A STUDY ON NANOSTRUCTURED OF ANODISED ALUMINIUM TEMPLATE SYNTHESISED BY THE MIXTURE OF PHOSPHORIC ACID AND ACETIC ACID

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A Study on Nanostructured of Anodised Aluminium Template Synthesised by The Mixture Of Phosphoric Acid and Acetic Acid

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TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

LIST OF ABBREVIATIONS

AAO	Anodic aluminium oxide
AC	Alternating current
Al	Aluminium
$Al(OH)_3$	Aluminium hydroxide
Al_2O_3	Aluminium oxide/alumina
Al^{3+}	Aluminium ion
Al-Si	Aluminium-silicon
CH_3COOH	Acetic acid
CH_3OH	Methanol
CVD	Chemical vapour deposition
DBD Reactor	Dielectric barrier discharge reactor
DC	Direct current
H^+	Hydrogen ion
H_2	Hydrogen gas
H_2O	Water
H_2PO^{4-}	Hydrogen phosphate
H_3PO_4	Phosphoric acid
$H_3PO_4+CH_3COOH$	Mixture of phosphoric acid+acetic acid
HPO_4^{2-}	Hydrogen phosphate
ICDD	International Centre for Diffraction Data
MDO	Micro-arc discharge oxidation

O^{2-}	Oxygen ion
OH^-	Hydroxide ion
PM Collection	Particular matter collection
PO_4^{3-}	Phosphate ion
PTFE	Polytetrafluoroethylene
PVD	Physical vapour deposition
RH SENSOR	Relative humidity sensor
SEM	Scanning electron microscope
XRD	X-Ray diffraction
α-Al_2O_3	Alpha-alumina
γ-Al_2O_3	Gamma-alumina
δ-Al_2O_3	Delta-alumina
ε-Al_2O_3	Epsilon-alumina
η-Al_2O_3	Eta-alumina
ι-Al_2O_3	Iota-alumina
κ-Al_2O_3	Kappa-alumina
φ-Al_2O_3	Phi-alumina
χ-Al_2O_3	Chi-alumina

LIST OF SYMBOLS

$(m_{Al})_{\eta}$	Mass of aluminium metal converted to oxide
$\|Z\|$	Impedance modulus
A_t	Anodized area
C	Capacitance
C_1	Capacitor
d	AAO thickness
e	Electrons
F	Faraday's constant
f	Frequency
g/cm^3	Gram per cube centimeter
g/mol	Gram per mol
GPa	Giga pascal
Hz	Hertz (unit of frequency)
i	Current density
j	Complex number, (√-1)
$Jkg^{-1}K^{-1}$	Joule per kilogram kelvin
k	Parameter dependent on anodising condition
kgm^{-3}	Kilogram per cube meter
kHz	Kilo hertz
M	Molar
mA^{-2}	Miliampere

M_{Al}	Molecular weight of aluminium
M_{Al2O3}	Molecular weight of oxide
m_d	Mass of oxide dissolved from the pores
m_f	Mass of aluminium sample after anodising
m_i	Mass of aluminium sample before anodising
m_p	Mass of porous oxide formed at any time
MPa	Mega pascal
m_t	Total mass of oxide formed
mV	Milivolt
R	Resistor
R_1	Film resistance
R_s	Solution resistance
t	Anodising time
V	Volt
$Wm^{-1}K^{-1}$	Watt per meter kelvin
wt%	Weight percent
X_c	Capacitance reactance
z	Number of electron used for oxide formation
Z	Impedance
Z’	Real part of impedance
Z”	Imaginary part of impedance
ε_o	Dielectric constant of vacuum ($8.8542 \times 10^{-12} Fm^{-1}$)
ε_r	Dielectric constant

η_{ce}	Current efficiency
θ	Phase angle of impedance
θ	X-Ray Diffraction angle
μ	Micro
ρ_p	Specific resistivity
Ω	Ohm
ω	Angular frequency (2π*f*)

Kajian Templat Nanostruktur Aluminium Teranod Menggunakan Campuran Asid Fosforik dan Asid Asetik

ABSTRAK

Pembentukan filem aluminium oksida teranod (AAO) dalam proses penganodan telah dikaji. Proses penganodan ini telah dijalankan dalam campuran asid fosforik dan asid asetik. Tujuan larutan campuran asid sebagai elektrolit adalah untuk meningkatkan keberkesanan pembentukan filem AAO. Kajian ini telah dijalankan untuk mendapatkan parameter penganodan yang optimum untuk membentuk filem AAO yang mempunyai pelbagai aplikasi dalam bidang elektronik. Kajian ini memfokuskan pengaruh parameter penganodan iaitu suhu penganodan dan voltan penganodan terhadap pertumbuhan filem AAO dalam larutan campuran asid ini. Suhu penganodan telah dikawal dalam lingkungan 5°C hingga 25°C dan voltan penganodan telah dikawal dari 70V hingga 130V. Sifat elektrik filem AAO juga dikaji melalui pengukuran galangan. Pertumbuhan, morfologi dan analisis komposisi filem AAO telah dikaji menggunakan teknik mikroskop imbasan elektron (SEM) dan pembelauan sinar-X (XRD). Keputusan kajian menunjukkan pembentukan filem AAO dipengaruhi oleh parameter-parameter penganodan. Purata diameter liang filem AAO adalah lebih besar pada suhu 15°C iatu 87nm dan liang-liang mempunyai susunan yang lebih teratur. Manakala filem AAO mempunyai diameter liang yang besar iaitu 92nm pada voltan penganodan yang tinggi pada 130V. Diameter liang filem AAO meningkat dengan peningkatan voltan penganodan. Filem AAO menunjukkan susunan keliangan yang teratur pada voltan penganodan 130V. Tindakbalas kinetik pembentukan filem AAO dinyatakan sebagai peratusan perubahan jisim dan ketebalan filem AAO. Pada suhu 15°C, peratusan perubahan jisim menunjukkan perubahan yang ketara iaitu 0.21% jika dibandingkan dengan suhu penganodan yang lain. Walau bagaimanapun, dengan peningkatan voltan penganodan, peratusan perubahan jisim telah meningkat. Di samping itu, filem AAO juga menunjukkan ketebalan yang tinggi pada suhu 15°C iaitu 2.82µm. Ketebalan filem AAO berkurang dengan peningkatan suhu pada 20°C dan 25°C. Pada suhu rendah, ketebalan filem AAO berkurangan. Manakala ketebalan filem AAO amat dipengaruhi oleh voltan penganodan. Voltan penganodan yang tinggi menunjukkan ketebalan filem AAO yang tinggi iaitu 2.82µm . Pengukuran galangan filem AAO menunjukkan bahawa kerintangan filem AAO bertambah dan kemuatan berkurangan apabila ketebalan filem AAO bertambah. Berdasarkan kepada keputusan kajian ini, parameter penganodan yang optimum adalah dalam lingkungan voltan 130V dan suhu penganodan 15°C untuk mendapatkan ciri-ciri filem AAO yang terbaik untuk dikaitkan dengan keperluan aplikasi elektronik.

A Study on Nanostructured of Anodised Aluminium Template Synthesised by the Mixture of Phosphoric Acid and Acetic Acid

ABSTRACT

The formation of anodic aluminium oxide (AAO) film in anodising process has been studied. The anodising process was done in a mixture of phosphoric acid and acetic acid. The purpose of mixed acid solution as electrolyte is to increase the efficiency of AAO film formation. This study was performed to determine optimum parameter of anodising process in order to develop AAO film with diverse application in electronic field. The studies were focused on the influence of anodising parameters which are anodising temperature and anodising voltage on the growth of AAO film. The anodising temperature was controlled in the range of 5°C to 25°C and the anodising voltage was controlled from 70V to 130V respectively. The electrical properties of AAO film also studied via impedance measurement. The growth, morphology and composition analysis of AAO film were investigated by scanning electron microscope (SEM) and X-ray diffraction (XRD) techniques. The results showed that the formation of AAO film was strictly influenced by the anodising parameter. The average pore diameter of AAO film was larger at temperature 15°C which is 87nm and the pores have more ordered arrangement. Meanwhile, the AAO film was shown have large pore diameter around 92nm at higher anodising voltage at 130V. The pore diameter of AAO film was gradually increased as the anodising voltage increase. The AAO film was shown to have highly ordered arrangement of pores at 130V of anodising voltage. The kinetic reaction of AAO film formation was expressed as percentage of mass change and AAO film thickness. At 15°C, the percentage of mass change showed a greater change which is 0.21% compared to the other anodising temperature. However, by increasing the anodising voltage, the percentage of mass change increased. Besides, the AAO film also showed greater thickness at 15°C which is 2.82µm. The thickness of AAO film decreased as the anodising temperature increased to 20°C and 25°C. At lower temperature, the thickness of AAO film is decreased. Meanwhile, the thickness of AAO film is strongly influenced by anodising voltage. Higher anodising voltage showed higher thickness of AAO film which is 2.8µm. The impedance measurement of AAO film revealed that the resistance of AAO film increased and the capacitance decreased as the thickness of AAO film increased. According to the results of this study, the optimum parameter of anodising should be in the range of 130V and the anodising temperature is about 15°C in order to obtain best characteristic of AAO film that can be related to the requirement of electronic applications.

CHAPTER 1

INTRODUCTION

1.1 Introduction

The development, growth and characterisation of nanostructured materials have been extensively investigated by the researchers either in industries or academic field. Nanostructures are defined as materials with structural units on a nanometer scale which is below 100nm (Eftekhari, 2008). These nanostructure materials have wide range of applications. The potential uses of those nanostructure materials are including electronic, optoelectronic and also magnetic devices (Nagaura et al., 2008; Su et al., 2008).

Porous anodic aluminium oxide (AAO) film is one type of ordered nanostructured material. AAO film is consisting of close-packed cells in a hexagonal arrangement with pore at their centres. AAO film growth has been studied since 1930 (Eftekhari, 2008). AAO film was used conventionally as a corrosion resistant material. Nowadays, the highly ordered structure of the AAO film is the advantage to design complex nanoscale structured devices with unique physical properties. The AAO film has been widely used as electronic devices in fabrication of dielectric films. The role of porous AAO within the nanostructure fabrication field can be divided basically into two wide classes. The first one is highly ordered porous structure working as a template to the preparation of nanodevice and the second one is AAO film acting as a nanodevice itself. The highly ordered structure combined with the physical and chemical properties of AAO are the key point to determine the AAO film usage (Eftekhari, 2008).

A highly ordered array nanoporous structure AAO film can be obtained by anodising which is relatively easy process for nanostructured material fabrication. Anodising process has been developed for aluminium, stainless steel, titanium and magnesium. However, aluminium anodising has been widely studied because aluminium always covered with a thin oxide film due to the high affinity for oxygen which makes the aluminium an excellent corrosion resistant metal (Hwang et al., 2002; Rajagopal et al., 2000). Aluminium is widely used in electronics because of the high strength-to-weight ratio, high thermal conductivity and good electrical conductivity. Anodising of aluminium has raised scientific and technological interest due to the diverse applications which include dielectric film production for use in electrolytic capacitors, sensors fabrication, increasing the oxidation resistance, abrasion resistance, corrosion resistance and wear resistance of materials (Eftekhari, 2008).

The anodising of aluminium can be resulted into two different types of oxide film which are barrier-type oxide film and a porous-type film. The type of oxide film mainly depends on the nature of the electrolyte solution used in the anodising. The group of electrolytes used for barrier-type film formation includes boric acid, ammonium borate and aqueous phosphate solutions, as well as perchloric acid with ethanol and some organic electrolyte such as malic, citric, succinic and glycolic acids (Eftekhari, 2008). In contrast, the porous-type films were reported formed in strongly acidic electrolytes such as sulphuric, oxalic, phosphoric and chromic acid solutions. Porous AAO films also have been obtained in mixed electrolytes including a mixed solution of phosphoric and organic acid with cerium salt (Wang et al., 2006), sulphuric and oxalic acids (Bai et al., 2008), a mixture of boric acid, sulfosalicylic acid and phosphate (Song-jiang et al., 2008) and a mixture of oxalic acid, sodium tungstate, phosphoric and hypophosphorous acid (Eftekhari, 2008). The mixed acid solution as anodising electrolytes can decrease the film dissolution rate, then increase the film formation efficiency and improve the film properties.

In this study, the mixture of phosphoric acid and acetic acid (H_3PO_4+CH_3COOH) was used to obtain nanostructured porous AAO film in anodising process in order to enlarge the application of this AAO film. The growth, structure and properties of porous AAO film formed in phosphoric acid is widely studied but the application of AAO film formed in phosphoric acid is limited because of the oxide film formed is thinner compared with those obtained in sulphuric acid and oxalic acid. In this study, the purpose of phosphoric acid is to develop larger pore diameter. According to Wang et al. (2005a), in phosphate anodising the H_3PO_4 is easy to ionized H^+ continuously. The H^+ ions contributed to the dissolution of oxide film and resulted to the larger pore diameter.

In the phosphate anodising PO_4^{3-} is difficult to adsorb on the surface to release much O^{2-} for formation of oxide. Therefore, Al^{3+} migrate to the electrolyte solution resulted to thin oxide film. Organic acid like acetic acid will be added in phosphoric acid solution to increase the efficiency of formation of AAO film and thus thick and hard oxide film formed (Froimovitch, 2006). Wang et al. (2005a) have been stated that carboxylic ion produced by the organic acid will produce complex compound in the electrolyte. This complex compound on the anode surface would remove H^+ ions from the surface to decrease the dissolving velocity of the oxide film. This reaction will result to high thickness of the film.

There are four major parameters need to be controlled in anodising process which are anodising voltage, anodising temperature, electrolyte and anodising time. All of the major anodising parameters are directly dependent on each other in order to form porous AAO films which have certain specific desirable characteristics. For example in AAO films, the pore diameter is shown to be a function of electrolytes which is the composition and operating temperature. Hence, solution of the electrolyte and the choice of operating temperature determine the applications where the pore diameter has specific influence. Other than that, large cell size and high wall thickness, small pore diameter and low pore density are favoured by high anodising voltages and lower anodising temperature. Since the AAO film characteristic were affected by anodising voltage, the controlling of the anodising voltage is essential in order to gain desired characteristic of AAO film for specific purpose (Rajagopal & Vasu, 2000).

1.2 Problem Statement

The application of AAO film as electronic device has drawn great attention because of the unique properties of AAO film. The AAO film can be developed in various technique including micro-arc discharge oxidation (MDO), gas-flame spray, plasma thermal spray, physical vapour deposition and high temperature glass enamelling method. These techniques of AAO films productions need high technology and high cost. However, anodising technique is one of the synthesis techniques of AAO film which provide good physical, chemical and mechanical properties of AAO. The anodising technique is simple and low cost process. Another advantage of anodising process is the dimension of aluminium substrate does not change because of the oxide layer is produced from the part of aluminium substrate. Therefore, anodising was needed to produce AAO film in order to obtained AAO film with desired applications.

The main problem in anodising process is to obtain large pore diameter and thick AAO layer on the surface of aluminium substrate. These kinds of AAO film properties can be achieved by selecting appropriate anodising electrolyte. According to Li et al. (2000) and Shih et al., (2000) better properties of AAO film can be obtained by using mixed solution of electrolyte. In this study, the mixture of phosphoric acid and acetic acid is used to produce thick layer of AAO film with large pore diameter. Wang et al., (2005b) have studied about the formation of AAO film in mixture of phosphoric acid, acetic acid and cerium salt. From the result, large pore diameter was obtained and the thickness of AAO film produced was about 20µm. These characteristics of AAO film are suitable for producing self-lubricating surface composite coating by dipped the PTFE particles into the pores of AAO film.

The type of anodising electrolyte plays an important role to create properties of AAO film. In this study, the mixture of phosphoric acid and acetic acid can create porous AAO film through oxidation and reduction reaction in anodising process. However, the optimum parameter is very difficult to achieve because the behaviours of the porous AAO film properties strictly influenced by anodising process parameter such as anodising voltage, electrolyte temperature, acid concentration and duration of anodising process.

The study approach on anodising process has been explored by using phosphoric and acetic acid to obtain the nanostructured porous AAO film on aluminium substrate for electronic applications such as a template to fabricate nanowires, nanotube and biosensors manufacturing. Furthermore, anodising can produce thin film with pore diameter between 5nm – 100nm with thickness in the range of 10µm. The physical, chemical and electrical properties of this oxide film also can be measured by anodising process. Thus, a new hypothesis has been generated to explore the relationship between anodising process parameter and substrate properties on nanostructured AAO film in microstructural, physical, chemical and electrical properties in order to enlarge AAO usage especially in electronic applications.