FABRICATION OF NANOSTRUCTURED ANODIZED ALUMINUM OXIDE (AAO) ON Si-Al SUBSTRATE FOR ELECTRONIC APPLICATIONS

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Fabrication of Nanostructured Anodized Aluminum Oxide (AAO) on Si-Al Substrate For Electronic Applications

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LIST OF ABBREVIATIONS

AAO	Anodized aluminum oxide
IUPAC	Internantional Union of pure and applied chemistry
PVD	Physical Vapor Deposition
MDO	Micro-Arc discharge oxidation
Si	Silicon
SiO_2	Silicon Dioxide
$C_2H_2O_5$	Oxalic acid
Al_2O_3	Aluminum oxide
H_2O	Water
HF	Hydrofluoric acid
HNO_3	Nitric acid
HCl	Hydrochloric acid
$HClO_4$	Perchloric
C_2H_5OH	Ethanol acid
$C_2H_2O_4$	Oxalic acid
α-Al_2O_3	Alpha-alumina

β-Al_2O_3	Beta-alumina
γ-Al_2O_3	Gamma-alumina
ζ- Al_2O_3	Delta-alumina
M_{Al2O3}	Molecular weight of Al_2O_3

LIST OF SYMBOLS

nm	Nanometer
V	Voltage
^{o}C	Degree Celsius
Ω^{-1} cm^{-1}	Conductivity constant
K	Kevin
eV	Energy gap
µm	Micrometer
α	Porosity
Dp	Pore diameter
Di	Interpore distance
ε^{0}	Permitivity
ε	Dielectric constant
Φ	Phase angle of impedance
Ω	Ohm
θ	X-ray diffraction angle
m_d	Mass of oxide dissolved from pores

m_f	Mass of aluminum sample after anodizing
wt%	Weight percent
µ	Micro
j	Passing current
η	Current efficiency
C	Capacitance
R	Resistance

Fabrikasi Nanostruktur Aluminium Oksida Teranod (AOT) ke atas Substrat Si-Al untuk Aplikasi Elektronik

ABSTRAK

Pembentukan filem aluminium oksida teranod (AOT) dalam proses penganodan telah dikaji. Proses penganodan itu dilakukan dengan asid oksalik. Tujuan memilih asid oksalik sebagai elektrolit adalah untuk menghasilkan filem AOT dengan liang sederhana diameter bersaiz nanometer. Kajian ini telah dijalankan untuk menentukan parameter yang optimum bagi proses penganodan untuk membentuk filem AOT pelbagai aplikasi dalam bidang elektronik. Kajian ini telah memberi tumpuan kepada pengaruh parameter penganodan seperti voltan, kepekatan elektrolit dan suhu elektrolit dalam pertumbuhan filem AOT. Voltan bagi proses penganodan telah dipelbagai dari 40V sehingga 55V, suhu dari 10^{o}C kepada 25^{o}C dan kepekatan dari 0.1M sehingga 0.7M. Sifat dielektrik juga dikaji melalui analsis spektroskopi impedans. Pembentukan AOT dikaji melalui komposisi, morfologi, dan analisis keratan rentas filem. Pencirian sifat-sifat fizikal dan kimia diperhatikan dengan menggunakan teknik mikroskop imbasan elektron (SEM) dan Pembelauan sinar-x (XRD). Keputusan menunjukkan bahawa purata diameter liang AOT adalah paling besar sebanyak 43.99nm di 40V. Pembentukan dan bentuk liang AOT yang terbaik terbentuk di voltan 45V. Sementara itu, purata diameter liang AOT pada suhu yang berbeza adalah yang terbesar pada 25^{o}C sebanyak 38.89nm. Untuk nilai kepekatan yang berbeza, nilai purata diameter liang AOT yang tertinggi diukur dalam kepekatan 0.3M iaitu 39.62nm. Struktur liang AOT yang lebih teratur telah terbentuk pada 45V pada suhu 20^{o}C didalam larutan 0.7M. Tindak balas kinetik untuk filem AOT telah dinyatakan dalam bentuk peratusan perubahan jisim dan ketebalan filem.Pada voltan penganodan yang lebih tinggi, peratusan perubahan jisim adalah paling tinggi iaitu 1.27% pada 55V. Pada 25^{o}C, ketebalan AOT yang diukur adalah yang tertinggi iaitu 1.382µm. Secara amnya, ketebalan filem AOT meningkat apabila suhu penganodan meningkat. Sementara itu, ketebalan AOT juga dipengaruhi oleh kepekatan elektrolit. Pada 0.5M, ketebalan AOT dicatatkan tertinggi iaitu 1.403µm. Sifat-sifat dielektrik diukur menggunakan penganalisis impedans. Berdasarkan keputusan, rintangan filem AOT berkurangan apabila voltan penganodan, suhu elektrolit dan kepekatan elektrolik meningkat. Walau bagaimanapun, kemuatan menurun apabila voltan dan kepekatan meningkat tetapi meningkat apabila suhu elektrolit bertambah. Berdasarkan data yang telah dianalisis, parameter yang optimum untuk penganodan seharusnya berada di dalam julat 45V, suhu penganodan harus pada 20^{o}C mendekati suhu bilik dan kepekatan elektrolit dalam julat 0.3M untuk menghasilkan filem AOT terbaik dengan ciri-ciri yang terbaik untuk aplikasi elektronik.

Fabrication of Nanostructured Anodized Aluminum Oxide (AAO) on Si-Al Substrate for Electronic Applications.

ABSTRACT

The growth of anodized aluminum oxide (AAO) film in anodizing process has been studied. The anodizing process was done in oxalic acid. The purpose of choosing oxalic acid as the electrolyte is to create AAO with a medium pore nanometer diameter. This study was performed to determine optimum parameters of anodizing process in order to develop AAO film for various applications in electronic field. This study focussed on the influence of anodizing parameters such as anodizing voltage, electrolyte temperature and electrolyte concentration to the growth of AAO film. The anodizing voltage was varied from 40V to 55V, temperature was controlled from 10^{o}C to 25^{o}C and the concentration was varied from 0.1M to 0.7M. The dielectric properties also studied via impedance spectroscopy. The growth of AAO was studied through the composition, morphology, and cross section analysis. Characterization for physical and chemical properties is observed by using Scanning Electron Microscopy (SEM) and X-Ray Diffraction (XRD) techniques. The results show that the formation of AAO film was strictly influenced by the anodizing conditions. The average pore diameter 43.99nm measured was the highest at 40V. Self ordering and great pore structures occurred whenever the voltage was 45V Meanwhile, the average pore diameter of AAO film at different temperature was the largest at 25^{o}C around 38.89nm. For varied concentration, the highest value of pore diameter observed in 0.3M which is 39.62nm. The most highly ordered structure of AAO pore was formed at 45V at temperature 20^{o}C and 0.7M of concentration. The kinetic reaction for AAO film was expressed in term of percentage of mass changes and thickness of the film. The higher anodizing voltage, the higher the percentage of mass change which is 1.27% at 55V. At 25^{o}C, the thickness of AAO measured was the highest value around 1.382µm. As general, thickness of AAO film increased as the anodizing temperature increased. Meanwhile, the thickness of AAO also strongly influenced by the concentration of the electrolyte. In 0.5M, the thickness of AAO is 1.403µm and was the highest value. The dielectric properties was measured using impedance analyzer. According to the result, the resistance of AAO film decreased when the anodizing voltage, electrolyte temperature and concentration increased. However, capacitance decreased when the voltage and concentration increased but increased as the temperature increased. Based on the analyzed data, the optimum parameter for anodizing should be in the range 45V ,the anodizing temperature should be at 20^{o}C near room temperature and the electrolyte concentration in the range 0.3M in order to develop the best AAO film with great properties for electronic applications.

CHAPTER 1

INTRODUCTION

1.1 Introduction

The growth, design, characterization and production of nanostructured materials has been extensively investigate by the researchers either in industry or academic field. Nanostructured materials are attracting a great deal because of their applications in areas such as electronics, optics, catalysis, ceramics, magnetic data storage and nanocomposites. These nanostructured classified as a material that are lie on nanometers scales ranging from 1 to 100 nm.

One of the nanostructured materials that have withdrawn scientific attention is porous anodized aluminum oxide (AAO). Porous AAO can be described as a close-packed array of hexagonally arranged cells which contained pores in each cell centre (Eftekhari, 2008). Porous AAO has been studied since 1930s due to the chemical stability of its passive layer and its honeycomb structure. Lots of research was done extensively in order to obtain this protective and decorative material. The most important feature of porous AAO is the versatility of its structures. By having highly ordered of AAO, it is possible to design a complex nanoscale structured devices with unique physical properties due to the size effects (Cojocaru et al., 2005)

The main role of porous anodized aluminum oxide within the nanostructure fabrication field can be classified into two main classes. First class is highly ordered alumina as template for nanodevice preparation which is a traditional application of this system, and the second class porous AAO acts as a nanodevice itself which applied in photonic crystal, electrochemical double layer of capacitors, light emitting diodes and medical applications. Nowadays, all of this nanodevice have been approached and presented at nanometer scale using porous AAO which can be considered as one of the key factor in development of nanotechnology.

An electrochemical formation of highly ordered porous AAO can be obtained by an anodic oxidation of aluminum metal which is known as anodizing. Anodizing has raised substantial scientific and technological interest due to its diverse applications which including dielectric film production for electrolytic capacitors, increasing the oxidation resistance of materials, decorative layers, increasing the abrasion wear resistance. Generally, a porous AAO was produced in an anodizing which conducted at low temperature 1^{o}C to 27^{o}C and employs mainly sulfuric, oxalic, phosphoric acids as an electrolyte. There are certain values of potential which can be applied for anodizing without burning or breakdown of the oxide film and the best arrangement of nanopores can be observed respectively. In order to have best arrangement of porous AAO, there are several anodizing conditions that should be considered before carry out the anodizing process which including operating voltage and temperature effect.

The structural features of porous AAO formed by anodization under a potentiostatic regime are highly depends on the electrolyte used. It has been believed that, a compact and dense anodic oxide layer has been obtained in strongly acidic electrolytes such as oxalic, sulfuric and phosphoric acids under certain potentials. However, recently reported by Eftekhari, (2008) that porous AAO formation for various acids such as malonic, tartaric, chromic acid, even in mixed solution of phosphoric and organic acids. In contrast, a strongly non-porous, non-conducting and dielectric compact of barrier type of anodic film can be formed in neutral solutions (pH=5-7) where the anodic layer is not chemically affected and stays practically insoluble. Acids used for forming the barrier type film includes boric acid, ammonium borate and some organics acids such as citric, malic and glycolic acids.

In this study, the oxalic acid is used as the electrolyte to develop nanostructured porous AAO in order to enhance the application of this nanoporous AAO film. The growth pores and wall structure and properties of porous AAO film formed in oxalic acid are extensively studied in order to broaden the applications of AAO film in nanoelectronics field. The purpose of using oxalic acid is to develop medium pore diameter because of electronics devices fabricated with AAO normally are using medium diameter compared to larger pore diameter in phosphate anodizing and smaller pore diameter in sulfuric anodizing (Wang, 2000).

There are four major parameters should be controlled in anodizing process which are anodizing voltage, the temperature of electrolyte, electrolyte concentration and anodizing time. All of these parameters are related and dependent to each other in forming high ordered porous AAO with a specific ideal characteristic. In addition, the characteristic features of fabricated nanostructured AAO including pore diameter, interpore distance, porosity and pore density also can be influenced by the anodizing parameters. For example, there are findings that obtained highest density of nanopores in sulfuric anodizing. Other than that, large cell size and high wall thickness, small pore diameter and low pore density can be obtained in high anodizing voltage and lower temperature (Sulka & Parkola, 2006). Therefore, choosing the most appropriate parameter is a necessary; therefore the main purpose of this study is to obtain an optimum parameter to generate a highly ordered of porous AAO.

1.2 Problem statement

The main purpose of this study is to develop AAO film with a highly ordered pores arrangement and specific pores characteristics. The production of this AAO film is to expand its application in nanoelectronic fields. Generally, AAO film can be developed by various techniques including gas flame spray, plasma thermal spray, physical vapour deposition (PVD), micro-arc discharge oxidation (MDO) and high temperature glass annealing method. In fact, all of these techniques require high technology and high cost. Due to this matter, research groups are seeking alternative, new routes of preparation. In this regard, anodizing has been chosen as the method to develop AAO film because its ability to provide good physical, chemical and mechanical properties. Besides, anodizing is a simple electrochemical technique, low cost process and is related to an ability to control the potential outcome of AAO.

The aim of this study is to develop the nanostructured AAO prepared using anodizing on silicon substrate. In general, the latter approaches, AAO film is treated on aluminum substrate. One interesting AAO configuration reported by Xiao et al., (2002) which showed a ramification along the porous structure which normal to substrate. This result was obtained by an anodization on aluminum film evaporated onto Si substrate, and the branch like of pores resulting due to an increase in the electrical resistance at the substrate interface.

Regarding to AAO formation, obtaining the desired pore specification with porous nature, medium pore diameter and thick AAO layer also become one of the main aims in this study. In order to meet this expectation, an appropriate anodizing electrolyte must be considered. According to (Eftekhari, 2008), porous AAO can be developed by anodizing of aluminum in strongly acidic electrolytes such as sulfuric, oxalic, phosphoric and chromic acid solutions. Ono & Masuko, (2003) have been studied about the formation of AAO film in sulfuric, oxalic and phosphoric acid. From the result, the pore diameters of AAO obtained in this three electrolyte are smaller in the order phosphoric > oxalic > sulfuric and the thickness of AAO film has been produced is in medium range of 15 to 30nm compared to larger value in phosphoric (25-75nm) and smaller in sulfuric (10-15nm).

Besides, the type of anodizing electrolyte also plays an important role to create great properties of AAO film. It should be noted that the rate of oxide growth during anodization depends significantly on the anodizing electrolyte. It have been reported that, the highest rate being observed is preceded by the sulfuric acids anodizing (Jagminiene, 2005). However, the aim of this study is to develop AAO film with a medium range of pore diameters. Therefore, oxalic acid have been chosen as the electrolyte, at the same time others parameters such as anodizing voltage, electrolyte temperature and electrolyte concentration also considered.

This study is approach on anodizing process which conducted in oxalic acid. Nanostructured AAO film will be obtained on Si substrate for electronic applications. The physical, chemical and electrical properties of this oxide also can be measured by anodizing process. Thus, a new hypothesis will be generated with this study approach to fabricate nanostructured AAO film on Si substrate, and to discover the relationship between anodizing parameters and substrate properties in order to broaden its application in electronic fields.

1.3 Objective of study

The objectives of this study are;

i. To produce the formation of nanostructured porous AAO films on Si substrate in oxalic acid by using anodizing technique.
ii. To study the influence of three major anodizing parameters which are anodizing voltage, electrolyte temperature and electrolyte concentration to the formation of AAO films
iii. To evaluate the physical, chemical and electrical properties of the AAO film formed in controlled anodizing parameters

1.4 Research approaches

In general, this study consist of five phase which contains fabrication and preparation of silicon as a substrate, fabrication and preparation of silicon/aluminum sample and pre-treatment, synthesis of AAO film by anodizing process and the final phase, AAO film characterizations and result analysis.

I. Phase I - Fabrication and preparation of silicon substrate
II. Phase II - Fabrication and preparation of silicon/aluminum sample
III. Phase III - Synthesis of AAO film by Anodizing process
IV. Phase IV - AAO film characterizations
V. Phase V - Electrical testing

The characterization of raw materials which is high purity aluminum pellets (99%) have been conducted before the substrate preparation process. The characterization process will be performed using X-ray Diffraction (XRD). Then the fabrication of silicon substrate was started by growing the oxide layer SiO_2 onto Si wafer using a conventional furnace. This