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Deposition and characterization of thin Films on Titanium Substrate: Review

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ABSTRACT: Titanium was considered a rare metal, and it was one of the most important metals in the industry. Synthesis and study of the thin films prepared onto titanium substrate by using different physical and chemical deposition methods have been reported by many researchers. Titanium was used as substrate due to good corrosion resistance and high strength weight ratio. The formation of the metal sulphide, metal selenide, metal telluride and metal oxide thin films was confirmed by X-ray photoelectron spectroscopy, Raman spectroscopy, and X-ray diffraction analysis. The compositional, morphological, and optical properties of thin films were investigated by using energy dispersive X-ray analysis, scanning electron microscopy, atomic force microscopy, and UV-visible spectrophotometer, respectively. The obtained thin films could be used in solar cells due to suitable band gap value and high absorption coefficient. On the other hand, these films have potential in super capacitor applications because of good power density, high energy density, excellent cycling stability and good rate capability.

Keywords: titanium, thin films, semiconductor, deposition, metal chalcogenide, solar cell.

I. INTRODUCTION

Titanium was once considered a rare metal, but nowadays, it is one of the most important metals in the industry. Titanium is a transition metal, and it has an incompletely filled *d*-shell in its electronic structure [1]. The melting point of titanium is 1668℃. It has hexagonal closely packed crystal structure (*hcp*) up to a temperature of 882.58℃. Above this temperature, it transforms into a body-centered cubic structure (*bcc*) [2]. Titanium alloys can be grouped into several categories such as *α*, near *α, α+ β,* metastable *β*, or stable *β* [3]. The *α* –stabilizers including Al, O, N, C while β-stabilizer such as Mo, V, Nb, Ta (isomorphous), Fe, W, Cr, Si, Co, Mn, and H. The properties of the materials depend on the composition such as α and near- α titanium alloys (superior corrosion resistance), α+ β alloys (higher strength) and the β alloys (low elastic modulus and superior corrosion resistance) [4, 5]. Figure 1 illustrates the overview of different titanium alloys and their distinct properties such as density, strain rate sensitivity, heat treatment behavior, weldability, and machining response.

Titanium and its alloys became one of the leading and most attractive material used for many applications due to all these significant characteristics. Currently, these materials are the metal of choice in the spatial of biomedical application. Stainless steel and cobalt alloys have also been used for biomedical implants, but they tend to react with the body fluid which usually yielded to corrosion of the material and resulted in damages of the tissues [6]. The main features that make titanium and its alloys to be distinguished and further biocompatible from other materials in the spectrum of biomedical applications including the low level of electronic conductivity, high corrosion resistance, thermodynamic state at physiological pH values, a low ion-formation tendency in aqueous environments, the isoelectric point of the oxide and titanium has a dielectric constant comparable to that of water with the consequence that the Coulomb interaction of charged species is similar to that in water [7-9].

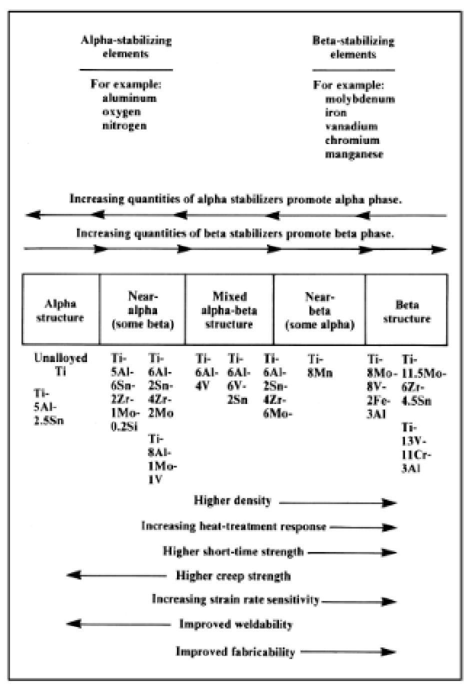

Fig. 1. Overview of variants of titanium and its alloys [1].

Commercially pure titanium is vastly used for dental implants due to its resistance to body fluid effect, surface properties behavior in the spontaneous build-up of a stable oxide layer and biocompatibility [10, 11]. Meanwhile, titanium alloy grade 5 has made a substantial impact in the orthopaedic and prosthesis development [12, 13]. There are several reasons for titanium is used in the body are due to its biocompatibilities of no toxicity, no dissolution out, good adaptability to the tissues, no biodegradation and no decomposition in the human body. Also, titanium has very good mechanical tensile strength, compressibility, ductility, sufficient fatigue strength, high elongation, bending and shearing abilities [14]. On the other hand, titanium has been widely utilized in aerospace and aviation industries owing to high strength to weight ratio, favorable working temperature, composite biocompatibility with polymer, good damage tolerance, mechanical properties and excellent corrosion resistance [15, 16]. The application of titanium alloys for aerospace components such as fan turbine blades, tubes, missile fins, and airframe structure [17, 18]. Titanium alloys have a lot of benefits over other materials including weight savings, space limitations, composites compatibility and low modulus. Researchers also point out that titanium alloys [19] could be used in automobile [20], marine [21] and space applications [22].

The deposition and characterization of nanostructured thin films have been deposited onto various substrates as reported by many scientists. Transparent conducting oxide glass substrate (indium tin oxide and fluorine doped tin oxide glass) is much more popular than titanium substrate because of excellent optical transmittance in visible wavelength, low electrical resistance and high electrical conductivity. In this work, the synthesis of thin films onto titanium substrate was reported. The obtained thin films were characterized by using various tools. The uses of these films will be highlighted as well.

II. LITERATURE SURVEY

Titanium and its alloys have unique properties such as good mechanical properties and corrosion resistance. However, these materials exhibit some limitations such as stress shielding phenomenon, biomechanical compatibility, poor biofunctional and low abrasion resistance [23-25]. Titanium and its alloys are regarded as reactive material and often generate a protective layer spontaneously when exposed to an ambient atmospheric condition which inhibited the propagation of corrosion in the presence of oxygen. However, they lose their ability to regenerate the protective oxide film and resulted in corrosion in an anhydrous condition. With all these limitations, it's imperative to protect the surface properties of titanium alloys with none or minimal change to the overall bulk properties of the material. Coating the surface with nanostructured materials in the form of the thin film is a potential way of mitigating these shortcomings since nanostructured materials increase the performance of the material with improved mechanical, surface properties and consequently enhances the yield of the surface reactions of interest. These limitations have been overcome by several methods. Surface modification and surface coating are the two distinct techniques, were used for addressing, modifying, and improving the challenges of surface properties without leading to any major alteration on the bulk properties.

The properties of the surface of materials could be changed through surface modification method including nitriding, heat treatment process, implantation and carburizing [26-28]. The surface coating method needs the deposition of thin films layer on the surface, and resulted in a change of the properties of the surface. Several examples of this technique including fusion process, physical & chemical vapor deposition, and solution-state processes. This type of process could be reached through the thin film deposition process, plasma enhancement, ion bombardment, self-assembly, nanomachining, and chemical treatment [29-33]. Thin film could be defined as 2-dimensional and has a thickness in the order of 0.1 micrometer, while thick films was around thousands time thicker. The properties of the obtained films showed unique properties such as from single crystal to amorphous, fully dense to less than fully dense, pure to impure, and thin to thick. Thin films offer enormous potential due to the followings [34-36]:

Selection of coating methods depends on the area of application and properties of the coating materials. Forbiomedical implants, the surface roughness of titanium plays a major role in the adhesion, bonding, and stiffness discrepancy between the implants and the bone tissue [37, 38]. It has been proven that increasing the surface roughness of the implant results in higher micromechanical retention than for smooth surfaces [39]. Higher surface roughness transposes to more pores on the surface which in turn enhances the bio-osseointegration interaction of the bone and implants [40].

Bioactive materials are usually used for biomedical coating. Hydroxyapatite (HA) is the most popular used bioactive material due to its exceptional properties like corrosion resistance, biocompatibility and meager contaminants. The coating can either be a unitary coating (single layer coating) or hybrid coating (two or more different materials are coated on the surfaces). Generally, hybrid coating was developed by using electrodeposition, micro-arc oxidation, electrophoresis, sponge replication process, sol-gel, and sputtering method [41-44]. There are many researchers investigated hybrid coating on titanium. It was discovered that the hybrid inorganic/organic coating was successfully deposited without the presence of foreign contaminants. The optimization of the coating process allows the achievement of an adherent, homogeneous, and protective film of tantalum oxidized on its surface (Ta_2O_5). It was also revealed that the modifications with organophosphorus acids allow surface functionalization with quite acceptable coverage regarding the complicate structures of these molecules, better corrosion resistance compares to single layer coating, and decreases in contact angle. Titanium oxide, which is the protective coating that occurred naturally on titanium was produced via micro-arc oxidation, and HA was deposited on it using a combination of plasma electrolysis and electrophoresis to form hybrid coating by Nie and co-workers. Their findings revealed that a hybrid combination of micro-arc oxidation and electrophoretic deposition can provide a phase-pure HA top layer and anticorrosive TiO_2 interlayer, which should show good mechanical and biochemical stability in the corrosive environment of the human body [42]. Their findings also agree with the observation from Lee and co-workers which proved that hybrid coating improved the osteoblastic activity of titanium [43]. Hybrid coating of hydroxyapatite and titania grew by sol-gel shows improvement in bonding strength and cell attachment density compare to single layer coating and also proven to be bioactive from the needle-shaped bone-like apatite formation after exposure to simulated body fluid. Hybrid coatings progress bone bioactivity by inducing the rapid precipitation of coatings on their surface when immersed in a simulated body fluid (SBF) [45]. It can be established that hybrid coating can further enhance the biomedical and mechanical properties of titanium and its alloys and coating has substantial significance on the properties of titanium alloys

Deposition of metal sulphide, metal selenide, metal telluride, and metal oxide thin films onto titanium substrate was investigated. Chemical bath deposition was used to produce cadmium sulphide. The obtained films were annealed to improve photocatalytic activity. Optical studies found that this material has a small band gap value [46]. The influence of sulfurization temperature on Cu_2ZnSnS_4(CZTS) films deposited onto titanium foils was studied. The strongest diffraction peak could be observed in (112) plane based on XRD data [47]. Magnetron sputtering method was used to produce CZTS films on titanium foil. CZTS films have lightweight, suitable for roll to roll manufacturing and flexible properties [48]. Hall effect studies indicated these films are p-type semiconductors, could be used as an absorber in solar cell technology. The growth of chemical bath deposited nickel sulphide thin films onto titanium was reported [49]. Chemical bath contains $Ni(NO_3)_2.6H_2O$ and CH_3CSNH_2 solution. The obtained films were used for the super capacitor application. These films showed good power density (3.05 kW/kg), high energy density (27.4 Wh/kg), good cycling stability (98% retention after 1000 cycles), excellent rate capability (640 F/g at 50 mA/cm^2), and high specific capacitance (788 F/g at 1mA/cm^2).

ZnSe films were synthesized by using electrodeposition method. Deposition was carried out at 60℃, pH 2-2.5 by using $ZnSO_4$ and H_2SeO_3. Voltammetry studies revealed that the reduction of Zn^{2+} ion to zinc metal at -0.95 V versus Ag/AgCl, and three cathodic peaks were detected (reduction of H_2SeO_3 to Se). EDX analysis indicated that the atomic percentage of zinc and selenium was 21.37%, 78.63%, and 26.11%, 73.89% for the films prepared at -0.85 V and -0.95 V versus Ag/AgCl [50]. The brush plating method was used to produce zinc selenide thin films under various temperatures. XPS analysis showed the existence of ZnSe. Photoluminescence studies revealed that the peak at 675 nm and the intensity of peak increased with increasing annealing temperature [51]. Pulse electrodeposition method was employed for the synthesis of ZnSe films in the presence of silicotungstic acid. The films displayed cubic structure and film thickness in the range of 1 to 2.5 µm. Optical investigations showed that an absorption coefficient of about 10^4 cm^{-1} and the band gap in the range of 2.64 to 2.68 eV [52].

Cadmium selenide thin films have been prepared by using the electrodeposition method. XRD data supported the existence of a hexagonal structure with polycrystalline. The crystallite size was 10.2 nm. Photovoltaic parameters were studied, indicated I_{sc}=0.1 mA/cm^2, V_{oc}=303 mV, fill factor=27.06%, and power conversion efficiency =0.0205% [53]. On the other hand, structural and optical properties of cadmium selenide thin films prepared on titanium were studied. The differences could be seen in the band gap, surface morphology, and crystallite size of both types of films (as-deposited and annealed films) [54].

Ternary compounds such as copper indium diselenide ($CuInSe_2$) films have been synthesized onto titanium substrate by using hydrothermally assisted chemical bath deposition technique. The XRD data confirmed all diffraction peaks belonging to the chalcopyrite phase. Experimental results showed that better crystallinity and bigger size could be observed at a higher hydrothermal temperature [55]. Electrode position was utilized to produce $CuInSe_2$ films from aqueous solutions by using different reactants. The nano crystalline structure of $CuInSe_2$ films was prepared using electrolytic bath contains $CuSO_4$, $In_2(SO_4)_3$, and SeO_2 solutions [56]. On the other hand, the ternary semiconductor has been synthesized from a bath containing $CuCl_2$, $InCl_3$, and SeO_2 [57]. The band gap, resistivity, and trap density were 1.08 eV, 10^3 ohm.cm, and 10^{14} cm^{-3}, respectively. Electrodeposition of $CuInSe_2$ films from an aqueous solution containing H_2SeO_3, $CuSO_4$, and $In_2(SO_4)_3$ was reported. The formation of chalcopyrite structure and excellent stoichiometry were found at deposition potential of -0.4 to -0.6 V versus Ag/AgCl after heat treatment [58]. TEM analysis confirmed that diffraction rings are very fuzzy due to the very bad crystallinity in as-deposited films. On the other hand, a complexing agent such as citrate ions was used during the thin film deposition process. The best electrodeposited $CuInSe_2$ films conditions were found at pH 3.3, deposition potential of -0.97 V versus Ag/AgCl [59].

Ternary nanostructured $CdSe_{0.65}Te_{0.35}$ thin films have been synthesized by using electrodeposition technique. The obtained films were stoichiometric and low band gap, which could be used in liquid junction solar cells [60]. The growth of indium doped zinc selenide thin films onto the titanium substrate was reported. Deposition was carried out at -0.8V versus standard calomel electrode (SCE) at room temperature. The film thickness (2.1 to 12 10^{-6} cm), and current density (0.11 to 0.26 mA/cm^2) increased, but the corrosion rate decreases as the composition of indium are increasing from 0.0001 M to 0.0004 M [61].

Electrodeposition of zinc telluride thin films onto titanium substrate have been carried out in the range of -0.6 to -0.8 V versus Ag/AgCl. EDX results showed that atomic percentage of zinc and selenium were 42.9%, 57.1%;

38.1%, 61.9% and 55%, 45% for the films prepared at -0.6 V, -0.7 V and -0.8 V versus Ag/AgCl [50]. Deposition of cubic zinc telluride thin films onto titanium was carried out in acidic bath using electrode position method. The best experimental conditions to produce ZnTe films at deposition potential of -0.8V and -0.9 V versus Ag/AgCl, 98 ℃, pH of 4.5, 0.02M of zinc concentration. Annealing process (450 ℃, argon, 60 minutes) was used to improve the optical and crystalline properties of films [62]. On the other hand, zinc telluride films were prepared via cathodic electrode position under different conditions. Experimental results showed that the best stoichiometric film with smooth surfaces could be produced by using a minimum concentration of zinc ions, pH =3.5, deposition potential of -1.1 V versus saturated calomel electrode, and 90 ℃ [63]. Electrode position of $CuInTe_2$ films from acidic solution containing $CuCl_2$, $InCl_3$ and TeO_2. Experimental findings concluded that the stoichiometry of films strongly depended on electrolytic bath composition and deposition potential [64]. Deposition of $CuInTe_2$ thin films was carried out in the alkaline bath. The as-deposited films were amorphous, uniform, adhered well to the substrate and fine grain structure [65].

The Cu_2O thin films have been deposited onto the titanium substrate by using electrode position method. The n-type (pH 5.4, pH 6.3 and pH 6.6; 0.005M, 0.008M and 0.01M of cupric ion) and p-type of films (pH 7.9; 0.0005M, 0.001M and 0.002 M of cupric ion) could be prepared under various pH values and the cupric ion concentration [66]. On the other hand, the influence of deposition potential on the electrodeposited Cu_2O films was studied. XRD data confirmed that the intensity of diffraction peaks decreased when the deposition potential was increased. Surface morphology investigation showed regular, well-faceted, octahedral to cubic, agglomerated particles with the increasing of deposition potential from -0.1V to -0.9 V versus Ag/AgCl. Optical properties showed that the band gap values are in the range of 1.69 eV to 2.03 eV [67]. Zinc oxide thin films were prepared onto titanium through electro deposition method. The strongest peak corresponding to (101) plane with hexagonal wurtzite phase. The larger crystallite size (46 nm) could be observed for the films prepared using 0.5 M of zinc nitrate if compared to 0.1 M of zinc nitrate (41.1 nm) [68]. The pulsed laser deposition technique was used to produce zinc oxide films under various substrate temperatures. The best substrate temperature was 500℃. The presence of TiO_2 could be seen at high temperature based on XRD, XPS, and Raman results. Experimental findings supported that these films could be used in the microwave and direct current, and medical applications [69].

The synthesis and properties of thin films onto various substrates were reported by many researchers. These substrates including Si (100) substrate [70], soda lime glass [71], Ge (100) substrate [72], microscope glass [73, 74], corning 7059 glass [75], indium doped tin oxide [76-78], fluorine doped tin oxide glass (FTO) [79], plastic foil [80], stainless steel [81], and mica [82]. Experimental results confirmed that the choice of substrate is a very important stepin order to achieve desire products. This is due to the substrate exerts considerable influence on film characteristics [83]. Researcher highlighted that successful product design needs knowledge about the choice of substrate. The obtained films have true potential for solar cell [84-86], and opto electronic applications [87-89].

III. CONCLUSION

The growth of thin films onto a titanium substrate has been successfully described by many researchers. Experimental results confirmed that the choice of substrate is a very important step in order to achieve desire products. Because of the substrate exerts considerable influence on film characteristics. The obtained films have great potential in solar cell, super capacitor and opto-electronic applications

IV. FUTURE SCOPE

Deposition of thin films onto other types of substrates will be studied.

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Conflict of Interest. No.

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