide, $Ta[OCH(CH_3)_2]_5$, were used as precursors and 1,3-propanediol, $HO(CH_3)_2OH$ was used as solvent. The films were deposited on the substrates by spinning coating of the solutions at a spin rate of 3000 rpm for 30 s. After each coating step, the films were given a pyrolysis heat treatment at 400℃ for 2 min to remove residual organics. The average thickness of a single-coated as-fired layer, measured by a α-step surface profiler, was found to be about 0.1 μm. The desired film thickness of approximately 0.5 μm was achieved by repeating the spin-coating and heating cycles. After multi-coating, $LiTaO_3$ thin films were annealed at 700 ℃ for 2 min by the rapid thermal processing in the oxygen atmosphere. The heating rates ranged from 600 ℃/min to

3000 ℃/min. The films annealed with heating rate of 600 ℃/min, 1200 ℃/min, 1800 ℃/min, 2400 ℃/min and 3000 ℃/min are designated as LT600, LT1200, LT1800, LT2400 and LT3000, respectively. To make contact with the platinum bottom electrode, a corner of the film was etched, using a 50 wt% solution of fluoroboric acid, HBF_4. Then, alumina (Al) was evaporated on the $LiTaO_3$ film as a top contact electrode. Finally, silver (Ag) black, a heat absorption material, was evaporated upon the top contact electrode to assist the absorption of incident IR radiation. Figure 1 shows a schematic diagram of the thin-film detector.

To measure the sensitivity of detectors, various light sources, such as a He-Ne laser (wavelength $\lambda = 0.633$ μm) and a blackbody radiation furnace (wavelength $\lambda = 2.3 \sim 3$ μm), were focused using a concave lens, and mechanically chopped at frequencies from 5 Hz to 1 kHz, then directly irradiated onto the surface of the sensing electrode. The pyroelectric voltage and current signals were measured using a lock-in amplifier and monitored by a digitizing oscilloscope, while the detector element was exposed to the incident chopped-IR radiation. These measurements were performed at room temperature, in a shielded room.

4. Results and Discussion

The materials characteristics of $LiTaO_3$ thin films have been discussed in a privious work [11]. The relative dielectric constant ε_r on various heating rate were measured at 10 kHz for films annealed at 700 ℃. The calculated dielectric constants increase from 28 to 45.6 with the heating rate from 600 ℃/min to 3000 ℃/min. It is obvious that ε_r increases as the heating rate increases. The pyroelectric coefficient γof the $LiTaO_3$ thin film heated at 700℃ with various heating rate of 600℃/min ~ 3000℃/min were measured by a technique initially used by Byer and Roundy [14]. The displacement current I parallel to the polar axis produced by the variation of spontaneous polarization was given by [15]

$$I = A\gamma(T)\frac{dT}{dt}, \qquad (1)$$

where $\gamma(T)$ is the pyroelectric coefficient evaluated at temperature T, dT/dt is the temperature change rate, and A is the area of the top electrode. In the direct measurement technique, the device is mounted in a shielding case to prevent the interference of the external noise. The pyroelectric current I was measured using a digital electrometer (TR8652). A temperature change rate of 3 ℃/min was adopted. Figure 2 shows the temperature dependence of the pyroelectric coefficient for the $LiTaO_3$ thin films heated at 700 ℃ with various heating rate of 600 ℃/min ~ 3000 ℃/min. The pyroelectric coefficient of LT3000 thin films increased slowly from 1.1×10^{-8} to 2.1×10^{-8} C/cm^2·K as the temperature increased from 20 to 50 ℃, and then increased markedly up to a maximum value of 4.25×10^{-8} C/cm^2·K at 70 ℃, as shown in Fig. 2. In addition, the pyroelectric coefficient increased from 2.5×10^{-8} C/cm^{2}K for 600 ℃/min to 4.25×10^{-8} C/cm^2·K for 3000 ℃/min at 70 ^{o}C.

The fundamental performance parameters of a pyroelectric detector are the

voltage responsivity (R_V) and current reponsivity (R_I), defined as the ratio of the output voltage and output current induced by the pyroelectric effect to the incident radiant power. In the pyroelectric measurement, the radiation energy is absorbed by the top metal layer, converted to thermal energy, and then conducted to the active $LiTaO_3$ thin film as well as to the underlying substrate. Figures 3 show the modulation frequency dependence of R_V and R_I of LT1800 thin film IR detectors, respectively. R_V increased with the increased modulation frequency from 5 to 20 Hz and varied proportional to f^{-1} above 20 Hz. In contrast, R_I increased with the increased modulation frequency, but the increase slowed down at higher frequencies. The current response of an infrared device can be expressed as follow:

$$R_I = \frac{\eta\gamma A\omega}{G\sqrt{1+\omega^2\tau_t^{\,2}}}, \qquad (2)$$

where η is the emissivity, γ is the pyroelectric coefficient, A is the detector area, ω is angular modulation frequency, G is the thermal conductance and τ_t is the thermal time constant (τ_t =H/G, where H is the thermal capacity). Thus, R_I is proportional to ω at low frequencies ($\omega << \tau_t^{-1}$) and is almost constant in the high-frequency region. R_V is obtained by multiplying R_I by the impedance of the electrical circuit with parallel resistance R and capacitance C, being:

$$R_V = \frac{\eta\gamma AR\omega}{G\sqrt{1+\omega^2\tau_t^{\,2}}\sqrt{1+\omega^2\tau_e^{\,2}}}, \qquad (3)$$

where τ_e (=RC) is the electrical time constant. R_V is almost constant in the low-frequency region. The decrease in R_V at high frequencies is due to the fact that R_V is inversely proportional to the frequency when the modulation frequency is above τ_t^{-1}. In this study, the results obtained are consistent with the above phenomenon. The maximum voltage responsivity R_V exists at the frequency of 20 Hz. R_V (max) was significantly increased by the increase of heating rate. However, it decreased when heating rate exceeded 1800℃/min, as shown in Fig. 4. The result also shows that the LT1800 detector exhibits the largest R_V of as high as 4227 (V/W) at 20 Hz.

The noise voltages (Vn) for pyroelectric IR detectors with various heating rate are measured at modulated frequency. The frequency dependence of the noise voltage per unit bandwidth (in units of $V/Hz^{1/2}$) for $LiTaO_3$ thin film detectors is shown in Fig. 5. It is obvious that Vn varies nearly proportionally to $f^{-1/2}$. This might be due to the fact that Johnson noise frequently dominates in pyroelectric detectors. Figure 5 also shows that Vn increases with the increase of heating rate. This might be due to the fact that the loss tangent (tan δ) noise increases with the increase of heating rate.

The sensitivity of a pyroelectric device can be expressed in terms of its noise equivalent power (NEP):

$$NEP = \frac{Vn}{R_V} = \frac{1}{R_V}\sqrt{\frac{4kTR(1+\omega\tau_e \tan\delta)}{(1+\omega^2\tau_e^{\,2})}}, \qquad (4)$$

where k is the Boltzmann constant and T is absolute temperature. The frequency dependence of the NEP and the specific

detectivity ($D^*=A^{1/2}/NEP$) of the LT1800 thin film IR detectors is shown in Fig. 6. D* is proportional to $f^{-1/2}$ when f > 300 Hz, because R_V varies proportionally to f^{-1} and Vn varies as $f^{-1/2}$. In contrast, D* decreases with decreased f when f < 70 Hz. This phenomenon is probably due that R_V almost saturates and Vn increases nearly proportionally to $f^{-1/2}$. The measured D* value at 300 Hz, at which the maximum D* exists, for detectors with various heating rate is shown in Fig. 7. D* was significantly increased with the increase of heating rate. However, it decreased when heating rate exceeded 1800 ℃/min. It was found that the LT1800 detector exhibits a large D* of 1.2×10^8 $cmHz^{1/2}/W$ at 300 Hz.

5. Conclusions

In this report, $LiTaO_3$ thin film detectors were fabricated on $Pt(111)/Ti/SiO_2/Si(100)$ substrates by a diol-based sol–gel process and RTA technology. $LiTaO_3$ thin films 0.5 μm thick were achieved using a five-layer spin-coating process. Dynamic analysis shows that the noise voltage (Vn) increases with the increase of the heating rate. The specific detectivity (D*) is proportional to $f^{-1/2}$ when f > 300 Hz and decreases with decreasing f when f < 70 Hz. D* is obviously increased by an increase of heating rate. However, D* decreases when the heating rate exceeds 1800℃/min. The LT1800 thin film IR detector has a largest voltage responsivity of 4227 V/W and a specific detectivity of 1.2×10^8 $cmHz^{1/2}/W$ at 20 Hz and 300 Hz, respectively. The corresponding results show that the obtained LT1800 thin film exhibited excellent pyroelectric properties and, thus, was suitable for application to highly sensitive pyroelectric IR devices. This work was sponsored by the National Science Council of the Republic of China under the grants No. NSC 94-2112-M-164-002-.

6. References

[1] R. W. Whatmore: Rep. Prog. Phys. **49,** 1335 (1986).

[2] R. Takayama, Y. Tomita, K. Iijima and I. Ueda: J. Appl. Phys. **61,** 411 (1987).

[3] R. Takayama, Y. Tomita, K. Iijima and I. Ueda: J. Appl. Phys. **63**, 5868 (1988).

[4] D. L. Polla, C. P. Ye and T. Tamagawa: Appl. Phys. Lett. **59,** 3539 (1991).

[5] D. H. Lee, J. S. Lee, S. M. Cho, H. J. Nam, J. H. Lee, J. R. Choi, K. Y. Kim, S. T. Kim and M. Okuyama: Jpn. J. Appl. Phys. **34,** 2453 (1995).

[6] A. Rauber: *Current Topics in Materials Science*, (North-Holland, Amsterdam, 1978).

[7] W. S. Hu, Z.G. Liu, D. Feng: Solid State commun. **97,** 481 (1996).

[8] W. S. Hu, Z.G. Liu, D. Feng: J. Appl. Phys. **80,** 7089 (1996).

[9] W. S. Hu, Z.G. Liu, Y.-Q. Lu, S.N. Zhu, D. Feng: Opt. Lett. **21,** 946 (1996).

[10] Y. Kuwano, T. Yokoo, K. Shibata: Jpn. J. Appl. Phys. **20,** 221 (1981).

[11] M. C .Kao, H. Z. Chen, C. M. Wang, Y. C. Chen and M. S. Lee: Appl. Phys. A **79**, 103 (2004).

[12] S. D. Cheng, C. H. Kam, Y. Zhou, Y.L. Lam, Y. C. C. K. Pita and W. S. Gan: Ferroelectricsn **232,** 979 (1999).

[13] T. A. Deis, P. P. Phule: Journal f Materials Science **11,** 1353 (1992).
[14] R. L. Byer and C. B. Roundy: IEEE Trans. Sonics Ultrason. **19** (1972) 333.
[15] R. W. Whatmore, P. C. Osbond and N. M. Shorrocks: Ferroelectrics **76** (1987) 351.

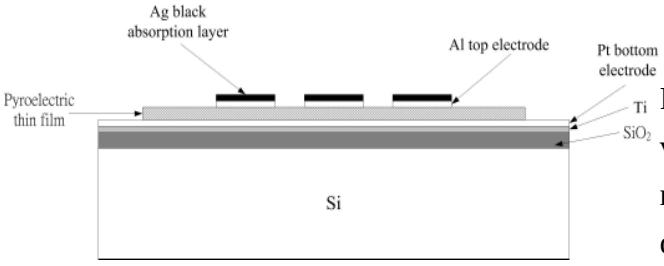

Fig. 1. A schematic diagram of the thin-film detector.

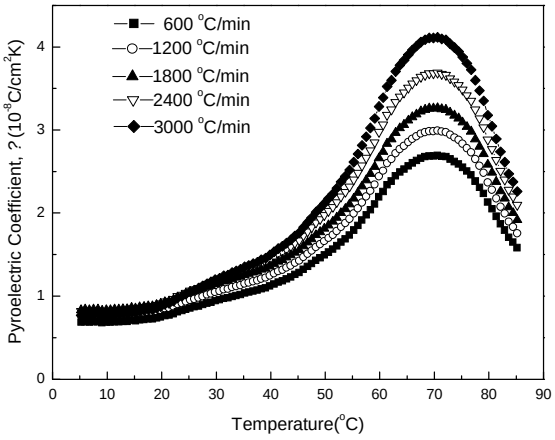

Fig. 2. The temperature dependence of the pyroelectric coefficient for the $LiTaO_3$ thin films heated at 700 ℃ with various heating rate of 600 ℃/min ~ 3000 ℃/min

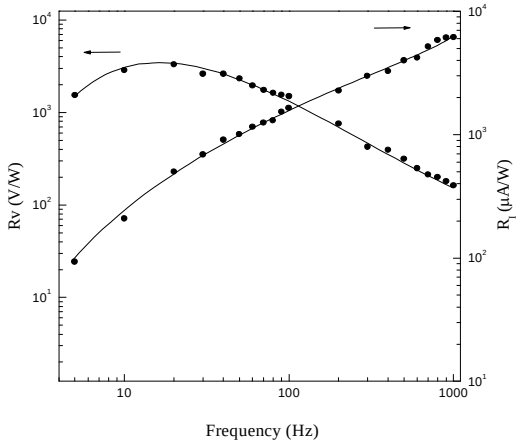

Fig. 3. Frequency dependence of the voltage responsivity (R_V) and current reponsivity (R_I) of $LiTaO_3$ thin film IR detector with heating rate of 1800 ℃/min.

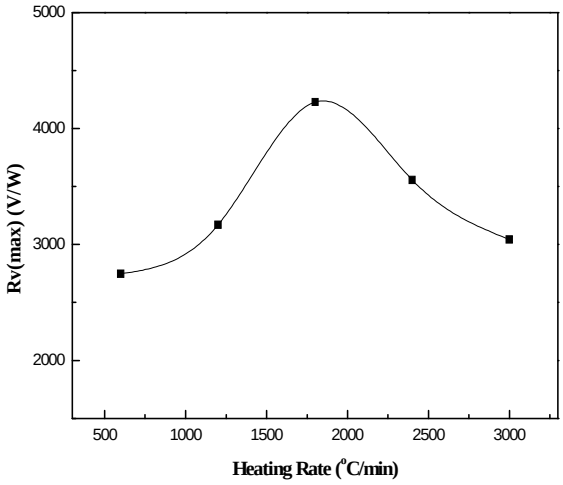

Fig. 4. Dependence of the maximum voltage reponsivity on heating rate at 20Hz.

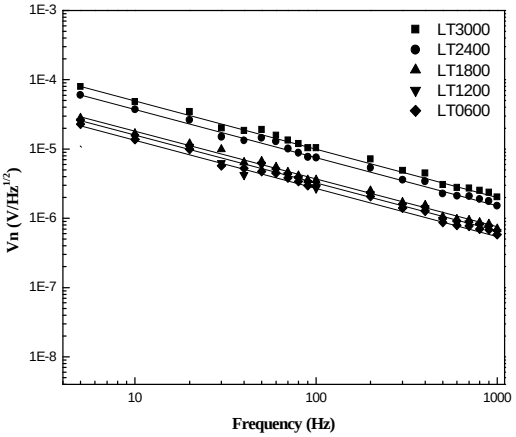

Fig. 5. Frequency dependence of the noise voltage per unit bandwidth for $LiTaO_3$ thin film IR detectors.

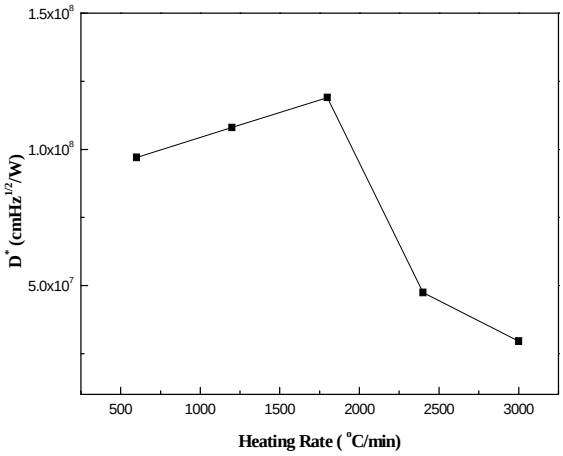

Fig. 7. Dependence of the maximum specific detectivity on heating rate at 300Hz.

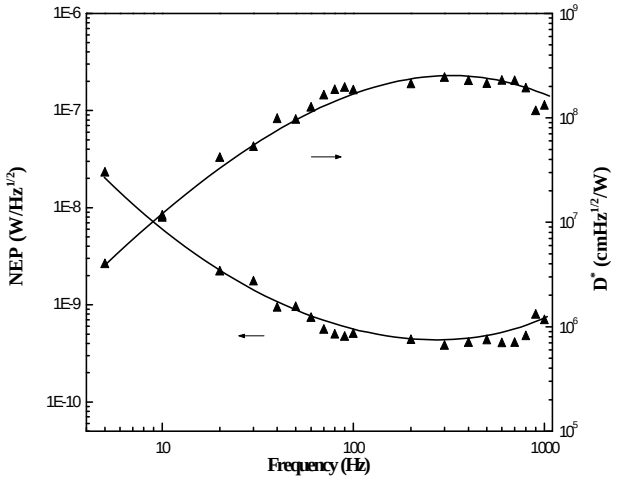

Fig. 6. Frequency dependence of the noise equivalent power and the specific detectivity of $LiTaO_3$ thin film IR detector with heating rate of 1800℃/min