UNIVERSITI TEKNIKAL MALAYSIA MELAKA

EFFECT OF SUBSTRATE ON THE MICROSTRUCTURE AND MORPHOLOGY OF Ag-TiO_2 SOL GEL COATING

This report submitted in accordance with requirement of the Universiti Teknikal Malaysia Melaka (UTeM) for the Bachelor Degree of Manufacturing Engineering (Engineering Materials) (Hons.)

by

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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 committee is as follow:

………………………………………..

(Prof Madya Dr. Zulkifli Bin Mohd Rosli)

ABSTRAK

Salutan perak titanium dioksida (Ag-TiO_2) telah didepositkan ke atas tiga jenis substrat yang mempunyai kehabluran berbeza iaitu kaca amorfus, wafer silikon kristal tunggal dan polikristal indium tin oksida (ITO) kaca dengan kaedah sol gel. Cecair titanium dioksida (TiO_2) disintesis pada suha bilik melalui proses pencampuran titanium tetraisopropoxide (TTiP) ke dalam etanol, asid hidroklorik (HCL) dan air suling. Sebanyak lima lapisan TiO_2 telah didepositkan atas setiap substrat melalui process celupan. Kemudian, substrat yang bersalut degan TiO_2 dicelup ke dalam cecair nanopartikel perak untuk memperkenalkan kesan antimikrobial. Suhu pensinteran pula ditetapkan pada 500°C untuk mendapat Kristal yang saiz kecil dan lebih fasa anatase. Pemerhatian fizikal dan morfologi salutan telah dijalankan dengan mikroskop imbasan electron (SEM). Penyelidikan SEM menunjukkan bahawa salutan TiO_2 yang deposit atas kaca amorfus dan kaca ITO tidak homogen manakala wafer silikon boleh membentuk lapisan yang telus dan padat. Sebaliknya, salutan Ag-TiO_2 tidak telus kepada ketiga-tiga substrat kerana nanopartikel perak telah teroksida. Lapian Ag-TiO_2 adalah tidak seragam. Nanopartikel perak tidak tertanam ke dalam lapisan TiO_2 tetapi membentuk satu lapisan di atasnya. Nanopartikel perak yang halus dan tidak teratur didapati atas kaca amorfus manakala kepingan perak diagragatkan di permukaan lapis kaca ITO dan wafer silikon. Kaedah pencirian tambahan perlu menjalankan dalam kajian masa depan untuk menjelaskan korelasi antara penghabluran substrat dan transformasi kristal salutan Ag-TiO_2.

ABSTRACT

Silver titanium dioxide (Ag-TiO_2) coatings obtained by a sol gel method were deposited on three substrates with different crystallinity : amorphous glass, single crystal silicon wafer (100) and polycrystal indium tin oxide (ITO) glass. First, titanium dioxide (TiO_2) sol was synthesized in room temperature and acidic condition by hydrolysis of titanium tetraisopropoxide (TTiP) in ethanol, hydrochloric acid (HCL) and deionized (DI) water. Five layers of TiO_2 coatings were deposited on all substrates using TiO_2 sol by a dip coating process. Then, TiO_2 coated substrate was dipped into pure silver nanoparticles solution to introduce antimicrobial effect. Sintering temperature was set at 500°C to produce small crystal size and more anatase phases. Physical observation and morphology of coating using scanning electron microscopy (SEM) had been conducted. SEM investigation revealed that the TiO_2 coating deposited on amorphous glass and ITO glass substrates was not homogenous whilst silicon wafer substrate can formed a transparent and dense coating. On the other hand, Ag-TiO_2 coating on three substrates was not transparent due to the presence of oxidized silver nanoparticles. The coatings were non homogenous. Silver nanoparticles did not embed into TiO2 coating and forming a layer on top of it. Fine and irregular shape of silver particles had found on the coating of glass substrate while silver flakes aggregated on coating surface of ITO glass and silicon wafer substrates. Additional characterization method should be conducted in future study to clarify the correlation between crystallinity of substrate and crystallite transformation of Ag-TiO_2 coating.

DEDICATION

I would like to dedicate this research to my beloved family, my supervisor and friend that has been supporting during the study of this research.

ACKNOWLEDGEMENT

I would like express my deepest gratitude to my supervisor, Prof Madya Dr. Zulkifli Bin Mohd Rosli for his excellent guidance and friendly advice during the research of this project. Without his patient guidance, I would not able to complete this research report.

Besides that, I would like to thank my research team members. They were always supporting me and sharing information with me to accomplish this project. And also thanks for everybody who has helped me out during my report preparation.

Thank you.

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AFM	-	Atomic Force Microscopy
Ag	-	Silver
$AgNO_3$	-	Silver Nitrate
$Ag\text{-}TiO_2$	-	Silver Doped Titanium Dioxide
Al_2O_3	-	Aluminium Oxide
CaO	-	Lime
CVD	-	Chemical Vapor Deposition
DI	-	Deionized Water
EDX/EDS	-	Energy-dispersive X-ray spectroscopy
F	-	Fluorine
FESEM	-	Field Emission Scanning Electron Microsopy
FTO	-	Fluoride doped Tin Oxide
H_2O_2	-	Hydrogen Peroxide
H_2SO_4	-	Sulfuric Acid
HCL	-	Hydrochloric Acid
HNO_3	-	Nitric Acid
In_2O_3	-	Indium (III) Oxide
ITO	-	Indium Tin Oxide
Na_2O	-	Sodium Oxide
PEG	-	Polyethylene Glycol
PET	-	Polyethylene Terephthalate
Pt	-	Platinum
PVD	-	Physical Vapor Deposition
SEM	-	Scanning Electron Microscopy
Si	-	Silicon

SiO_2	-	Silicon Dioxide
SnO_2	-	Tin Dioxide
TEM	-	Transmission Electron Microscopy
Ti	-	Titanium
TiO_2	-	Titanium Dioxide
TTiP/TIP	-	Titanium (IV) Isopropoxide
XRD	-	X-Ray Diffraction

CHAPTER 1

INTRODUCTION

This chapter explains the background study of this research and problem statement had been justified. Objectives and scope also included in this chapter.

1.1 Background study

Importance of maintaining personal hygiene is taught from an early age. Hygiene in daily life settings is needed to prevent spread of infection diseases when human come in contact with other substrates. Thus, people had introduced a coating on substrate surface to provide self cleaning effect. Titanium dioxide (TiO_2) had become the best choice for self-cleaning material due to its high photocatalytic properties, inexpensive and easy to deposit as a coating. This coating can choose to deposit on variety type of substrates such as ceramic, fiber glass, stainless steel and silica according to the substrate properties and its application.

However, self cleaning effect is not enough for maintain cleanliness particularly in medical industry. Since TiO_2 has high photocatalytic activity, some researcher doped TiO_2 coating with silver (Ag) nanoparticles to prepare a photocatalytic antimicrobial coating. Antimicrobial coating is a surface coated by antimicrobial agent that able to diminish the ability of microorganisms to grow. Ag has good antibacterial properties. Low concentration of Ag nanoparticles is harmless to human body but able to kill microorganisms such as bacterial. (Kumar et al., 2013)

According to Yu et al.(2011), Ag-TiO_2 coating had successfully deposited on silicon wafer using sol gel method and exhibiting a strong antimicrobial behavior. This Ag-TiO_2 solution can be coated on the medical device using different coating techniques. Other than medical device, Ag-TiO_2 solution also can be coated on other substrates surface such as windshield and wall tiles to obtain the antimicrobial and self cleaning effect.

There is numerous coating techniques have been used to coat the Ag-TiO_2 sol gel on the substrates surface for example sputtering, electron beam evaporation as well as sol gel process. According to Alzamani et al. (2013), sol gel dip coating is preferred due to its advantages like low operation temperature, low equipment cost and able to control microstructure of coating in order to achieve high homogeneity.

1.2 Problem statement

Generally, properties of coating deposited using sol gel technique are strongly influence by the type of precursor, solvent, catalyst and additive. Changing in the molar ratio of materials or heat treatment temperature definitely bring different results. From the literature studies, substrate type used will also affect the coating properties as well as the adhesive between substrate and coating.

Study found that the surface roughness of substrate affects the surface roughness of coating. For example, glass, FTO and silicon substrates had different surface roughness. Smooth surface of glass and silicon substrate produce thinner coating surface where the rough surface such as FTO substrate produces thicker coating surface (Anastasescu, 2014). Coating deposited on FTO also consists of larger pore size compare with glass. Hence, by comparing the bare surface roughness and coating surface roughness, the relation between substrate and coating can be justifying.

Some of the researches state that the crystallinity of substrate affects the final microstructure and surface morphology of the coating. Phase composition of coating depends on the crystallinity substrate. Crystalline substrate consists of higher phase transformation rate. With the same heat treatment temperature, TiO_2 coating on the silicon single crystal consists of both anatase and rutile phases where TiO_2 coating on amorphous glass does not undergo any phase transformation.

However, those studies were not conducted systematically on the how the substrates bring effects on the Ag-TiO_2 coating properties. Therefore, the aim of this study is to provide a systematic study on the effect of different substrates (soda lime glass slide, indium tin oxide (ITO) glass and silicon wafer) with different crystallinity and surface roughness towards the morphology of the Ag-TiO_2 coating via sol gel technique.

1.3 Objectives

1. To deposit Ag-TiO_2 coating on various substrates with different crystallinity via sol gel process.
2. To analyses the effect of substrates' crystallinity on the morphology of Ag-TiO_2 coatings

1.4 Scope

The scope of this research will focus on the effect of three types of substrates on the microstructure and morphology of the Ag-TiO_2 .The three substrates are soda lime glass, Indium Tin Oxide (ITO) glass and silicon wafer. The significant of this research is to ensure the effect of crystallinity of substrate toward morphology of Ag-TiO_2 coating and provide a guideline of choosing suitable substrate based on its application in the future. Coating method chosen in this research is sol gel technique with constant chemical composition and deposit parameter. Different characterization methods will use to analyze the properties of Ag-TiO_2 coating.

CHAPTER 2

LITERATURE REVIEW

This chapter explains about the surface and coating technology, application of TiO_2 and the advantage after doped with silver nanoparticles. Factors that affect the coating properties will discuss in this section based on the result of previous researches' report. The function and properties of substrate as well as the coating deposition technique also compare to make the selection.

2.1 Surface and coating technology

Coating can be defines as a thin layer or covering of something. When the coating thickness is less than few micrometers, it can be describe as thin film. Coating can be use for various applications. For example, colour coating was used to enhance the appearance of object where functional coating use to manipulate the surface properties such as improve the corrosion resistance or wear resistance. Currently, the technology of coating still undergoes intense development to achieve the better coating properties in different application.

2.1.1 Self cleaning properties of titanium dioxide (TiO_2) coating

One of the popular engineering materials in our daily life is titanium dioxide (TiO_2). Titanium dioxide (TiO_2) as known as titania is a high chemical stability, nontoxicity and low cost material. TiO_2 exists in three main crystal structure namely brookite, anatase and rutile. When TiO_2 coating undergoes heat treatment process, it will transform from amorphous phase into crystalline anatase. Further heating will produce pure rutile phases. However, anatase phase is the most photoactivity among the rest.

A thin layer of TiO_2 coating can deposited on the glass surface to introduce self cleaning properties. The first self-cleaning window announced by the Pikington Glass. Photocatalytic behavior of TiO_2 allow dirt chemically break down when the TiO_2 coating exposed to light. Then the dirt is washes away by rain during a hydrophilic process which the dirt molecule is tend to attracted and dissolved by rain. Thus, it brings a significant effect on the self-cleaning properties. At the present, TiO_2 coating is broadly use in medical, food, and paint and coatings industry.

According to Alzamani et al. (2013), a transparent TiO_2 coating that prepared by sol gel method can deposited on glass substrate using dip coating technique. High photocatalytic activity and superhydrophilic behavior cause TiO_2 coating become competent in self cleaning application.

2.1.2 Antimicrobial silver doped titanium dioxide (Ag-TiO_2) coating

Since TiO_2 has high photocatalytic activity, some researchers combine TiO_2 with silver nanoparticles to prepare a photocatalytic antimicrobial coating. According to Yu et al. (2011), Ag-TiO_2 coating had successfully deposited on silicon wafer using sol gel method and exhibiting a strong antimicrobial behavior. Silver (Ag) nanoparticlel is well known antimicrobial agents that have strong antibacterial effect. Ag ions can cause the inactivation of bacteria and virus. Ag mixed with titanium dioxide (TiO_2) in a solvent and then the mixed solution use to forms a coating on substrate surface for self-cleaning and antimicrobial purpose. High reactivity and low raw material cost makes silver doped titanium dioxide (Ag-TiO_2) become the most preferred antimicrobial coating used.

Antibacterial coating plays an important role in hygiene protection and prevention of bacterial diseases. The application of antimicrobial coating is infinite as it can apply at any surface that requires hygienic protection, for example healthcare industry, food industry, and household product. Antimicrobial flooring system is the antimicrobial coating applies on the floor. It successfully offer protection against bacteria, virus as well as fungi comes into contact with the floor.

2.1.3 Coating deposition method and factors influence the coating performance

There are many techniques can be use to deposit coating on the substrate surface. Based on the Table 2.1, sol gel dip coating technique is the most preferred technique use in preparing TiO_2 or Ag-TiO_2 coating. Preparation condition has effect on the performance of coating that prepares using sol gel process. Those factors was summarise as precursor, solvent, additive, catalyst, annealing temperature and substrate.

Table 2.1: Comparison table of coating deposition method

References	Coating	Deposit method	Variable	Substrate
Guo et al. (2013)	TiO_2	Laser chemical vapor deposition	Deposition parameter	Pt/Ti/SiO_2/Si substrate
Giolli et al. (2007)	TiO_2	Physical vapour deposition system	Substrate	Copper , stainless steel, glass
Bazmara and Mohammadnejad (2014)	TiO_2	Sol gel spin coating	Additives and precursor	Glass
Kaewwiset et al. (2008)	TiO_2	Sol gel dip coating	Annealed temperature	glass
Nikolic et al. (2005)	TiO_2	Sol gel dip coating	Annealed temperature, substrate	Quartz glass, quarts single crystal, silicon single crystal, polycrystalline alumina
Alzamani et al. (2013)	TiO_2	Sol gel dip coating	Catalyst	Glass
Wang et al. (2013)	TiO_2	Sol gel dip/spin coating	Coating technique	α-Al_2O_3 substrate
Lim et al. (2010)	TiO_2	Sol gel	pH	-

Golobostanfard and Abdizadeh (2012)	TiO_2	Sol gel spin coating	Solvent	glass
Anastasescu et al (2014)	TiO_2	Sol gel dip coating	Substrate	Glass, FTO, Silicon Wafer
Baglio et al.(2011)	TiO_2	Spray coating	Coating Thickness	FTO
Adochite et al. (2011)	Ag-TiO_2	Magnetron sputtering	Present of silver, Annealed temperature	Silicon and quartz substrate
Wodka et al. (2010)	Ag-TiO_2	Photoreduction treatment	Concentration of silver	-
Amin et al. (2009)	Ag-TiO_2	Sol gel	Calcined temperature	-
Kadziola et al. (2014)	Ag-TiO_2	Sol gel dip coating , reactive magnetron sputtering	Coating method	Silicon wafer
Kumar et al. (2013)	Ag-TiO_2	Sol gel, electron beam physical vapour deposition	Coating method	glass
Peerakiatkhajohn et al. (2011)	Ag-TiO_2	Sol gel dip coating	Concentration of silver	PET
Yu et al.(2011)	Ag-TiO_2	Sol gel spin coating	Concentration of silver	Silicon wafer
Piwonski et al. (2011)	Ag-TiO_2	Sol gel dip coating	Deposition parameter	Silicon Wafer
He et al. (2002)	Ag-TiO_2	Sol gel Dip coating	Present of silver	glass
Zhao, B. and Chen, Y. (2011)	Ag-TiO_2	Sol gel dip coating	Present of silver	Glass
Ubonchonlakate et al. (2012)	Ag-TiO_2	Sol gel dip coating	Present of silver, additive	glass
Prasad et al. (2011)	Ag-TiO_2	Sol gel spin coating	Present of silver	Glass, quartz, silicon substrate

Alzamani et al. (2013) claimed that coating using sol containing acidic catalyst can form no defects, transparent and smooth surface. Besides that, to obtain a self-cleaning surface with high photocatalytic activity, the particles size has to be as small as possible and high anatase phase percent. He found that when the coated substrate undergo heat treatment temperature at 500°C produce smaller particle size and more anatase phases compared to 700°C as shown in figure 2.1. This is because in a sol gel process of transition metal alkoxides, hydrolysis and condensation happen rapidly in high temperature lead to larger crystalline size and non uniform particle form.