UNIVERSITI TEKNOLOGI MARA

FERROELECTRIC PROPERTIES OF PVDF-TRFE (70:30 mol%)/MgO NANOCOMPOSITE THIN FILM

MOHAMAD HAFIZ BIN MOHD WAHID

Thesis submitted in fulfilment
of the requirement for the degree of
Doctor of Philosophy

Faculty of Applied Sciences

July 2017

ABSTRACT

This research proposed study on new nanocomposite material for the application of electrical devices, which utilized fluoropolymer and nanofiller. Nanocomposite thin films with MgO loading percentages of 1, 3, 5, and 7 % incorporated in PVDF-TrFE polymer matrix were produced by spin coating technique on Al-glass substrates. The PVDF-TrFE thin films were annealed and recrystallized in accordance to the transition temperatures (T_c, T_m and T_{crys}) of PVDF-TrFE determined through the observation of the DSC spectra. The annealed PVDF-TrFE thin film (AN113) showed significant improvement in the ferroelectric properties with rectangular shape hysteresis loops for a range of applied voltage. Most importantly, the annealed AN113 film sustained electrical breakdown unlike the recrystallized thin films (RC154, RC135 and RC55). The P_r value recorded for AN113 thin film at applied voltage of 100 V was 77 mC/m^2, with E_c of 88 MV/m. The morphology of AN113 thin film was also observed to be defect free, as evident from FESEM images. The high intensity peaks at 1288 cm^{-1} and 845 cm^{-1}, observed from the FTIR spectrum showed most of the dipoles in AN113 thin film were aligned parallel to the b-axis. Further annealing of PVDF-TrFE thin film at 120°C (AN120), showed a significant increased in the P_r to a value of 93 mC/m^2 and E_c of 74 MV/m at 100 V applied voltage. With the incorporation of MgO nanofiller in PVDF-TrFE, the AN120/3%MgO nanocomposite thin film showed the highest P_r of 88 mC/m^2 with E_c of 79 MV/m at 100 V, relative to the P_r and E_c values obtained for nanocomposite thin films filled with MgO at loading percentages of 1, 5 and 7%. Further increased in MgO loading percentage, produced a drop in crystallinity, as shown by the decrement in the XRD peak diffraction at 2θ = 19.2°. It is noteworthy to mention that from the observation of the XRD peak diffraction patterns, peak at 2θ = 17.5°emerged for AN120/5%MgO and AN120/7%MgO films, which indicated the presence of α phase crystals in these nanocomposite films. These unfavourable non-polar crystals have little contribution to ferroelectric properties of the nanocomposite thin films. Therefore, it is established in this study, the favourable thin film produced with enhanced ferroelectric was the annealed PVDF-TrFE thin film at 120°C and loaded with 3% MgO nanofiller.

ACKNOWLEGEMENTS

Alhamdulillah, all praises to Allah S.W.T for His strength and blessings in completing this thesis. I would like to express my greatest and sincere gratitude to my supervisor, Assoc. Prof. Dr. Rozana Mohd. Dahan for her continuous support, encouragement and motivation during my study. Her guidance helped me in the research and writing of this thesis.

My sincere thanks also goes to my co-supervisors, Assoc. Prof. Dr. Siti Zaleha Sa'ad, Prof. Dr. Mohamad Rusop Mahmood (Faculty of Electrical Engineering, UiTM) and Prof. Dr. Wan Haliza Abd Majid (Faculty of Science, Universiti Malaya), who had provided me an opportunity to join their research team and had given access to their laboratories and research facilities. Without their precious support, it would not be possible for me to complete this study.

I would also like to express my appreciation to the Faculty of Applied Sciences, Institute of Graduate Study (IGS) and Institute of Research Management and Innovation (IRMI) of Universiti Teknologi MARA for the financial supports and funding towards the research. I wish also to acknowledge all laboratory and administration staffs of Faculty of Applied Sciences, NANO-SciTech Centre, NANO-Electronic Centre and Microwave Technology Centre of UiTM Shah Alam, especially En. Khairul Nizam, En. Anuar, En. Hayub, En. Abul, Puan Nurul Wahida, En.Salifairus, En.Azlan, En.Shahril, En.Azwan and En Khairil for their continuous untold cooperation throughout the journey of my study.

I also wish to take this opportunity to say thanks, especially to good friends Adillah Nurashikin Arshad, Muhamad Naiman Sarip and Siti Munira Yahaya, to my fellow colleague Dr. Habibah Zulkefle, Dr. Lyly Nyl Ismail, Dr. W.C. Gan (Universiti Malaya), for their critical comments, suggestions and enthusiasm in publishing research papers and most of all, for their never-ending words of encouragement.

Finally, I must express my very profound appreciation to my beloved parents, Mohd Wahid Israh and and my lovely wife, Siti Zulaikha Ibrahim for providing me with unfailing support and continuous encouragement throughout my years of study. This accomplishment would not have been possible without them.

TABLE OF CONTENT

CHAPTER ONE
INTRODUCTION

1.1 INTRODUCTION

Researchers in the field of atomic and molecular interactions are continuing to push the frontiers by enhancing knowledge needed to progress in the technology of miniaturization. The current global research interest focuses on the manufacture of structures that are few microns or nanometer thick. Rapid growth in electronic products forces manufacturers to design small and light weight multifunctional devices for the current demanding lifestyle.

Conventional electronic components such as sensors, transducers, capacitors, and memory devices are conventionally made of highly dense and brittle ceramic materials, which is a challenge especially for intricate and miniature parts made of ceramic due to its high temperature and several complex stages of processing. However, these problems can be overcome with the utilization of both polymeric material and ceramic, also known as composite materials [9]. Composite materials comprise of materials with two different phase or more [10]. Polymers with their high flexibility, lightweight and high mechanical properties are usually utilized in combination with ceramic materials. Interestingly, these polymer-based composites can be fabricated into many shapes and sizes at relatively low temperatures. The cost and time taken to produce these polymer composite parts are far much less in comparison to ceramic products.

Homopolymer polyvinylidenefluoride (PVDF) and its copolymer, polyvinylidenefluoride-trifluoroethylene (PVDF-TrFE) stand out from other polymers owing to its good relative permittivity value ($\varepsilon = 7 \sim 13$), excellence performance as piezo-, pyro- and ferroelectric materials [2-3]. The ferroelectricity in PVDF-TrFE copolymer is induced by the parallel packing of the all-trans conformation of chain molecules, which resulted in large spontaneous polarization [11]. This makes PVDF-TrFE a suitable polymer to be employed in memory and storage devices. The performance of PVDF-TrFE in memory device depends mainly on the value of its remnant polarization (P_r), which is largely affected by the crystallinity of the β phase