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Effect of Different TiO_2 Preparation Techniques on the Performance of the Dielectric Bolometer $Ba_{06}Sr_{0.4}TiO_3$ as a Distance Sensor

(Kesan Kaedah Penyediaan TiO_2 yang Berbeza Terhadap Prestasi Bolometer Dielektrik $Ba_{06}Sr_{0.4}TiO_3$ sebagai Pengesan Jarak)

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ABSTRACT

In this study TiO_2 films have been prepared using two different techniques i.e. sol-gel and electron gun evaporation (e-gun) techniques. The films were annealed at 300, 350 and 400°C in air. The microstructure study using field emission scanning electron microscope and x-ray diffractometer showed nanometer grains size and only the film prepared by sol-gel and annealed at 400°C has anatase phase while others are amorphous. To study the effect of the films (as buffer layer) onto the dielectric bolometer $Ba_{0.6}Sr_{0.4}TiO_3$ as distance sensor, sensors with the configuration of Al/BST/TiO_2/RuO_2/SiO_2/Si were built. Two different measurements i.e. with and without infrared source were carried out to measure the sensitivity and repeatability of the sensors. The sensors which contained sol-gel TiO_2 films gave reading for both type of measurements, indicating that the sensor can act as active and passive sensors. However, the sensors which contained e-gun TiO_2 films only gave responses when the IR source was used, indicating that they can only act as passive sensors. The most sensitive sensor was TiO_2 film prepared by sol gel and annealed at 350°C. In general sensors which contained TiO_2 films prepared by sol gel showed good repeatability.

Keywords: Sol-gel; thin film; TiO_2

ABSTRAK

Dalam kajian ini, filem TiO_2 telah disediakan dengan dua teknik yang berbeza iaitu teknik sol-gel dan penyejatan senapang elektron (senapang-e). Filem kemudiannya disepuhlindap pada 300, 350 dan 400°C dalam udara biasa. Kajian mikrostruktur menggunakan mikroskop elektron imbasan pemancaran medan (FE-SEM) dan pembelauan sinar-X menunjukkan kesemua filem mempunyai saiz butiran nanometer dan hanya filem yang disediakan dengan sol-gel dan disepuhindap pada 400°C mempunyai fasa anatas sementara yang lain adalah amorfus. Untuk mengkaji kesan filem tersebut (sebagai lapisan penimbal) ke atas bolometer dielektrik $Ba_{0.6}Sr_{0.4}TiO_3$ sebagai pengesan jarak, sensor dengan konfigurasi Al/BST/TiO_2/RuO_2/SiO_2/Si telah dibina. Dua pengukuran yang berbeza iaitu dengan dan tanpa punca inframerah telah dijalankan untuk mengukur kesensitifan dan kebolehulangan pengesan. Pengesan yang mengandungi filem TiO_2 sol-gel memberikan bacaan untuk kedua-dua jenis pengukuran, menandakan pengesan ini boleh bertindak sebagai pengesan aktif dan pasif. Namun begitu, pengesan yang mengandungi filem TiO_2 senapang-e hanya memberi tindak balas apabila punca inframerah digunakan, menandakan pengesan hanya boleh bertindak sebagai pengesan pasif. Pengesan yang paling sensitif adalah pengesan dengan filem TiO_2 yang disediakan dengan sol-gel dan disepuhindap pada 350°C. Secara amnya pengesan yang mengandungi filem TiO_2 yang disediakan dengan sol-gel menunjukkan kebolehulangan yang baik.

Kata kunci: Filem nipis; sol-gel; TiO_2

INTRODUCTION

Titanium dioxide (TiO_2) thin film is an interesting material as it has high dielectric constant and can be used in various applications such as high-density dynamic memory (Stamate et al. 2000), gas sensors (Garzella et al. 2000) and distance sensors (Dewi 2009; Hanani 2005). In a distance sensor which contains barium strontium titanate (BST) as an active layer, TiO_2 has been used as a buffer layer. Dewi (2009) and Hanani (2005) have reported on the performance of passive distance sensors which consist of BST as the active layer and micrograins TiO_2 as a buffer layer however their buffer layers were not being properly studied. Recently it has been reported that the microstructure and electrical properties of (Pb,Sr)TiO_3 ferroelectric films can be improved by controlling the TiO_2 buffer layer (Chen et al. 2008). The microstrucure and electrical properties of $Ba_{0.5}Sr_{0.5}TiO_3$ can also be improved by controlling La_2O_3 buffer layers (Fan et al. 2009). The TiO_2 buffer layer can be prepared using various methods such as radio-frequency(rf) sputtering, ion-beam sputtering, laser ablation, metal-organic chemical vapor deposition, electron gun evaporation and sol-gel technique. However, sol-gel technique has become famous compared will the other techniques because it needs only low cost apparatus and its ability to produce high purity and homogen samples (Tsuzuki et al. 1998; Wu et al.

2000). The sol is made of solid particles of diameter of few hundreds nanometer suspended in a liquid phase. Then the particles are condensed in a new phase (gel) in which the solid macromolecule is immersed in a liquid phase (solvent) (Brinker et al. 1990). To transfer the gel into thin film form, two techniques can be used i.e. dipping and spin coating techniques. The electron gun evaporation technique (e-gun) is a form of physical vapor deposition. In this technique, the target material is bombarded with high energy electrons under high vacuum, resulting in formation of plasma. This plasma is then collected onto a substrate to produce thin film. In this study nano grains TiO_2 have been prepared using 2 different techniques i.e. sol-gel and e-gun techniques. The physical properties of the films were characterized and studied. Then the same films were used as buffer layers in dielectric bolometer $Ba_{0.6}Sr_{0.4}TiO_3$ sensors and the effect of the TiO_2 on the performance of the sensors was also investigated. To our knowledge, there is no report yet on the effect of these different TiO_2 preparation techniques (sol-gel and e-gun) on the performance of the dielectric bolometer $Ba_{06}Sr_{0.4}TiO_3$ as a distance sensor.

MATERIALS AND METHODS

The p-type silicon substrates were cleaned using acetone, methanol and distilled water. Then SiO_2 (150 nm) and RuO_2 (100 nm) films were deposited onto the substrates using electron gun evaporation technique. These substrates were used in both TiO_2 preparation techniques.

Titanium butoxide (1 mL) was disolved in 5 mL ethanol and stirred for 6 h at room temperature. Without stopping the stirring process, 0.3 mL ion free water and 0.4 mL hydrochloric acid were added to the solution. Then the stirring process was continued for another hour. The composition of the obtained gel was $Ti(OC_4H_9)_4:C_2H_5OH:H_2O:HCl = 1:26.5:1:1$. To transfer the gel into thin film form a spin coater was used. The spinning rate was 2,500 rpm within duration of 30 s. All of the films were dried at 50°C in air for an hour in order to get rid of the solvent, followed by the annealing process at 300, 350 and 400°C for 30 min in air.

The microstructures of the films were studied using X-ray diffractometer (XRD) (Bruker D8 Advance) and field emission scanning electron microscope (FE-SEM) (model Supra 55VP). The FE-SEM was also used to measure the films thickness. As the annealing temperature increased, the films thickness also increased (Table 1).

To study the effect of the prepared TiO_2 films on the performance of the dielectric bolometer, $Ba_{0.6}Sr_{0.4}TiO_3$ (BST) were prepared on the films by sol-gel process. The detail of the BST preparation technique has been reported elsewhere (Dewi et al. 2009). Aluminium film (100 nm) which acts as the upper electrodes were deposited by e-gun technique. The final configuration of the sensor was $Al/BST/TiO_2/RuO_2/SiO_2/Si$.

TiO_2 (0.25 g) was pressed into pellet form using hydraulic pump and was used as a target in the e-gun technique. Table 2 shows the preparation parameters. The thickness of the films follow the thickness of the sol-gel films.

Then the films were annealed at 300, 350 and 400°C for 30 min in air. Similar procedures were also applied to the e-gun films in order to investigate the effect of the e-gun films onto the performance of the dielectric bolometer.

RESULTS AND DISCUSSION

The XRD patterns of all of the films prepared using the sol-gel and e-gun techniques are shown in Figure 1. All of the films except the sol-gel film annealed at 400°C are amorphous. The sol-gel film annealed at 400°C has crystallized into an anatase phase. These results showed that all of the films need higher annealing temperature in order to be crystallined.

TABLE 1. The TiO_2 sol-gel films thicknesses measured by FE-SEM

Annealing temperature (°C)	Film thickness (± 0.1 nm)
As deposited	190.0
300	218.1
350	222.8
400	230.1

TABLE 2. The e-gun preparation parameter for TiO_2 films

Parameter	Value
Power (watt)	120
Pressure ratio of $Ar:O_2$	3:1
Thickness (nm)	190, 218.1,222.8,230.1
Distance between target and substrate(cm)	5
Pressure (Mbar)	2.5×10^{-5}

The size of the films grains were measured using the FE-SEM. Figures 2 and 3 show the micrographs of the sol-gel and e-gun prepared films, respectively. The average values (Table 3) clearly show that both sol-gel and e-gun techniques were capable in producing films with nanometer grain size. All of the films showed that the thickness increased with the annealing temperature, which could be due to the increment of the grain size. However, film with the same thickness but produced by different technique have different grain size, in other word sol-gel technique produce films with smaller grains compared with the e-gun technique.

In order to investigate the effect of the TiO_2 films on the performance of BST distance sensor, $Ba_{0.6}Sr_{0.4}TiO_3$ films (~ 430 nm) were deposited using sol-gel technique onto the TiO_2 films followed by Al (~ 100 nm) using e-gun technique. The final configurations of the sensors were $Al/BST/TiO_2/RuO_2/SiO_2/Si$. The upper and lower electrodes were Al and RuO_2, respectively. Two different measurements i.e. with and without IR source were carried out in order to measure the farthest distance that the sensor can detect. The schematic diagram of the sensor setup is shown in Figure 4. Details of the setup have been discussed elsewhere (Efil et al. 2010). For the measurement with IR, the source was fixed throughout the measurement while the distance of the sensor was varied in a sraight line with respect to the IR source. The IR source was replaced by a piece of paper during the measurement without the IR souce. The results are tabulated in Table 4.

Sensors with sol-gel TiO_2 films gave reading for both type of measurements, indicating that the sensors can act as active and passive sensors. However, the sensors with e-gun TiO_2 films only gave response when IR source was used, indicating that the sensors can only act as a pasive sensor. The farthest distance i.e. 100 cm was measured using the sensor with TiO_2 film prepared by sol-gel and annealed at 350°C. The active layer of the sensor i.e. BST

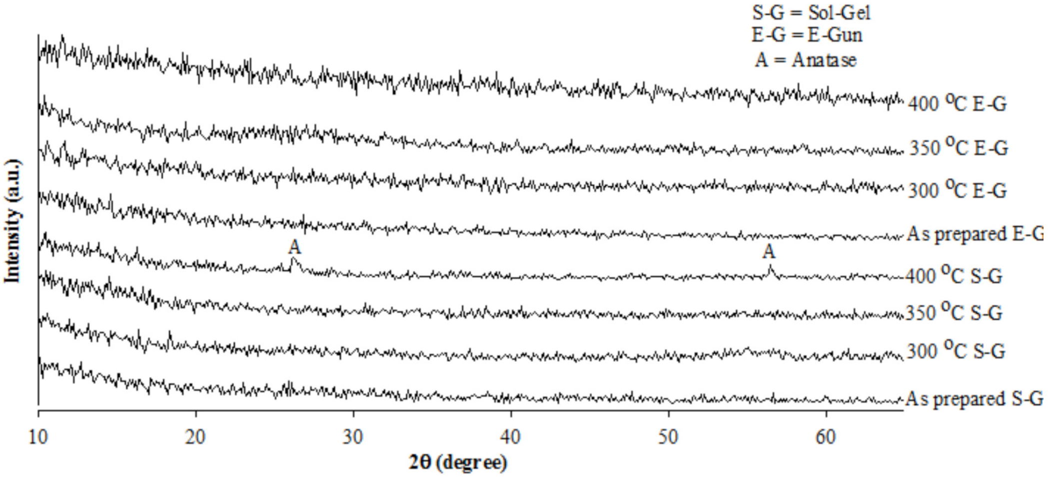

FIGURE 1. X-ray diffraction patterns of TiO_2 thin films prepared by sol-gel and e-gun techniques

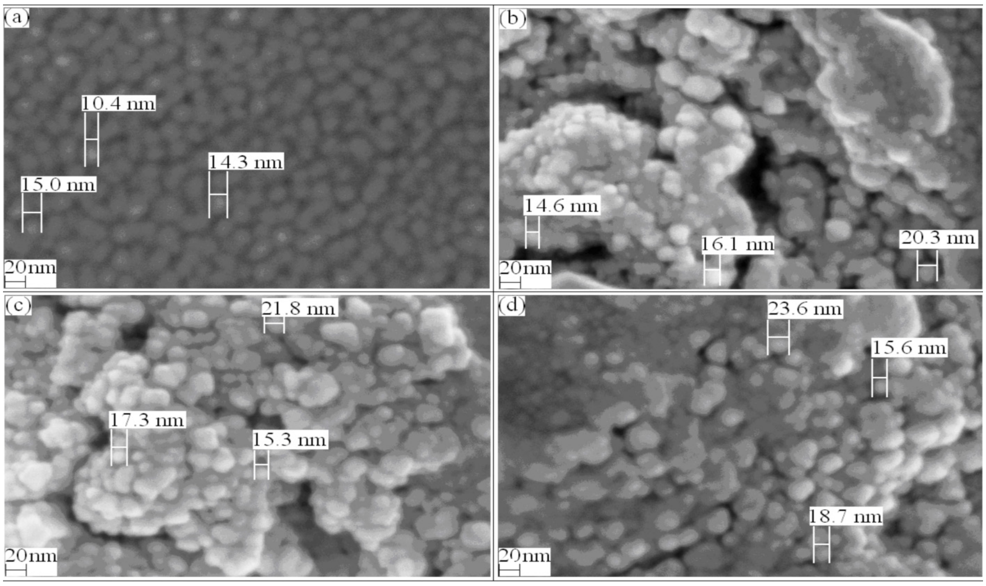

FIGURE 2. FESEM micrographs of the films prepared using sol-gel technique,
(a) as prepared, annealed at (b) 300, (c) 350 and (d) 400°C

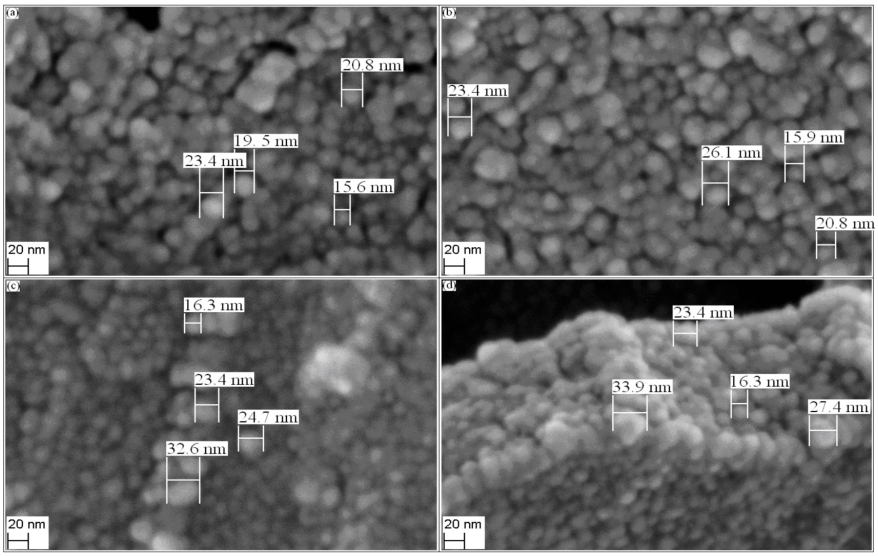

FIGURE 3. FESEM micrographs of the films prepared using e-gun technique, (a) as prepared, annealed at (b) 300, (c) 350 and (d) 400°C

TABLE 3. The summary of the thickness and grain size of the films prepared by sol-gel and e-gun technique

Preparation technique	Annealing temperature (°C)	Thickness (±0.1) nm	Average grain size (±0.1) nm
Sol gel	As prepared	190.0	13.2
	300	218.1	17.0
	350	222.8	18.1
	400	230.1	19.3
E-gun	As deposited	190.0	19.8
	300	218.1	21.6
	350	222.8	24.2
	400	230.1	25.2

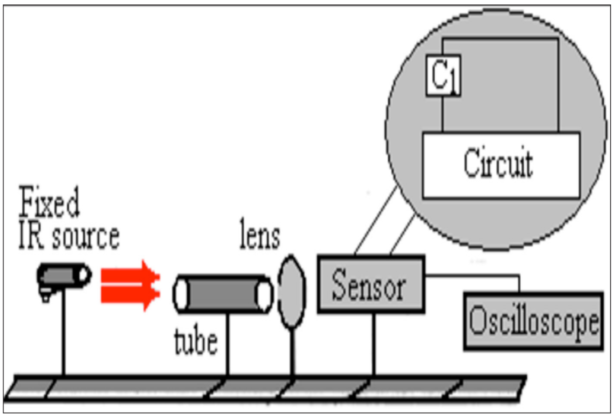

FIGURE 4. Schematic set-up for measuring the sensitivity and repeatability of the sensors

TABLE 4. The summary of the average grain size, sensor sensitivity and repeatability (with and without IR source)

Preparation technique	Annealing temperature (°C)	Average grain size (±0.1) nm	Sensor sensitivity with IR source (±2) cm	Sensor sensitivity without IR source (±2) cm	Sensor repeatability with IR source (±2) cm	Sensor repeatability without IR source (±2) cm
Sol gel	As deposited	13.2	0 - 20	0-5	Bad	Bad
	300	17.0	0 – 110	0-10	Good	Good
	350	18.1	0-140	0-40	Good	Good
	400	19.3	0-100	0-15	Good	Bad
E-gun	As deposited	19.8	0-15	None	Good	None
	300	21.6	0-30	None	Good	None
	350	24.2	0-20	None	Good	None
	400	25.2	0	None	Bad	None

films were directly deposited onto the TiO_2 bufer layer. Smaller grains TiO_2 are closed pack and the distance between grains were small. Hence the possibilty of the BST leaking to the buffer layer was small and thus the current leakage was also small. To confirm these we measured the current density of the sensors and the results are shown in Figures 5 and 6. Sensors with e-gun films showed higher current leakage compared with the sensors with sol-gel films.

The repeatability of the sensors were also measured and Figure 7 shows the typical results. Table 4 summarises the results for all of the sensors. For the measurement with IR source, only sensor with the as prepared sol-gel film does not show good repeatability while others show good results. The sensors with sol-gel films annealed at 300 and 350°C also show good repeatability for the measurement without IR source.

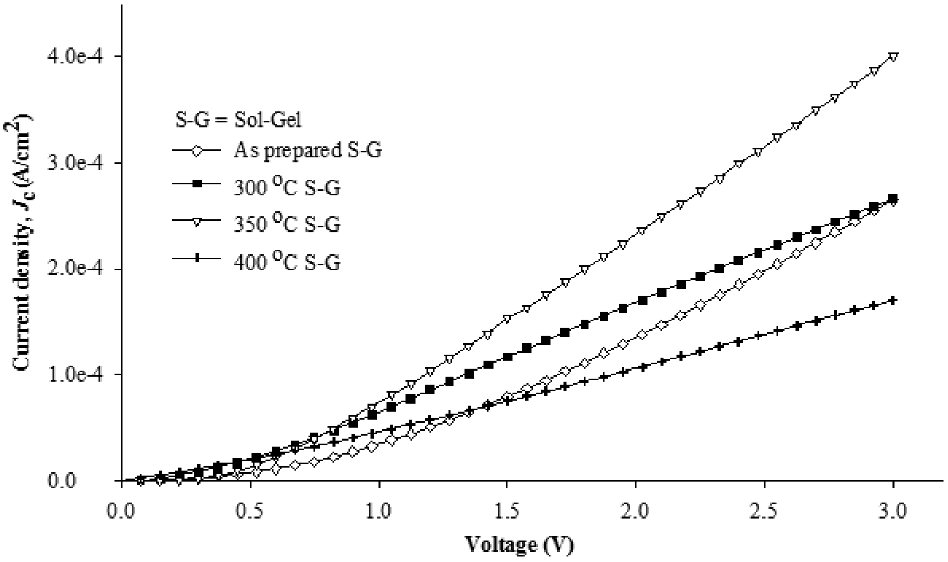

FIGURE 5. Current density of TiO_2 thin films prepared by sol-gel technique

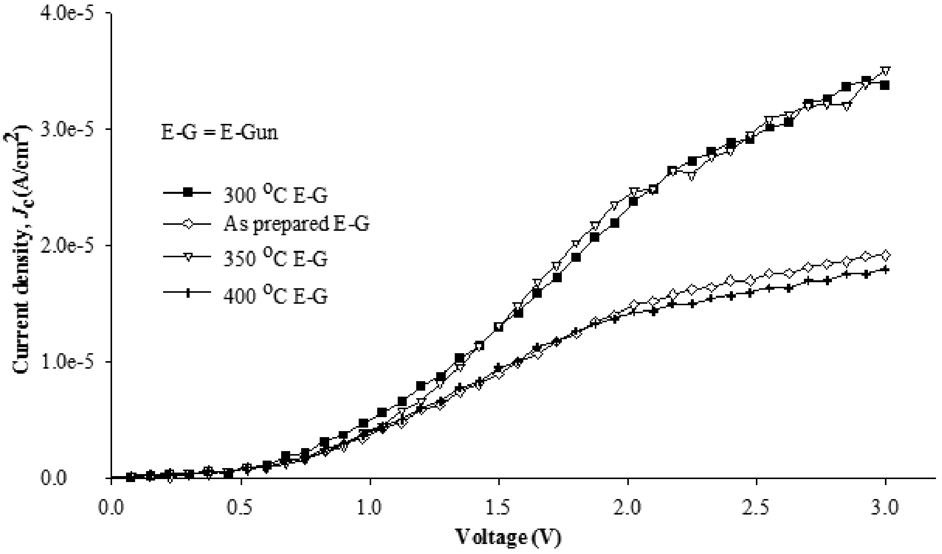

FIGURE 6. Current density of TiO_2 thin films prepared by e-gun technique

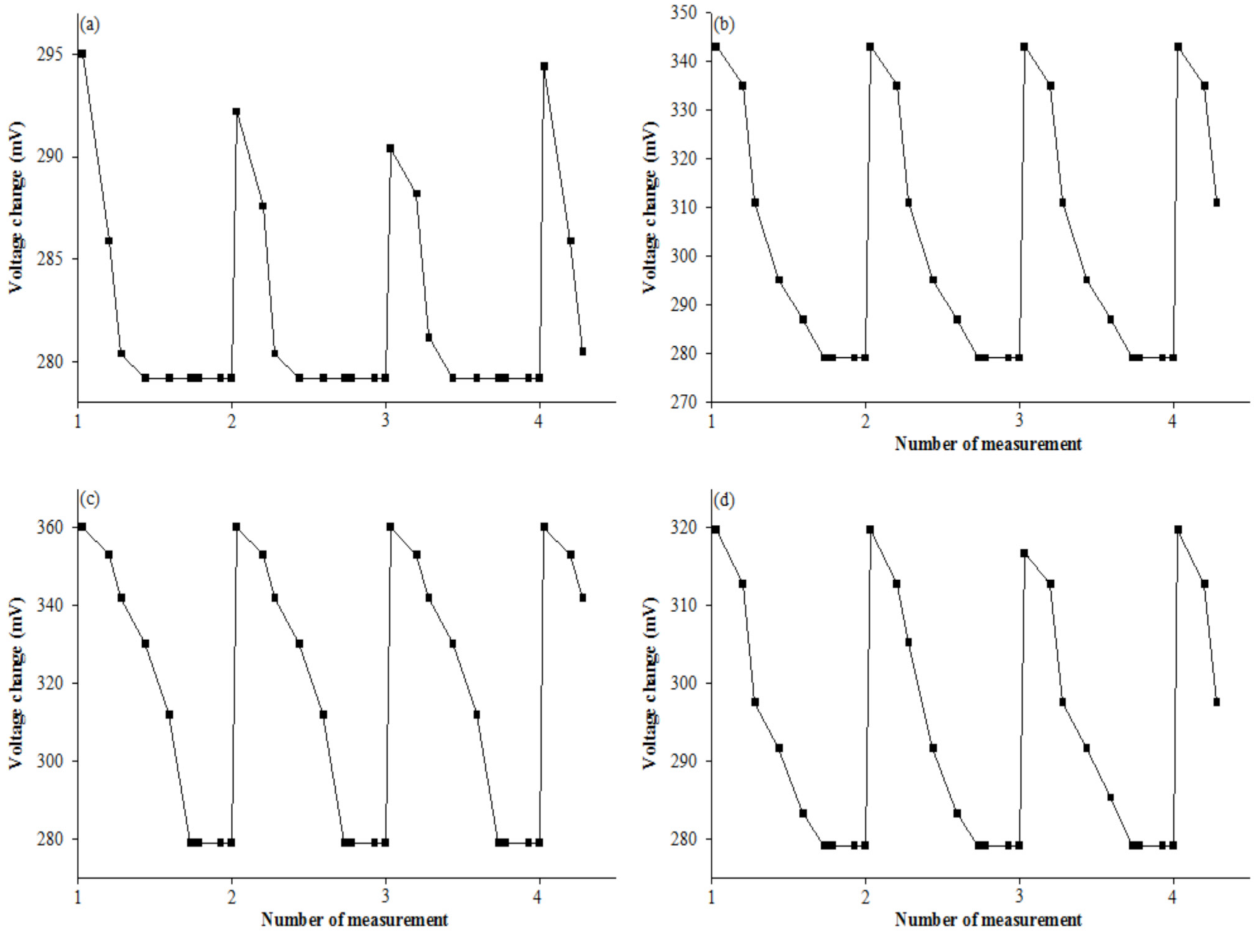

FIGURE 7. Typical results of the repeatability of the sensors with sol-gel TiO_2 (a) as prepared, annealed at (b) 300, (c) 350 and (d) 400°C

CONCLUSION

Both sol-gel and e-gun techniques were capable in producing films with nanometer size grains, however the sol-gel technique produced smaller grains films. Sensors with sol-gel TiO_2 can act as active sensors and also showed good repeatability. This could be due to the smaller grains in the film thus increasing the current density of the sensors. The farthest distance was measured by sensor with TiO_2 sol gel annealed at 350°C. This sensor also showed the best repeatability.

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REFERENCES

Brinker, C.J. & Scherer, G.W. 1990. *Sol-Gel Science: The Physics and Chemistry of Sol-Gel Processing*. New York: Academic Press.

Chen, L., Shen, M., Fang, L. & Xu, Y. 2008. Microstructure control of $(Pb,Sr)TiO_3$ films on Pt/Ti/SiO2/Si substrates by a TiO_2 buffer layer. *Thin Solid Films* 516: 1285-1289.

Dewi, R., Baa'yah, N.I. & Talib, I.A. 2007. The effect of spin coating rate on the microstructure, grain size, surface roughness and thickness of $Ba_{0.6}Sr_{0.4}TiO_3$ thin film prepared by the sol-gel process. *Materials Science-Poland* 25(3): 657-662.

Dewi, R. 2009. Distance sensor based on nanoparticles of barium strontium titanate. PhD Thesis. Universiti Kebangsaan Malaysia, Bangi (unpublished).

Efil Yusrianto, Noor Baa'yah Ibrahim & Zahari Ibarahim. 2010. The effect of TiO_2 thin films on the sensitivity, repeatability and current density of the dieectric bolometer $Ba_{0.6}Sr_{0.4}TiO_3$ as a distance sensor. *Solid State Science and Technology* 18(2) 52-60.

Fan, Y., Yu, S., Sun, R., Li, L, Du, R. & Yin, Y. 2009. Microstructure and electrical properties of $Ba_{0.5}Sr_{0.5}TiO_3$ thin films prepared on copper foils with La_2O_3 buffer layers. *Applied Surface Science* 255: 8319-8323.

Garzela, C., Comini, E., Tempesti, E., Frigeri, C. & Sberveglieri, G. 2000. TiO_2 thin films by a novel sol-gel processing for gas sensor applications. *Sensors and Actuators B*(68): 189-196.

Hanani, N. 2005 The development of barium strontium titanate ceramics bolometer as a distance sensor. Master Thesis. Universiti Kebangsaan Malaysia, Bangi (unpublished).

Stamate, M.D. 2000. Dielectric properties of TiO_2 thin films deposited by a DC magnetron sputtering system. *Thin Solid Films* 372: 246-249.

Tsuzuki, A., Kato, K., Kusumoto, K. & Torh, Y. 1998. Preparation and characterization of $Ba_{1-x}Sr_xTiO_3$ films by sol-gel processing. *J. Mater. Sci*. 33: 3055-3058

Wu, D., Li, A., Ling, H., Yin, X., Ge, C., Wang, M & Ming, N. 2000. Preparation of $(Ba_{0.5}Sr_{0.5}TiO_3$ thin films by sol-gel method with rapid thermal anneaing. *J. Appl. Surface Sci*. 165: 309-314.

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