UNIVERSITI TEKNIKAL MALAYSIA MELAKA

UNIVERSITI TEKNIKAL MALAYSIA MELAKA (UTeM)

EFFECT OF DIFFERENT COATING LAYER OF ALKALI NIOBATE (KNN) THIN FILM THROUGH SOL-GEL TECHNIQUE

This report is summited with requirement of the Universiti Teknikal Malaysia Melaka (UTeM) for the Bachelor Degree of Manufacturing Engineering (Engineering Materials)

(Hons.)

By

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I hereby, declared this report entitled 'Effect of different coating layer of alkali niobate (KNN) thin film through sol-gel technique' is the results of my own research except as cited in references.

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APPROVAL

This report is submitted to the Faculty of Manufacturing Engineering of UTeM as a partial fulfillment to the requirements for the degree of Bachelor of Manufacturing Engineering (Engineering Materials) (Hons.). The member of the supervisory is as follow:

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PM Dr Mohd Warikh Bin Abd Rashid)

ABSTRACT

Piezoelectric ceramic thin film has become worldwide attention as current used materials for the application contains hazardous substances. In this report, the alternative material for piezoelectric ceramic thin film which is various coating layer of alkali niobate through sol-gel technique is investigated. Alkali niobate are used as the raw material in this research. The requirement in this research is to analyse the physical and mechanical properties of various coating layer of Alkaline niobate. In this experiment, the raw materials were mix with 2-metoxyethanol and acetylacetone as solvent and chelating agent respectively to obtain 1.0M sol concentration, using Sol-gel technique at 2000 rpm for 30s. Sol precursor preparation and substrate preparation are fabricated and processed in parallels and both were combined in spin coating process. Sol precursor and prepared Ti/Pt substrate is then sputtered using spin coating machine. Coated substrate is then calcined at 350°C for 3 minutes and annealed at 650°C for 1 hour. The sample is then tested physically and mechanically in order to determine the physical and mechanical properties of rare earth doped KNN thin film. The test involves in this research X-ray diffraction (XRD), Raman spectroscopy and Scanning electron microscopic (SEM).

ABSTRAK

Piezoelektrik filem nipis seramik telah menjadi perhatian di seluruh dunia sebagai bahan-bahan yang digunakan semasa bagi permohonan itu mengandungi bahan berbahaya. Dalam laporan ini, bahan alternatif untuk piezoelektrik filem nipis seramik yang pelbagai lapisan lapisan niobate alkali melalui teknik sol-gel disiasat. Niobate alkali digunakan sebagai bahan mentah dalam kajian ini. Keperluan dalam kajian ini adalah untuk menganalisis sifat-sifat fizikal dan mekanikal pelbagai lapisan lapisan niobate Alkali. Dalam eksperimen ini, bahan-bahan mentah adalah campuran dengan 2-metoxyethanol dan acetylacetone sebagai ejen chelating pelarut dan masing-masing untuk mendapatkan sol kepekatan 1.0M, dengan menggunakan teknik Sol-gel pada 2000 rpm untuk 30-an. Sol penyediaan pelopor dan penyediaan substrat adalah direka dan diproses dalam persamaan dan kedua-dua telah digabungkan dalam proses salutan putaran. Sol pelopor dan disediakan Ti / Pt substrat kemudiannya terpercit menggunakan mesin salutan putaran. Substrat dilapisi kemudian calcined pada 350 ° C selama 3 minit dan disepuh lindap pada 650 ° C selama 1 jam. Sampel ini kemudiannya diuji dari segi fizikal dan mekanikal untuk menentukan sifat-sifat fizikal dan mekanikal nadir bumi didopkan KNN filem nipis. Ujian ini terlibat dalam penyelidikan ini pembelauan sinar-X (XRD), spektroskopi Raman dan Mengimbas elektron mikroskopik (SEM).

DEDICATION

To my parents and family member for their continuous support through my study.

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LIST OF ABBREVIATIONS, SYMBOLS AND NOMENCLATURE

°C	-	degree celsius
µm	-	micrometre
ALD	-	atomic layer deposition
$CH_3COCH_2CH_2OH$	-	acetylacetone
CH_3COOK	-	potassium acetate
CH_3COONA	-	sodium acetate
$CH_3OCH_2CH_2OH$	-	2-metoxyethanol
CVD	-	chemical vapour deposition
FWHM	-	full width half maximum
g	-	Gram
g/mol	-	gram per mol
GaAS	-	gallium arsenide
IC	-	integrated circuit
InP	-	indium phosphide
KNN	-	potassium sodium niobate
min	-	minute
ml	-	millilitre

nm	-	nanometre
Pt	-	platinum
PVD	-	physical vapour deposition
PZT	-	lead zirconate titanate
RoHS	-	restriction of hazardous substance
rpm	-	rotation per minutes
SEM	-	scanning electron microscope
Si	-	silica
SOI	-	silicon on insulator
T_C	-	curie temperature
TEM	-	tunnelling electron microscope
Ti	-	titanium
WEEE	-	waste electrical and electronic equipment
XRD	-	x-ray diffraction
ϴ	-	theta

CHAPTER 1

INTRODUCTION

1.1 Background

Rapid development in electronic industry nowadays has given a huge impact on the studies of the piezoelectric materials. The impact effected by this the demand of new material with better properties is always sought to fulfil the industry need to producing a better feature with green technology to the user. Materials like ceramics have been greatly improvised with research and development of the ceramics into a better generation of fine ceramic or also known as advance ceramic.

Advance ceramics can be made to have a wide variety of unique properties characteristic through variations in raw material, synthesizing method and processing. These unique properties can be obtained by altering the raw materials selection such as zirconia, alumina, silicon carbide and aluminium nitrate. As results, the properties of each advance ceramic material can be uniquely formulated for a specific properties, behaviour and functional according to various desired application.

With excellence dielectric and piezoelectric properties, advance ceramic have been served as based material for essential electronic component including highly efficient capacitor, actuators, sensors, resonator and thin film. Microelectronic chip manufacturing has considered as one of the fastest industry in term of utilize advance ceramic uses for its application.

One of advance ceramic that is fabricate for this purposes is piezoelectric material based on $(K,Na)NbO_3$ due to its moderate dielectric constant and optimum piezoelectric response as well as its friendly properties of lead-free materials. KNN has been a priority of thin film fabrication to replacing widely used lead zirconate titanate or PZT due to the facts that this ceramics contain about 60% lead, and therefore represent a possible ecological hazard, Malic et al., (2005). The switch idea of PZT to KNN is supported by the law that enforced in 2006, that the Waste Electrical and Electronic Equipment (WEEE) and restriction of the use of certain Hazardous Substances in electrical and electronic equipment (RoHS), with purpose of protecting health as well as environment by exclusion of hazardous substances in electronic devices, Li et al., (2012).

Active research was never stop to seek the best outcome possible out of advance ceramics which leads to idea of properties enhancement and manipulate of KNN structure by varies the deposition layer of KNN on Si substrate.

1.2 Problem statement

In past years, potassium sodium niobate (KNN) has been actively researched. As the only known lead free system compared to commonly use lead zirconate titanate (PZT), according to Wang, (2002) large amount of lead contained in PZT materials has drawn much attention due to environmental concern as well as regulation against hazardous substances. KNN has become the best option for replacing PZT in electrical devices, including in thin film application.

In order to utilize the KNN thin film application by enhancing the piezoelectric, ferroelectric reliability and coupling constant, different number of coating layer was deposited. Since different layer of deposition alter its own unique properties in particular their ferroelectric and piezoelectric compatible properties. It is interesting to note that Du, (2006) concluded from the investigation various layers that processing comparable influence on the piezoelectric and mechanical properties of KNN to doping.

The increment of KNN coating layer was effectively proved to enhance the insulating and ferroelectric properties because of the reduced oxygen vacancies Yao, (2005). The thin films were reported to have relatively low Curie temperature, high-fatigue resistance, low-processing temperature and large remnant polarization. Watanabe, (2002) explained that the role of alkaline substituting volatile Bi-site is to suppress the A-site vacancies accompanied with oxygen vacancies which act as space charge is varies as different coating layer.

Therefore, some researchers suggested the possibility for the thin film to reduce the processing temperature and leakage current density and improve ferroelectric properties. Noguchi et al., (2002) investigate that the effect of concentration and distribution of defects controlled by quenching and doping of high-valence electron vacancies on ferroelectric properties.

The deposition of thin film technique fall into two categories which is chemical deposition and physical deposition. However, the physical deposition technique is preferred in advance thin film industry. Physical deposition technique uses mechanical, electromechanical to produce a thin film of solid. One of the techniques in physical deposition is sputtering, which relies on plasma to knock material from a 'target' a few atoms at a time. Sputtering is a fast technique and also provides a good thickness control of a thin film (micrometre) in thickness.

With a high stress on producing a non-hazard product in industries, lead-free piezoelectric with better properties is required. However, in many cases the doping mechanism and defect chemistry remain poorly understand.

1.3 Objective

The objectives of this project are:

i. To fabricate multiple layers of KNN thin film via sol-gel method
ii. To analyze properties enhancement of KNN thin film on physical, electrical and morphological properties

1.4 Scope

The scope of this research is to analyze the crystal structure, crystal plane, polarization, dielectric and morphology of pure potassium sodium niobate (KNN) in thin film. Multiple layers of KNN will be deposited onto silicon (Si) substrate. The sample will be prepared for 5 different layers and analyzed later on.

The research is start with mixture of raw material Potassium acetate (CH_3COOK), sodium acetate (CH_3COONa) and niobium pentaethoxide ($Nb(OCH_2CH_3)_5$ with 2-metoxyethanol ($CH_3OCH_2CH_2OH$) and acetylacetone ($CH_3COCH_2CH_2OH$) as solvent and chelating agent, using Sol-gel technique. Sol solution and Si substrate is then sputtered using spin coating machine before calcined and annealed.

The raw material preparation and substrate preparation will be fabricate and processed in parallels and both will be combined in spin coating process later on. The sol precursor of raw material via sol-gel technique will be spin coated onto SOI substrate.

Further detail in the methodology will be mainly based on different deposition layer of KNN based materials using sol-gel method. The mixing will then prepared to be at 1.0M in concentration. The sol precursor will then spin-coated with spin coating technique on silicon on insulator (SOI) substrate prepared using sputtering technique. The substances will be followed up with calcined and annealing processes into thin film. Finally, the sample surface morphology will be checked with SEM and analysis of crystal structure and plane will be done with X-ray diffraction (XRD) machine.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

This chapter is describing about the basic fundamental of piezoelectric material mainly on potassium sodium niobate (KNN) which is focused on thin film. This chapter also give brief description of the fundamental processing method of thin film piezoelectric. The characteristic of pure KNN will also be elaborated in this chapter.

2.2 Piezoelectric

Piezoelectric material is refers to materials that generate charges on the surface of the material with pressure. The word "piezo" itself is originated from the Greek word meaning pressure. In other words, crystals which gain a charge when it is compressed, distorted or twisted are claims to be piezoelectric materials. This behaviour provides a convenient transducer effect between mechanical and electrical properties. Based on Castleman et al.,(2007) If an electrical oscillation is applied to piezoelectric ceramic wafers such as PZT, they will respond with mechanical vibrations which provide the ultrasonic sound source. This is how piezoelectric material is used in electronic industry.

2.2.1 Piezoelectric effect

Piezoelectric effect is also known as either generator or sensor effect; the effect converts mechanical energy into electrical energy, Priya, S. (2007). The mechanism of the piezoelectric effect is relatedly similar to the mechanism of electric dipole moments in solids. The piezoelectric effect can be found not only in monocrystalline materials but also in polycrystalline ferroelectric ceramics. In single crystal structure, the condition for the effect to occur is simply by formation of asymmetry in structure crystal lattice unit cell, which is generally a form below the Curie temperature T_c.

The decisive consequentiality for the piezoelectric effect is whenever a mechanical stress is applied to the piezoelectric material, the polarization P is changes Ok, K. M. et al., (2006). This phenomenon might either be caused by a re-configuration of the dipole-inducing or by re-orientation of molecular dipole moments resulting from the influence of the external stress.

2.2.2 Piezoelectric Coefficient

The piezoelectric coefficient is the parameter in piezoelectric a ceramic material that is aim to be controlled and altered to achieve certain value and controlling the piezoceramic properties suitable to application of the material. Some of the related piezoelectric coefficient are permittivity ε, piezo modulus d_{ij}, piezoelectric voltage coefficient g_{ij}, mechanical quality factor Q_m, coupling Factors, k.

2.2.2.1 Permittivity ε

The permittivity, ε is the ratio of the absolute permittivity of the material by the permittivity in vacuum ($\varepsilon_0 = 8.85 \times 10^{-12}$ F/m), as the absolute permittivity is a quantification of the polarizability in the electrical field. The dependency of the dielectric displacement and the dielectric coefficient from the orientation of the electric field is designated by the corresponding indices, Yokoyama, S. et al.,(2006).

2.3 Electrical properties

2.3.1 Piezoelectric

Piezoelectric materials are utilized for fabrication of electrical devices that convert mechanical forces into electrical signals (direct piezo effect), inverse piezo effect where electrical signals is changes into mechanical forces, or electrical signals into electrical signals (utilization of both direct and inverse effects).

2.3.2 Piezoresistive effect

The piezoresistive effect is a transmutation in the electrical resistivity of a semiconductor when mechanical strain is present. Compare to the piezoelectric effect, the piezoresistive effect only affecting changes in electrical resistance.

The piezoresistive effect in semiconductor materials can be several orders of magnitudes much greater than the geometrical effect. Thus, the semiconductor strain gauges with a significant coefficient of sensitivity can be created. For exact measurement, the piezoresistive effects are usually much complicated to handle rather than metal strain gauges, due semiconductor strain gauges that are much more sensitive to environmental surrounding, Mootanah, & Bader, (2006).

In silicon, the factors are two orders of magnitudes more sizeable voluminous than in metal. The resistance of n-conducting silicon mainly varies due to a shift of the three different conducting valley pairs, Sapmaz, et al., (2006). The shifting results to a spreading of the carriers between valleys with different mobility. This results in varying mobility dependent on the direction of current flow. The minor effect is due to the efficacious mass change cognate to transmuting shapes of the valleys. In p-conducting silicon the behaviour are more intricate and additionally result in mass changes and aperture transfer.

2.4 Piezoelectric Ceramic

Intrinsic piezoelectric ceramics have an unstructured polarization, Kong, & Wang, (2003) as the charge concentrations of the unit cells are discrete from each other. Plus, the axis of the lattice elongates in the direction of both the spontaneous strain occurs and polarization. The piezoelectric effect of natural monocrystalline materials Rochelle salt is relatively minuscule. However, for polycrystalline ferroelectric ceramics such as lead zirconate titanate (PZT) and barium titanate ($BaTiO_3$) exhibit more sizably voluminous displacements or induce more immensely colossal electric voltages.

Lead zirconate titanate (PZT) piezoceramic materials are exist in large variations and are most actively utilized for actuator and sensor applications. According to Watanabe et al., (2002) doping of the PZT ceramics with alkali earth and rare earth metal such as Bi, Ni, Nb, La, Nd ions make it possible to categorically optimize parameters of piezoelectric and dielectric.