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### ABSTRACT

## CHARACTERIZATION AND CORROSION OF BCC-TANTALUM COATING DEPOSITED ON ALUMINUM AND STEEL SUBSTRATE BY DC MAGNETRON SPUTTERING

### by Chirag Joshi

Tantalum is one of the most versatile highly refractory corrosion-resistant metals. Tantalum coating can be used as an effective corrosion barrier if it is continuous, free from defects and it adheres well to the substrate. A DC magnetron sputtering technique was used to deposit tantalum on aluminum and steel. X-ray diffraction measurements revealed that the tantalum films produced by sputtering had two crystallographic structures: a body centered cubic  $\alpha$ -phase and a metastable tetragonal  $\beta$ -phase. Tough and ductile alpha phase tantalum is preferred over the hard and brittle beta phase tantalum, as a protective coating. Alpha phase coatings were successfully deposited on aluminum and steel at room temperature by depositing interlayer of tantalum nitride prior to tantalum and also on heated substrates of aluminum and steel at 400°C with argon sputtering gas. Alpha phase was also obtained on sputter-etched aluminum at room temperature, while beta phase was obtained at room temperature if aluminum was not sputter-etched. The tantalum nitride films were investigated by X-ray diffraction and by four-point probe resistivity measurements. The resistivity was found to increase, as concentration of nitrogen in sputtering gas was increased.

Corrosion resistance of tantalum coating was evaluated using potentiodynamic and potentiostatic methods. Potentiodynamic test carried out on bcc tantalum coated aluminum and steel revealed a very low corrosion current density, indicating good corrosion resistance. Tetragonal tantalum coated on aluminum was evaluated by potentiostatic test, which indicated some corrosive effects after four days of continuous testing. This study confirms that high quality coatings of tantalum can be deposited on steel and aluminum by DC magnetron sputtering. The coatings of alpha phase tantalum on metal such as steel and aluminum have potential applications as corrosion barriers.

## CHARACTERIZATION AND CORROSION OF BCC-TANTALUM COATING DEPOSITED ON ALUMINUM AND STEEL SUBSTRATE BY DC MAGNETRON SPUTTERING

By Chirag Joshi

A Thesis

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### **APPROVAL PAGE**

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With all my love to

My dearest Mom, Dad and Brother

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vi

Cł	apte	r	Page		
1	INT	TRODUCTION			
	1.1	Objective			
	1.2	2 Application of Tantalum			
	1.3	Properties of Tantalum and its Crystallographic Structure	4		
	1.4	The Scope in this Work	8		
2	SPU	TTERING AS A DEPOSITION PROCESS	9		
	2.1	Coating Technology	9		
		2.1.1 Deposition Process	9		
	2.2 Sputtering				
		2.2.1 Ion - Surface Interaction	10		
		2.2.2 Mechanism of Sputtering	12		
	2.3	Thin Film Formation	14		
	2.4	Sputtering Techniques			
		2.4.1 Diode Sputtering	16		
		2.4.2 Magnetron Sputtering	18		
		2.4.3 Sputtering Method	21		
3	COF	ROSION	26		
	3.1	Definition	26		
	3.2	Corrosion Principles	26		
	3.3	Polarization	29		
		3.3.1 Activation Polarization	31		

## TABLE OF CONTENTS

## TABLE OF CONTENTS (Continued)

Chapter			Page
		3.3.2 Concentration Polarization	33
	3.4	Passivity	34
	3.5	Electrochemical Techniques	36
		3.5.1 Potentiodynamic Polarization	37
		3.5.2 Potentiostatic Polarization	40
	3.6	Tafel Plot	40
4	EXF	PERIMENTAL SET-UP PROCEDURE	43
	4.1	Mechanical Cleaning	43
	4.2	Electrochemical and Ultrasonic Cleaning	45
	4.3	DC Magnetron Sputtering System	47
	4.4	Sputter-Etching	52
	4.5	Deposition Procedure	53
5	CH	ARACTERIZATION TECHNIQUES	55
	5.1	Dektak Profilometer	55
	5.2	X-ray Diffraction	56
	5.3	Four Point Probe Technique	59
	5.4	Corrosion Testing Method	61
6	AN	ALYSIS OF DEPOSTED FILMS	64
	6.1	Deposition of the Film	65
	6.2	Resistivity Measurement	68

## TABLE OF CONTENTS (Continued)

Cl	napte	r	Page
	6.3	X-Ray Analysis	69
		6.3.1 Tantalum Deposition on Steel and Aluminum Substrate at Room Temperature	69
		6.3.2 Tantalum Deposition on Heated Substrates	71
		6.3.3 Tantalum Deposition with Interlayer of Tantalum Nitride	74
	6.4	Corrosion Testing	78
7	CON	NCLUSION	84
	APP	PENDIX A STANDARD POWDER DIFFRACTION PATTERNS FOR $\alpha$ -TANTALUM AND $\beta$ -TANTALUM	87
	APP	ENDIX B SPUTTERING DEPOSITION DETAILS OF SAMPLES REPRESENTING THE DATA POINTS IN FIGURE 6.2, 6.3 AND 6.7	89
	APP	PENDIX C SPUTTERING DEPOSITION DETAILS	90
	REF	ERENCES	92

## LIST OF TABLES

Table		Page
1.1	Properties of Tantalum	6
4.1	Grinding Process and Parameters	44
4.2	Polishing Process and Parameters	44

## LIST OF FIGURES

Figure		Page
2.1	Interactions of ions with surfaces	11
2.2(a)	Sputtering – the atomic billiards game	12
2.2(b)	Collision process responsible for sputtering and fast neutral generation	13
2.3	Formation of a thin film	14
2.4	Schematic of a diode sputtering system	11
2.5	Schematic of magnetron sputtering	19
2.6	Motion of an electron ejected from a surface with velocity v into a region of magnetic field B parallel to the surface: (a) with no electric field, and (b) with a linearly decreasing field	20
2.7	Schematic of RF sputtering system	22
2.8	Ion beam sputtering	23
3.1	Schematic Diagram for a Metal Corroding in an acid	27
3.2	Hydrogen reduction reaction under activation control	31
3.3	Concentration polarization during hydrogen reduction	33
3.4	Corrosion characteristics of an active-passive metal as a function of potential	35
3.5	Theoretical and actual Potentiodynamic polarization plot active–passive metals	38
3.6	Tafel Plot	40
4.1	MINIMET 1000 Grinder/Polisher	43
4.2	Planer DC magnetron sputtering system at NJIT	47
4.3	Substrates mounted on a holder	48
4.4	A view of the vacuum chamber lid	49

## LIST OF FIGURES (Continued)

Figure		Page
4.5	Inner view of deposition chamber	50
5.1	Dektak II Profilometer	55
5.2	Diffraction of x-rays by planes of atoms (A-A1 and B-B1)	56
5.3	Schematic diagram of an x-ray diffractometer	57
5.4	Schematic of the in line-four point probe	59
5.5	Resistivity meter	59
5.6	Experimental set-up measurements	62
6.1	Sputter etching current as a function of time at constant voltage (400 V) for for aluminum and steel substrates	65
6.2	Step Profile of a SiO <sub>2</sub> substrate with Ta deposition	66
6.3	Deposition rate of the TaN films deposited at various $N_2$ -Ar ratios	67
6.4	Resistivity of the TaN films deposited at various N2-Ar ratios	69
6.5(a)	XRD spectrum of Ta deposited on aluminum sample	70
6.5(b)	XRD spectrum of Ta deposited on steel sample	71
6.6	XRD spectra of aluminum and steel substrate heated to 400°C	72
6.7(a)	Microscopic image of Ta on steel substrate	73
6.7(b)	Microscopic image of Ta on Al substrate	73
6.8	XRD spectra of tantalum coating deposited on nitride interlayer on sputter etched aluminum and steel substrate	75
6.9	Comparison of XRD spectra of tantalum nitride film $(1 \ \mu m)$ deposited on sputter-etched steel substrates	76
6.10	XRD spectra of tantalum coating deposited on nitride interlayer on non-sputter etched aluminum and steel substrates	77

## LIST OF FIGURES (Continued)

Figu	re	Page
6.11	Tafel plot of Potentiodynamic test performed at room temperature in water pH 5 for alpha Ta coating deposited on aluminum and steel substrates	79
6.12	The corrosion current density vs the time plot measured by Potentiostatic test in pH 5 water at room temperature on (a) tetragonal Ta coated aluminum and (b) bare aluminum	81
6.13	Microscopic image of Ta deposited on Al substrate before potentiostatic Test	82
6.14	Microscopic image of Ta deposited on Al substrate after potentiostatic Test	83

## CHAPTER 1 INTRODUCTION

### 1.1 Objective

Metals and alloys still constitute the most important group among engineering materials, and the demand for metallic materials with higher strength and a special properties is on the increase with the advancement of technology. However, these metallic materials deteriorate due to its chemical or electrochemical interaction and can be released to environment through corrosion process. Often this leads to economical loss, environmental pollution, and in some cases risk to human lives [1]. In the U.S., costs currently exceed \$300 billion a year to replace the corroded materials [2]. These problems caused by corrosion lead to the development of corrosion protection methods.

The application of coating, metallic or nonmetallic, is widely used technique for protection against corrosion. The primary goal of coating is to provide a physical barrier between the metal and the environment [1]. Coating can also enhance the surface properties. For example, chromium because of it high corrosion resistance and hardness is used to coat steel, subject to erosive and corrosive wear, in medium and large caliber gun tubes [3]. However, chromium is a carcinogen and can cause stomach, kidney and liver damage, convulsions, and in large doses leads to death. The disposal of chromium waste is hazardous to environment [4].

As environmental regulations become increasingly stringent alternative coating materials are being evaluated. Metallic tantalum (Ta) is one material that has received

1

attention as a potential replacement for chromium in some applications. In the case of gun tubes it can satisfy new, more demanding service required with rate of high-energy propellants.

Tantalum is one of the most versatile corrosion-resistant metals, highly refractory, and is chemically resistant to propellant gases. Tantalum has a relatively low thermal conductivity, and is much more ductile than chromium. Tantalum pentoxide, which forms on its surface acts as a passivating barrier [3][5]. Effects of tantalum in the environment are under investigation, but there is no known health hazard associated with this metal. Sputtering of tantalum is an environmentally friendly and clean process.

The purpose of this research is to investigate and characterize the properties of tantalum coating deposited on steel and aluminum by D.C.- magnetron sputtering and to test the corrosion resistance of tantalum films.

This thesis is a part of a larger project of U.S. Army for deposition of Ta coating carried out at the Ion Beam and Thin Film Research Laboratory at NJIT.

### **1.2 Application of Tantalum**

The investigation of tantalum thin films over the past 30 years has been stimulated by its applications in electronic devices, such as thin film capacitor and resistor [6] and as a biomedical material in orthopedics [7]. Tantalum films are also of interest for application in X-ray optics [8] and as absorbers for X-ray lithography [6]. Since the advent of copper interconnects for deep sub-micron multilevel integrated circuits (ICs), tantalum has become a highly promising diffusion barrier material for copper interconnects integrated circuits [9], polish stop and adhesion layer for chemical-

mechanical polishing of damascene process [10]. Tantalum [8] and tantalum nitride (TaN) thin films [10] are the most promising diffusion barriers to prevent highly diffusing copper, used for conductor line metallization from penetrating to the silicon substrate and into SiO<sub>2</sub> dielectric layers [8]. A desirable feature of such barriers is low resistivity, which depend on the crystalline phase viz. body centered cubic ( $\alpha$ -Ta) and tetragonal metastable phase ( $\beta$ -Ta), as described in Section 1.3 [11].

The nearly ideal, low loss, dielectric properties of tantalum oxide  $(Ta_2O_5)$  layers grown on Ta films are desirable for superconducting tunnel junctions produced with  $Ta_2O_5$  tunnel barriers on Ta base electrodes for producing quantum-limited millimeter-wave receivers [12].

Tantalum oxide is used to make a glass with a high index of refraction, with applications including use for camera lenses [13].

Other applications of Ta include:

- Components for chemical plants, nuclear power plants, airplanes and missiles.
- Tantalum can be used to fabricate valves for corrosive liquids and to manufacture heaters for acids and heat shields for rocket motors.
- Tantalum mill products are used in the fabrication of corrosion resistant process equipment including reaction vessels, columns, bayonet heaters, shell and tube heat exchangers, U-tubes, thermowells, spargers, rupture diaphragms, and orifices.
- Heat transfer units made from tantalum are also used in pickling lines in steel production.
- Tantalum is alloyed with steel to increase steel's ductility, strength and melting point [14].

- It is also used as a component of ion implanters in the manufacture of semiconductors.
- Sutures as well as orthopedic implants, such as artificial joints and cranial plates. Tantalum does not react with bodily fluids and is a non- irritating metal [13] [15].

### **1.3 Properties of Tantalum and its Crystallographic Structure**

Tantalum is strong, ductile metal that is nearly immune to chemical attack at room temperature. It combines the inertness of glass with the strength and ductility of lowcarbon steel and has a much higher heat transfer capability than glass [5]. Tantalum metal possesses excellent resistant to erosion, chemical stability, histocompatibility [7] and robust mechanical properties [12] to make it a particularly desirable material. Outstanding corrosion resistance and inertness of tantalum are attributed to thin, impervious, protective oxide film  $(Ta_2O_5)$  that forms upon exposure of the metal to anodic or oxidizing condition [5]. It offers the same level of corrosion resistance as platinum and glass [15] and equals glass in resistance to acids and is far superior to Titanium, Zirconium, and Niobium. It is impervious to liquid metals up to 1650°F. It shows exceptional corrosion resistance to most of corrosive environments. Only a few reagents - hydrofluoric acid, fuming sulfuric acid, and strong alkalis - will begin to break through tantalum's corrosion barrier. Therefore it can be used for hydrochloric acid or sulfuric acid condensers, surface treatment equipments, and electro-plating equipments [16].

The properties and crystal structure of tantalum thin films are dependent on the deposition techniques and conditions [6]. Tantalum films produced by sputtering occur

in two crystallographic structures: a body centered cubic  $\alpha$ -phase (*Im3m* space group, a=3.304 Å) and a metastable tetragonal  $\beta$ -phase (P42/mnm space group, a=5.313 Å, c=10.194 Å) [18], which have very different physical and electrical properties [12].

In bulk,  $\alpha$ - Ta, possesses good chemical, thermal, and mechanical properties, including a high melting temperature, elastic modulus similar to that of steel, good ductility and formability, and resistance to acids [18]. It is highly refractory (mp=2996°C) and has a relatively low thermal conductivity (57 W/m°C). The bcc-Ta has a superconducting transition temperature T<sub>c</sub> of 4.4 K [12] and a low resistivity of  $\rho \sim$  15-60  $\mu\Omega$ -cm, which makes it good choice for the thin film interconnection and for protective coatings [6].

The physical properties of  $\beta$ -phase tantalum are not well know, except that it is hard, brittle, and thermally unstable, as it transforms to  $\alpha$  -phase tantalum at 750-1000°C [18]. Typical knoop microhardness values for  $\beta$ -Ta are greater than 900 vs. knoop values of 300-400 for  $\alpha$ -Ta. These properties make  $\beta$ -Ta more susceptible to crack formation and failure, and hence less desirable for protective coating applications where thermal shock and high shear forces are present [19]. There is only one report on  $\beta$ -Ta grown in the bulk form [12]. The  $\beta$ -Ta has a superconducting transition temperature of T<sub>c</sub> of 0.5 K [12] and resistivity of 170-210  $\mu$ Ω-cm [6]. The metastable  $\beta$  phase and mixed phase Ta is usually observed in sputtering deposited films [6] [19]. Properties of the two phases of tantalum are listed in the Table 1.1 below [20]:

	Density		Temperature	Super	
Tantalum	(theoretical)	Resistivity	Coefficient	Conductivity	Structure and
[Phase]	[gm/cc]	[μΩ-cm]	of Resistance	T <sub>c</sub> [K]	lattice
		-	[Ppm/°C]		constant [Å]
Bulk	16.55	13	3800	4.4	Bcc
Tantalum					a=3.304
Sputtered	16.55-16.27	24-50	+500 +1800	3.25	Bcc
Bcc					a=3.3-3.4
Tantalum					
Sputtered	16.9	180-220	-100 +100	0.5	Tetragonal
Beta					a=5.313
Tantalum					c=10.194

 Table 1.1 Properties of Tantalum

The mechanisms that lead to the formation of  $\alpha$ -Ta or  $\beta$ -Ta in deposited films are not clearly identified even though a large number of papers have been published [12]. Lee and Windover [17] proposed that  $\beta$ -Ta is an impurity-stabilized phase formed to accommodate oxygen or nitrogen when their concentrations in the coating exceed their solubility limit. Lee et al. [18] concluded that the  $\beta$ -phase is always obtained on substrate, which contain oxygen or have surface oxide. Several author have found that the nature of the substrate [12], impurity content, substrate bias, temperature and surface preparation, [17] have a large effect on the nucleation of either  $\beta$ -Ta or  $\alpha$ -Ta. Vacuum system impurities have also been found to have large effect on the nucleation and growth of Ta films [12].

The ability to control the structure of Ta films has been highly desirable for coatings and thin film applications. Choice of substrate or underlayer material is often decisive for the structure of the sputtered Ta layer [8]. Interfacial layer of Ti is reported to promote growth of  $\alpha$ - Ta phase [21]. Face and Prober [12] has suggested that a niobium underlayer, as thins as 1nm, ensured  $\alpha$ -Ta formation. Niobium and bcc-Ta has

the same crystal structure and the lattice mismatch of less than 0.1%. Also, Nb underlayer will neutralize the effect of O or OH formed by the reaction of H<sub>2</sub>O with the surface, which favors the nucleation of  $\beta$ -Ta. Lee and Windover [17] studied the impurity effects on nucleation, and reported that for the same sputtering conditions, tantalum phases depend on the type of substrate. Lee et al. [18] suggested that substrate with high resistance to oxidation always nucleate in the  $\alpha$ -phase, such as Au, Pt, Rh, Be. Lee and Windover [17] reported sputtered  $\alpha$ -Ta on cylindrical bore surfaces using Nb underlayer. Lee et al. [18] found that interface layer of Ta (N) promoted the growth of  $\alpha$ -phase tantalum thin films. Pure  $\alpha$ -Ta is also obtained on steel substrate, which is heated at 250°C and 300°C in presence of Kr and Ar sputtering gases respectively [9]\*. Tantalum deposited on SiO<sub>2</sub> (thermally oxidized Si wafers), Corning 7059 glass, BeO and sapphire (layer thickness up to 15nm) lead to the formation of tetragonal  $\beta$ -Ta, while bcc  $\alpha$ -Ta is formed on Al and Cr. Using evaporation techniques the formation of  $\alpha$ -Ta has been reported. In addition,  $\beta$ -Ta layer can be transformed into the equilibrium  $\alpha$ phase by annealing [8].

Note: \* From the recent experiment it was found more accurately that pure  $\alpha$ -Ta is obtained on steel substrate when heated at 350°C and 400°C in presence of Kr and Ar sputtering gases respectively.

### **1.4 The Scope of this Work**

In this research, tantalum films were deposited in planar DC magnetron sputtering system, on aluminum and steel substrate, under various process parameters. Obtained tantalum films were characterized using different characterization technique.

Chapter 1 deals with the application of Tantalum coating for protection against corrosion. It also describes the properties and crystallographic structure of tantalum. Chapter 2 describes sputtering as a deposition process. Thin film formation and different sputtering technique are also described. Description of the corrosion principles is given in Chapter 3. The polarization, passivity and electrochemical technique like potentiodynamic and Potentiostatic are explained. Chapter 4 deals with the description of the experimental set-up of planar DC magnetron sputtering system and deposition procedure. It also explains the surface preparation of the substrate before mounting inside the deposition chamber. Chapter 5 explains the analysis of the films by technique like XRD, potentiodynamic and potentiostatic. Results and discussion are discussed in Chapter 6, followed by conclusions in Chapter 7.

### **CHAPTER 2**

### SPUTTERING AS A DEPOSITION PROCESS

### 2.1. Coating Technology

Coating is the process in which a layer of material is applied to the surface of another material resulting in a combination of materials that function properly both on the surface and as a bulk. Normally, the materials used as the coating may have significantly different properties than bulk material.

Thick film deposition is the traditional coating technique. Many coating techniques belong to this category, e.g., painting, sol-gel, dipping and sintering. [22]. The main emphasis of this thesis is on thin films deposited by sputtering technique.

### **2.1.1 Deposition Process**

A large variety of "thin films" are used in today's industry for the fabrication of various microelectronic, optical and bioengineering devices [23]. The Thickness of these films is usually from a few angstroms (1 Å =  $10^{-10}$  m) or a few monolayers of material, up to a micron. Thin films are of interest not only because they are thin, but also because the ratio of the surface area to the bulk volume is so high that the surface properties become very important [24].

Physical vapor deposition (PVD), term that includes both evaporation and sputtering, and Chemical vapor deposition (CVD), together with all of their variant and hybrid processes, are basic film deposition methods. Chemical vapor deposition is the process of formation of stable solids by decomposition of gaseous chemicals using heat, plasma, ultraviolet, or other energy sources, or a combination of sources [24]. The basic

mechanism behind physical vapor deposition is that materials are vaporized by heat, radiation, electrical discharge, or energetic bombarding, and then the vaporized species are condensed on the substrate resulting in deposition of thin film.

The formation of thin film by PVD includes the processes of sputtering and evaporation. In evaporation, atoms are removed from the source by thermal means, whereas in sputtering through impact of gaseous ions. These techniques can also produce thicker coatings. The deposition of a liquid on a substrate to form thin films is most commonly done by spin coating, which involves the acceleration of a liquid puddle on a rotating substrate [22][23][26].

### 2.2 Sputtering

### **2.2.1 Ion – Surface Interactions**

When an energetic ion approaches the surface of a solid usually called the target, the following phenomena may occur as shown in Figure. 2.1.

- The ejection of surface atoms or molecules of a solid due to the momentum transfer associated with surface bombardment by energetic particles (i.e. ions), called secondary electron.
- The ion may become buried in the target. This is ion-implantation, extensively used in integrated circuit technology and in other applications, such as surface treatment of steels.
- The ion may be reflected, being neutralized in the process.
- The ion impact may be responsible for some structural rearrangements in the target material.

• The ion impact may set up a series of collisions between atoms of the target, leading to the ejection of one of the target atom. This ejection process is known as sputtering [26].



Figure 2.1 Interactions of ions with surfaces [26].

### 2.2.2 Mechanism of Sputtering

Sputtering is a process operating on an atomic or molecular scale whereby an atom or molecule of surface is ejected when the surface is struck by a fast incident particle. The ejected atom and/or molecules are deposited on the surface of different material (substrate) and condensed to solid thin films. Since sputtering removes and transports the target material, it can be used as a method of film deposition or etching. The process is often linked to a game of atomic snooker as shown in Figure. 2.2, since the scattering process employs similar mechanics. In snooker the cue ball (the bombarding ion) strikes the neatly arranged pack (the atomic array of the target), scattering balls (target atoms) in all directions, including some back towards the player, i.e. out of the target surface [22][24].





(Target)

Figure 2.2 (a) Sputtering – the atomic billiard game [26].



**Figure 2.2(b)** Collision process responsible for sputtering and fast neutral generation [27].

In the sputtering process, the interatomic potential (the variation of interatomic repulsion or attraction with separation distance) is different from the hard sphere in snooker, but snooker model is not too unrealistic [26].

Sputtering is a versatile process. It has become dominant technique for depositing a variety of metallic films in VLSI and ULSI fabrication, including aluminum alloys, titanium, titanium nitride, tantalum and cobalt. It is now widely used in manufacturing of cutting tools, forming tools, injection molding tools and common tools such as punches and dies, to increase wear resistance and service life. Both reactive and non-reactive process can be used with contemporary sputtering techniques [22][26][27].

In sputter deposition, ultra thin films of thick coatings of target material can be deposited on to the substrate surface. The material arrives at the substrate mostly in an atomic or molecular form.

(a) Single Atom Arrives



(b) Migration Re-evaporation



(c) Collision & Combination of Single Atoms



(d) Nucleation









## (g) Coalescence



(h) Continuity



Figure 2.3 Formation of a thin film [26].

As shown in Figure 2.3, atom diffuses around the substrate with a motion determined by the impingement energy to the substrate and substrate temperature (Figure 2.3a). An atom after arriving at substrate either jumps over the energy barriers into adjacent adsorption sites (migrate) or might re-evaporate (Figure 2.3b). After certain time, if the atom will not evaporate form the surface it will join with another diffusing single atom to form a doublet, which is less mobile but more stable than the single atom and has a lower chance to re-evaporate (Figure 2.3a). In time, the doublets will be joined by other single atoms to form triplets, quadruplets and so on. This is the nucleation stage (Figure 2.3d) of thin film growth, leading to the formation of quasi-stable islands (Figure 2.3e), each containing tens or hundreds of atoms and typically having densities of  $10^{10}$ /cm<sup>2</sup>. In island growth stage, islands grow in size rather than in number (Figure 2.3f) to touch each other leading to agglomeration or coalescence stage (Figure 2.3g) that proceeds until the film attains uniformity (Figure 2.3h), but this may not occur in some cases until the film is several hundred angstroms in average thickness. This is the phenomenon of epitaxy. This collective set of events occurs during the early stages of deposition, leading the thin film formation of desired thickness.

Depending upon the type of substrate, the resulting film may have crystallographic orientation. If the substrate is made of single crystal or amorphous, the film is randomly oriented or uniformly oriented [24][26].

### 2.4 Sputtering Techniques

A wide variety of sputtering techniques have been used in the preparation of tantalum thin films. They fall in to two categories:

- 1. Diode Sputtering
- 2. Magnetron Sputtering

In addition, the modifications, which are necessary to make the sputtering methods work with all materials, will be discussed. These methods are:

- 1) RF Sputtering.
- 2) Ion Beam Sputtering.
- 3) Reactive Sputtering.
- 4) Bias Sputtering.

### **2.4.1 Diode Sputtering**

In Diode Sputtering, a large potential between the cathode (target) and anode (substrate) with the presence of gas at lower pressure (generally argon) will result in the formation of plasma containing electrons and ion. When ions, accelerated by high electron energy, strike the cathode, they sputter some of the target atoms off. They may also liberate secondary electrons form the target and it is these secondary electron, which are responsible for maintaining the electron supply and sustaining the glow discharge. The sputtered atoms fly off in random directions, and some of them land on the substrate, condense there, and form a thin film layer. A Schematic of system is shown in Figure 2.4.

It is necessary to provide a uniform and abundant supply of ions over the surface of the target to maintain the movement of the sputtered atoms across the gap between the target and the substrate.



Figure 2.4 Schematic of a Diode sputtering system [25].

DC sputtering can only be used to deposit coatings, which are electrically conductive. This method of deposition cannot be used to deposit insulators, since charge will build up on the target surface [22][26] [29].

### **2.4.2 Magnetron Sputtering**

In Diode Sputtering, most secondary electrons emitted from the target do not cause ionization events with Ar atoms. They end up being collected by anode, substrates, etc., where they cause unwanted heating. Since most electrons pass through the discharge region without creating ions, the ionic bombardment and sputtering rate of the target is low because only some electrons are involved in ionizing collisions. To increase ionization efficiency and sputtering rate, magnetron sputtering is used.

In magnetron sputtering technique, the material of which the coating is to be made (target) has magnets arranged behind it, which create a magnetic trap for charged particles. When the power is applied, the target at a negative voltage attracts argon ions to its surface. When they hit it, two processes occur,

- Atoms are knocked out of the target surface by the ions this is sputtering. It is these atoms, which impact the substrate to form the coating.
- The surface also releases electrons, which are negatively charged sub-atomic particles. These are held in the magnetic trap near the target, where they produce more argon ions. This means that the ions, which are attracted to the surface, are replenished all the time. More ions hitting the target increase the sputtering rate.

Magnetron sputtering is a powerful and flexible technique, which can be used to coat virtually any substrate with a wide range of materials – any metal or alloy and a variety of compounds. A schematic diagram of magnetron is shown in Figure 2.5 [30].



Figure 2.5 Schematic of Magnetron sputtering [30].

### Fundamentals of Magnetron sputtering

Consider the motion of charged particle of charge q, mass m, and initial velocity  $v_0$ , that is perpendicular to uniform magnetic field, B, as shown in Figure 2.6. The charged particle experiences a magnetic force F perpendicular to both velocity and the direction B, where

$$\mathbf{F} = \mathbf{q} (\mathbf{V} \mathbf{x} \mathbf{B}) \tag{2.1}$$

Electron moves in circular path with radius r due to perpendicular force F if the electron does not collide. It will return to the surface with velocity v. The radius r is given by,

$$\mathbf{r} = (\mathbf{m} \mathbf{v})/\mathbf{q} \mathbf{B} \tag{2.2}$$


**Figure 2.6** Motion of an electron ejected form a surface with velocity v into a region of magnetic field B parallel to the surface: (a) with no electric field (b) with a linearly decreasing field [26].

To examine the situation of electron, which is emitted from the target surface, consider magnetic field, B, parallel to the surface, and an electric field perpendicular to the surface (due to dark space). The magnitude of the electric field is given by:

$$E = E_o (1-y/L)$$
(2.3)

Where  $E_0$  is the magnitude of target surface and L is length of dark space and y is vertical distance above the target. An electron will get accelerated away from the target in a direction perpendicular to the target surface by electric field and experience force F due to magnetic field B. If magnetic field is strong enough to deflect electron velocity, its motion will be decelerated by the electric field and will come to rest at target surface. At this point cycloid period will be initiated, with electron again being repelled by the E-field.

The net result is that the electron is trapped near the target, by combination of magnetic field and electric field, so less electron going to anode. Such trapped electrons

are needed to make lot of ionizing collision to sustain the glow. Sputtering also leads to the heating of the target due to energetic ion bombardment, so the magnetron target mounting incorporates channels for water-cooling during operation to save the life of magnet [26] [27].

## 2.4.3 Sputtering Methods

**2.4.3.1 RF Sputtering.** If an insulating coating is to be deposited, DC sputtering cannot be used to deposit due to following reasons:

- In this case, the target will block the DC current and no stable gas discharge can be produced.
- If an insulating coating is deposited by a DC reactive process, the growing insulating film on the substrate and anode area is charged up which then generates arcs.

RF Sputtering can be used to deposit both conductors and insulators. In such a system, the RF power alone is capable of generating the plasma and accelerates ions to the target, followed by electrons so as to avoid charge build up, to cause sputtering. However, deposition rate is generally lower than that of DC sputtering.

In RF sputtering, the sign of the electrical field at every surface inside the plasma chamber is changing with the driving rf frequency. This avoids charge-up effects and reduces arcing. Magnetic field is not necessary when no magnet is used or very lower target erosion is achieved. RF sputtering system requires a very well designed matching network and components [22][26][28].

A schematic diagram of a RF sputtering system is shown in Figure 2.7.



Figure 2.7 Schematic of RF sputtering system [25].

2.4.3.2 Ion Beam Sputtering. In Ion Beam Sputtering, a high-energy ion beam impacts the sputtering target. Material is sputtered off of the target upon impact and reflected at an oblique angle to the incident ion beam. The material is reflected towards the sputtering substrate where it is deposited to form a film.

Ions are generated by an external ion beam source. This means that the substrate can be located in virtually field-free high vacuum environment, and this has several implications for the growth of the film. A typical arrangement is shown in Figure 2.8. This system requires that the ion does reach the target without being diverted by collisions with gas atoms. This type of sputtering allows one to have control over the energy and the current density of the incident ions on the substrate surface [24][29]. The deposition rate is relatively low. It can be used to deposit both conductive and non-conductive films [22].



Figure 2.8 Ion beam sputtering [24].

**2.4.3.3 Reactive Sputtering.** In reactive sputtering, reactive gases are introduced in to sputtering chamber during deposition process allowing material sputtered from the target to combine with such gases to obtain chemical compound films. The reaction could take place at any of all or three locations i.e. target, in gas phase or at substrate surface [24]. The resulting film is either a solid solution alloy of the target metal doped with the reactive element (e.g.,  $TaN_{0.01}$ ), a compound (e.g., TiN), or some mixture of two.

The advantages of this method are:

- Compounds can be formed using metallic targets.
- Insulating film can be deposited.
- Films can be of graded composition.
- It offers a mean of controlling the stoichiometry of the film.

The disadvantages of this method are,

- The gas injection rate affects the film properties in a non-linear fashion that is difficult to predict. The effects are evident in the growth rate, composition and film structure [29].
- Target poisoning (a compound layer formed on the target due to excess of reactive gas) which lead to instabilities like sparks and plasma extinguishing. By increasing the pumping rate of the chamber and decreasing the concentration of reactive elements in the working gas atmosphere the problem can be resolved.

Reactive sputtering can be applied to any of the sputtering methods that have been discussed.

2.4.3.4 Bias Sputtering. Bias Sputtering is the process of negatively charging the substrate with respect to the plasma potential creating an attraction between ions and the substrate.

With ions bombarding the film, and with the sensitivity of the nucleation and growth processes to this bombardment, changing the flux and energy of incident particles can control properties of film. It is difficult to control the motion of the neutral particles, but changing the local electric field can control the charged particles. This is the basis of bias sputtering, which can be applied to any of the previous methods of sputtering that have been discussed (dc, RF, magnetron, and reactive).

With the target voltages of -1000 to -3000 V, bias voltage of -50 to -300 V are typically used. Due to charge exchange processes in the anode dark space, very few discharge ions strike the substrate with full bias voltage. As a result substrates is not heated substantially [26].

Bias sputtering has been effective in altering a broad range of properties in deposited film e.g. resistivity, hardness and residual stress, dielectric properties, etch rate, adhesion, step coverage [25].

# CHAPTER 3

### CORROSION

## 3.1 Definition

Corrosion is a natural phenomenon [2] and can be defined as the destruction or deterioration of a substance (usually a metal) or its properties because of a reaction with its environment [31]. Most metals in natural state exist in the form of oxides. These metal oxides (or other metal compounds) must be refined to create the pure metals or alloys, which become useful structural materials that can be used to build things. Pure metals and alloys have a much higher energy state and there is a natural tendency to return to their lower energy state. Corrosion is the process nature uses to return metals to their original state [32]. It is extractive metallurgy in reverse i.e. rusting of steel [33]. The rate of corrosion depends upon the environment and the type of material. It can be very rapid in a highly corrosive environment or take thousands of years in a slightly corrosive environment [33].

#### **3.2 Corrosion Principles**

Most Corrosion phenomena are of electrochemical in nature. Corrosion is governed by both thermodynamics and kinetics of the partial reactions. They imply two or more electrode reactions: the oxidation of a metal (anodic partial reaction) and the reduction of an oxidizing agent (cathodic partial reaction) [1].

As shown in Figure 3.1, the oxidation reaction results in the generation of electrons at anodic areas of the corroding metal. These electrons flow through the metal to the cathodic sites, where they are consumed (reduction reaction). Current flow

(positive) is in the opposite direction of electron flow (negative current). Positive current is discharged form anodic sites, flow through the electrolyte (solution, soil, etc) by ionic conduction, is picked up at cathodic sites, and completes the circuit in the metal by electron conduction. The potential difference between the anodic and cathodic reaction on the metal surface is the driving force for the corrosion reaction [38].



Figure 3.1 Schematic Diagram for a Metal Corroding in an acid [38].

Anodic, or oxidation, reactions produce metal ions and electrons, for example, metal dissolution:

$$\mathbf{M} \rightarrow \mathbf{M}^{+} + \mathbf{e}^{-} \tag{3.1}$$

$$Fe \to Fe^{++} + 2e^{-}, E_0 = 0.44 (V)$$
 (3.2)

Where, E<sub>o</sub> is standard redox potential (referring to the hydrogen electrode).

Cathodic, or reduction, reactions consume electrons and yield various products, according to the nature of the environment:

Metal reduction: 
$$M^{2+} + e^- \rightarrow M^+$$
 (3.3)

Hydrogen evolution: 
$$2H^+ + 2e^- \rightarrow H_2$$
 (gas),  $E_0 = 0$  (V) (3.4)

Oxygen reduction (acid solutions):  $O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$ ,  $E_0 = 1.229$  (V) (3.5)

Oxygen reduction (alkaline solutions):  $O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$ ,  $E_0 = 0.401$  (V) (3.6)

Since these reactions involve the transfer of electrons (electric current) and chemical change, they are called " electrochemical" reactions. When metal oxidation occurs in an acid solution, hydrogen evolution or acidic oxygen reduction occurs to maintain electronic neutrality. The standard redox potential associated with hydrogen evolution or acidic oxygen reduction are 0.44 (V) and 1.229 (V), respectively. A positive standard redox potential ( $E_0$ ) indicates the corrosion process is spontaneous and negative standard redox potential ( $E_0$ ) indicates the corrosion process is not spontaneous [35].

Anodic corrosion reactions always involve one or more cathodic reactions, and the sum of the oxidation and reduction reactions must be equal. Corrosion control is possible by eliminating either the anodic or the cathodic processes, or by eliminating the environment. Coating is used to minimize corrosion, however, a poorly applied coating on an anodic surface will leave small unprotected areas (anodes) that will surely corrode more rapidly [2].

## **3.3 Polarization**

The concept of polarization is briefly discussed because of its importance in understanding corrosion behavior and corrosion reactions [33]. When two processes as shown in Figure 1.1 occur over a single metallic surface, the potential of the material will no longer be at an equilibrium value. This deviation form equilibrium potential (Ecorr) is called polarization. Electrodes can also be polarized by the application of an external voltage or by the spontaneous production of voltage away form equilibrium. The magnitude of polarization is usually described as an overvoltage ( $\eta$ ), which is measure of polarization with respect to the equilibrium potential of an electrode (E<sub>eq</sub>) [36].

Equilibrium potential (Ecorr) can be defined as the potential at which the rate of oxidation is exactly equal to the rate of reduction. A specimen at  $E_{CORR}$  has both anodic and cathodic currents present on its surface. However, these currents are exactly equal in magnitude so there is no net current to be measured [37]. The polarization is said to be either *anodic*, when the anodic processes on the electrode are accelerated by changing the specimen potential in the positive (noble) direction or *cathodic* when the cathodic processes are accelerated by moving the potential in the negative (active) direction.

There are three distinct types of polarization in any electrochemical cell, the total polarization across an electrochemical cell being the summation of the individual elements:

$$E_{(applied)} - E_{eq} = \eta_{total} = \eta_{act} + \eta_{conc} + iR$$

Where,

 $\eta_{act}$  = activation overpotential, which depend on the charge transfer kinetics of the electrochemical processes. Activation overpotential is predominant at small polarization currents or voltages.

 $\eta_{conc}$  = concentration overpotential, which depend on the mass transport limitations associated with electrochemical processes. Concentration overpotential is predominant at large polarization currents or voltages.

iR = ohmic drop. iR follows Ohm's law and describes the polarization that occurs when a current passes through an electrolyte or through any other interface such as surface film, connectors, etc. The ohmic drop is the simplest of the three polarization terms and can be evaluated either directly with a conductivity of the cell or using conductance data [36].

The two types of polarization are

- 1) Activation polarization
- 2) Concentration polarization

## 3.3.1 Activation Polarization

Activation polarization is controlled by the reaction sequence at the metal-electrolyte interface. This is illustrated by considering hydrogen-evolution reaction on zinc during corrosion in acid solution.

Figure 3.1 shows some of the possible steps in hydrogen reduction on a zinc surface. The species must first be absorbed or attached to the surface before the reaction can proceed according to step 1 followed by electron transfer (step 2), resulting in a reduction of the species. Two hydrogen atoms then combine to form hydrogen molecule (step 3), which combine to form a bubble of hydrogen gas (step 4). The speed of reduction of the hydrogen ions will be controlled by the slowest of these steps [33]. Therefore, in order to have a higher rate of reaction, expressed in terms of current density, an increase in potential is to be effected.



Figure 3.1 Hydrogen reduction reaction under activation control [33].

The relationship between current density and change in potential (overvoltage) is expressed by the Tafel equation [1]:

$$\eta_a = \beta \log \frac{i}{i \text{ corr}}$$

Where

 $\eta_a$  = overvoltage activation polarization, in volts.

 $\beta$  = Tafel constant and is usually of the order of 0.1 V

i = anodic or cathodic current,  $\mu A$ .

 $i_{corr}$  = exchange current density, which can be defined as rate of oxidation or rate of reduction at equilibrium or corrosion current, which is obtained form a Tafel plot (Section 3.6)

Activation polarization controls [3] [6],

- Dissolution reactions (anodic) in corrosion where the salvation of ion is the probable rate-controlling step.
- Hydrogen evolution reactions (cathodic reactions) where the concentration of hydrogen ions is high.
- Corrosion in media containing a high concentration of active species e.g., concentrated acids.

## 3.3.2 Concentration Polarization

Concentration polarization refers to electrochemical reactions, which are controlled by the diffusion in the electrolyte. This is illustrated in Figure 3.3 for the case of hydrogen evolution.



Figure 3.3 Concentration polarization during hydrogen reduction [33].

Here, the number of hydrogen ions in solution is quite small, and the region close to the metal surface will become depleted of hydrogen ions because these are being consumed by the cathodic reaction. Under this condition, the reduction rate is controlled by the diffusion of hydrogen ions form the bulk of the solution to the metal surface [1]. A maximum or limiting value of this reduction reaction is given by [33],

$$i_{\rm L} = \frac{{\rm DnFC}}{{\rm x}}$$

Where  $i_L$  is called the limiting diffusion current density, amp/cm<sup>2</sup>

D is the diffusion coefficient for  $H^+$  ion

n is the number of electrons transferred

F is the Faraday number, 96485 C mol<sup>-1</sup>.

C is the bulk concentration of H<sup>+</sup> ions in the solution

x is the thickness of diffusion layer.

A mathematical expression for concentration polarization involves  $i_L$  and is given by [33],

$$\eta_{\rm c} = \frac{2.3 {\rm RT}}{{\rm F}} \log(1-\frac{{\rm i}}{{\rm i}_{\rm L}})$$

Where,  $\eta_c$  is overvoltage due to concentration polarization, in volts.

Concentration polarization predominates when the concentration of the reducible species is small e.g., dilute acids, aerated salt solutions etc. It is small during metal dissolution and can be neglected; it is only important during reduction reactions [1].

#### **3.4 Passivity**

Passivity refers to the phenomenon of loss of chemical reactivity of a metal or an alloy under particular environmental conditions. It results form the formation of a thin, oxidized, protective film on the surface of a metal. Many metals active in the emf series, including important structural metals like aluminum, iron, nickel, chromium, titanium, and their alloys, can be passivated simply by exposure to strong oxidizing media or by anodic polarization or both. Other metals that show passivity include silicon, tantalum, niobium, molybdenum and zirconium [1].



Log (Current density)

**Figure 3.4** Corrosion characteristics of an active-passive metal as a function of potential [33].

Figure 3.4 illustrates the typical behavior of a metal, which demonstrates passivity effects. The behavior is divided into three regions, active, passive, and transpassive. The current required to shift the potential in the anodic direction from the corrosion potential  $E_{corr}$  can be several orders of magnitude greater than the current necessary to maintain the potential at a passive value. In the active region, the behavior of this material is identical to that of normal metal. As applied potential is increased (more positive), metal specimen corrodes. If more oxidizing agent is added, the increase in the corrosion rate ceases and the onset of passivation begins. This point is

characterized by two coordinate values, the primary passive potential ( $E_{PP}$ ) and the critical current density (i<sub>c</sub>). Although a high current density may be required to cause passivation (> i<sub>c</sub>), only a small current density is required to maintain it, and that in the passive region the corrosion rate corresponds to the passive current density (i<sub>p</sub>). Further increases in oxidizing agents produce little if any change in the corrosion rate of the material. Finally, at very high concentrations of oxidizers, or in the presence of very powerful oxidizers, the corrosion rate again increases with increasing oxidizer power. The passivating film begins to break down in region termed as transpassive region [33].

#### **3.5 Electrochemical Techniques**

Electrochemical techniques of corrosion measurement are currently experiencing increasing popularity, primarily due to the rapidity with which these measurements can be made. Long-term corrosion studies, such as weight-loss determinations, may take days or weeks, while an electrochemical experiment will require, at most, several hours. The speed of electrochemical measurements is especially useful for those metals or alloys, which are highly corrosion resistant like tantalum.

Polarization methods such as potentiodynamic polarization, potentiostaircase, and cyclic voltammetry are often used for laboratory testing. These techniques can provide useful information regarding the corrosion mechanisms, corrosion rate and susceptibility of specific materials to corrosion in designated environments. It involves changing the potential (Section 3.3) of the working electrode and monitoring the current, which is produced as function of time or potential [36].

#### 3.5.1 Potentiodynamic Polarization

This method is best known for its fundamental role in electrochemistry in the measurement of Evans diagrams. A three-electrode corrosion probe is used to polarize the electrode of interest. Here, potential of the electrode is varied at a selected rate by application of a current through the electrolyte and current response is measured. It is probably the most commonly used polarization-testing method for measuring corrosion resistance, the Tafel constants and is used for a wide variety of functions. The formation of passive films and the onset of pitting corrosion can also be identified at characteristic potentials, which can assist in assessing the overall corrosion risk [36].

Potentiodynamic polarization is the characterization of a metal specimen by its current-potential relationship. Since the measured current can vary over several orders of magnitude, usually the log current function is plotted vs. potential on a semi-log chart. This plot is termed a potentiodynamic polarization plot. A complete plot can be measured in a few hours, or in a few minutes.

This plot can yield important information such as,

- The ability of the material to passivate spontaneously in the particular medium.
- The potential region over which the specimen remains passive
- The corrosion rate in the passive region.

Whether the specimen will or will not be passivated depends on the form and intersection of the individual anodic and cathodic polarization plots as shown in Figure 3.5.



**Figure 3.5** Theoretical and actual Potentiodynamic polarization plot active–passive metals [37].

Figure 3A, 3B and 3C are theoretical examples of an anodic curve (label a), upon which are three superimposed cathodic curves (label c). In this figure  $E_{corr}$ corresponds to the intersection point(s) of the individual anodic and cathodic plots – the point(s) at which the anodic current exactly equals the cathodic current. At  $E_{corr}$  the net measured current is exactly zero. Figure 3D, 3E and 3F correspond to the experimentally determined curves for Figure 3A, 3B and 3C, respectively.

As shown in Figure 3A, if the cathodic current intersects the anodic curve in the active region then the specimen will corrode rapidly e.g., titanium in dilute, air-free sulfuric or hydrochloric acid. Figure 3D shows similar shape to the anodic portion of 3A and anodic portion predominates.

As shown in Figure 3B, if the cathodic current intersects the anodic curve then the specimen can exhibit either high corrosion rates or low corrosion rates e.g., Cr in air free sulfuric acid or iron in dilute nitric acid. In Figure 3E cathodic current loops are observed after the peak-shaped active to passive transition has already occurred. Metals that exhibit this behavior are undesirable

As shown in Figure 3C, if cathodic curve intersects the anodic curve in the passive region only then the material will passivate spontaneously e.g., S.S. and Ti in acid solution containing oxidizers. Figure 3F does not exhibit the peak-shaped active to passive transition because the specimen has already been fully passivated. This condition is most desirable.

In summary, potentiodynamic polarization measurements are valuable in rapidly identifying desirable materials-environment combination and in predicating material behavior when exposed to a particular environment [37].

#### **3.5.2 Potentiostatic Polarization**

The Potentiostatic polarization technique measures the polarization behavior of a working electrode by applying a series of discrete potential steps and monitoring the current response at each applied potential. Potentiostatic polarization permits a steady-state current to be attained before applying the next level of potential. Here, the desired working electrode potential is maintain by application of a current through the electrolyte and keeping the applied potential constant. This technique is no longer used for measuring the potential behavior [38].

#### **3.6 Tafel Plot**

Tafel plots can provide a direct measure of the corrosion current, which can be related to corrosion rate. This technique is extremely rapid compared to weight-loss measurements. The rapid determination of corrosion rates can be advantageous for studies such as inhibitor evaluation, oxidizer effect or alloy comparisons [36].

As shown in Figure 3.5 at  $E_{corr}$ , since  $i_{ox} = i_{red}$ , the current is at a minimum. The curved portions of the plot are due to enhancements of  $i_{red}$  at potentials slightly negative (cathodic) of Ecorr, or  $i_{ox}$  at potentials slightly positive (anodic) of Ecorr. At larger polarization values, the plot became linear. Extrapolation of these linear regions yields straight lines with slopes known as Tafel constants ( $\beta$ ) (both anodic and cathodic) and corrosion current  $i_{corr}$  is obtained. Tafel constants are expressed in terms of volts per decade of current and can be derived theoretically in terms of the kinetics of oxidation and reduction reactions [38].



Figure 3.5 Tafel Plot [9].

As indicated in Figure 3.5, if the straight line fitted to the anodic or cathodic Tafel plot is extended to Ecorr,  $i_{corr}$  can be determined, and is related to the corrosion rate. Corrosion rate in mils per year (mpy, or thousandths of 1inch/y) is given by equation [38]:

$$CorrosionRate(mpy) = 1.248 \times 106 \frac{i_{corr}M}{FZD}$$

Where,  $I_{corr}$  = corrosion current density, Amp/m<sup>2</sup>

M = molecular weight in, g/mole.

D = density of the corroding species,  $g/cm^{23}$ 

Z = valence state of metal in oxidized form (number of equivalents/mole)

F is the Faraday number, 96485 C mol<sup>-1</sup>.

#### CHAPTER 4

### SPUTTER DEPOSITION - EXPERIMENTAL SET-UP AND PROCEDURE

Deposition of tantalum was done on aluminum and steel substrates using Planar DC magnetron Sputtering. Besides aluminum and steel substrates, tantalum coating is also deposited on Si and SiO<sub>2</sub> substrates, which in turn were used for resistivity measurements (four-point probe method) and thickness measurement (Dektak Profilometer) as explained in Chapter 5. Silicon and SiO<sub>2</sub> substrates were highly polished, so they were directly subjected to ultrasonic cleaning (Section 4.2).

#### 4.1 Mechanical Cleaning

Aluminum and 4340 steel were used as substrates for tantalum coating deposition. The substrates were cut into small square pieces of 0.5" x 0.5" size and thickness 0.2" at machine shop practice at NJIT. The substrates are subjected to produce a bright, mirror-like reflecting surface, commonly referred to as polished surface.

The surface preparation operations can be done manually or can be mechanized. Mechanized processes are less time consuming and laborious than the manual operations. It is important if large number of specimen have to be prepared. The specimen should be held and rotated with appropriated speed and pressure such that specimen rotated exactly in horizontal plane against the abrasive surface. Than specimen should be properly washed away to remove unwanted material on it and to prevent the further carrying away of such unwanted material, which may result in, more scratches. Above-mentioned step is repeated using successively finer grades of abrasive paper.



Figure 4.1 MINIMET 1000 Grinder/Polisher at NJIT.

As shown in Figure 4.1, MINIMET 1000 Grinder/Polisher (Buehler Company) was used for substrates surface preparation. It is fully automatic and provides the control of rotation speeds (1-9 units), pressure applied (0-50 N) on the specimen and polishing time (up to 99 minutes at a time). It employs a variably loaded arm, which moves the specimen in a unique geometric pattern within a stationary polishing bowl. Abrasive paper (i.e. Emery paper) or cloth (i.e. Kempad and Vel-cloth) is attached to a glass platen, which rests on the bottom of the bowl and provides the surface needed to produce flat polished specimen. The bowl is held in space by means of a square protrusion on its underside.

The sequence and polishing parameter established for preparation of substrates viz. aluminum and steel are shown in Table 4.1 and Table 4.2.

Abrasive, Size, average	Abrasive				
particle size	carrier	Lubricant	Load	Speed (units)	Time
SiC, 240 grit	Emery paper	DI water	30-40 N	6-7	4-5 min
SiC, 320 grit	Emery paper	DI water	30-40 N	6-7	4-5 min
SiC, 400 grit	Emery paper	DI water	30-40 N	6-7	4-5 min
SiC, 600 grit **	Emery paper	DI water	30-40 N	6-7	4-5 min

 Table 4.1 Grinding Process and Parameters

**Table 4.2** Polishing Process and Parameters

Abrasive, Size	Abrasive carrier	Lubricant	Load	Speed (cm/s)	Time
Diamond, 15 µm	Kempad	-	25-35 N	5-6	4 min
Diamond, 10 µm	Kempad	-	25-35 N	5-6	4 min
Diamond, 6 µm **	Kempad	-	25-35 N	5-6	4 min
Diamond, 3 µm	Kempad	-	25-35 N	5-6	4 min
Diamond, 1 µm	Kempad	-	25-35 N	5-6	4 min
Diamond, 0.5 µm **	Kempad	-	25-35 N	5-6	4 min
Alumina suspension,					
0.05 μm **	Vel-cloth	DI water	50-0 N *	6-9 *	2 min

Note:

\*\* Steps for polishing aluminum. Speed and Load for polishing aluminum are 2-3 units and 10–15 N respectively for all steps.

\* For the 0.05  $\mu$ m final polish the load is gradually decreased from 50 N to 0 N and speed is gradually increased from 6 to 9 units in 2 minutes.

## 4.2 Electrochemical and Ultrasonic Cleaning

Electrochemical cleaning involves the cleaning of steel substrates from any impurities like oil, dust, grease, etc. Electrochemical cleaning utilizes two electrodes (anode and cathode) in an electrolyte, connected to a power supply. In this work, 'Electrocleaner 59 Special', an alkaline solution (product of Northwest Company) is used as an electrolyte to

carry out an anodic electrochemical cleaning.

The operating conditions used are as follow:

Cathode: Copper

Anode: Steel substrates

Temperature: 75 - 95°C

Concentration of the electrolyte: 60-75 g/l (DI water)

Voltage: 6-8 V

Cleaning time: 15 minutes

Aluminum substrates were not electrochemically cleaned, as it would lead to the formation of aluminum oxide, which is much harder than natural aluminum and has good corrosion resistance. This could affect the study of tantalum coating on aluminum substrates. The electrochemically-cleaned steel substrates were than rinsed in DI water to remove ay residual alkaline cleaner, before carrying out ultrasonic cleaning.

Ultrasonic cleaning is done in liquid medium, using high frequency sound waves (~33,000 Hz), which generate bubbles traveling at ultrasonic speeds through the medium. The specimen is surrounded by bubbles, which implode, causing dirt to be lifted from the surface.

The aluminum, steel, Si and SiO<sub>2</sub> substrates were subjected to three cycle of ultrasonic cleaning. In first cycle, all specimens were cleaned with alcohol for 10 minutes, followed with acetone for 5 minutes and again with 10 minutes of alcohol. Finally, to prevent specimen from atmospheric exposure, before placing in sputtering system for tantalum deposition, the samples were put in a desiccator.

#### **4.3 DC Magnetron Sputtering System**

Planar DC magnetron sputtering system was used to deposit Tantalum (Ta) coating on steel and aluminum (Al) substrate. The system was designed and assembled at the Ion Beam and Thin Film Research laboratory at NJIT, and fabricated by Kurt J. Lesker Company. A schematic of Planar DC magnetron sputtering system is shown in Figure 4.2.

The sputtering chamber is cylindrical in geometry with a volume of approximately 80 liters. The dimensions of the chamber are 20" inside diameter and 15" height. This system has capability of carrying out deposition form more than one source/gun. However, this work employed only one source for sputtering. The system consist of,

- Cryogenic vacuum pump (CTI Cryotorr 8) with a motorized control gate valve, which pumps the system to a base pressure of  $1.0 \times 10^{-7}$  torr.
- Two turbo-molecular pumps, viz. Turbovac 150 and Turbovac 50 (Leybold-Heraeus), are used to pump the system during deposition process.
- Rotary Mechanical pump (Leybold-Heraeus) to back up the turbo pumps and to pump the system to a base pressure of 100 mtorr.
- Ionization gauge to measure high vacuum pressure inside the chamber and thermocouple vacuum gauge to measure low pressure developed by mechanical pump alone.
- Residual gas analyzer (RGA) (Inficon Quadrex-200 Model form Leybold-Heraeus) was attached to the system through throttling valve and was capable of analyzing the partial pressure of the residual gases.



Figure 4.1 Planar DC magnetron sputtering system at NJIT.

- Two Mass Flow controllers (MFC) (MKS Instruments) control the flow of gases i.e., argon and nitrogen. MFC are attached to the 4-channel readout, which reads the gas flow.
- Three halogen bulbs (500 W, 120 V) are mounted inside the chamber to bake it for 6-8 hours to about 300° C. After baking, the chamber is cooled overnight before sputtering.

The substrates to be sputtered are mounted on a circular substrate holder of 2.75" diameter with the help of screws as seen in Figure 4.3. These substrates are mounted above the target facing downwards to prevent the falling of metal flakes, which, can form, on the source shield or other fixtures. The distance between the substrates and the target was set to 2 inches. Rotating substrate platter of 16.50" diameter is suspended vertically in the center of the lid of the chamber. This platter can hold at the most eight substrate holders.



Figure 4.3 Substrate mounted on holder.



Figure 4.4 A view of the vacuum chamber lid.

As shown in Figure 4.4, lowering manual linear positioner to the substrate holder and applying DC voltage carries out sputter etching. Typical DC voltage used for sputter etching was in the range of 300-400V at a pressure of 200-230 mtorr. The sputter etching time varied form 10-60 minutes on each substrate holder. Platter rotator facilitates the rotation of substrate platter form the top of the chamber. A substrate shield of 17" diameter is supported by four poles is mounted above the sputtering source to protect the substrate platter form the sputtered material as shown in Figure 4.5. Both substrate shield and platter are designed in such a way that only one substrate holder at a time can be sputtered and other substrate holders are shielded form the deposited material. Moreover, a shutter was provided just above source to close the opening in the substrate shield in

certain circumstances like plasma being extinguished in middle of deposition or due to unstable plasma. After stabilizing the process parameters of the chamber, a shutter is taken over to continue with the deposition process.



Figure 4.5 Inner view of deposition chamber.

The Tantalum target of 2" diameter and 0.125" in thickness with 99.999% purity is mounted on a TORUS 2A magnetron-sputtering source obtained form Kurt J. Lesker Company. The target is sputter cleaned for 10 minutes with all substrates shielded from the gun prior to deposition.

To carry out the deposition process, power is supplied from a D.C. power supply that can operate in either voltage control or current control mode. To prevent the target overheating and damaging of the permanent magnets of the source due to high power at the target, sufficient water-cooling of the source is necessary during sputtering. The sputtering gases, viz. argon (99.999%) and nitrogen (99.999%) of ultra high purity were passed through mass flow controllers into the chamber at specific rate. Argon gas with a flow rate of 18 sccm is admitted to maintain a pressure of 1-5 mtorr inside the chamber during sputtering. Argon gas pressure during sputtering is measured by a capacitance manometer (MKS Baratron model Type 626) with a range from 0-1 torr. Nitrogen gas along with argon was used for reactive sputtering. After deposition, the system is vented by flowing nitrogen through the vent valve.

#### **4.4 Sputter Etching**

Solvent cleaning usually removes only oils and greases, leaving more tenacious materials such as surface oxides. This is overcome by sputter etching.

Sputter etching is the process of removal of material forms a surface by sputtering. Here, substrate is subjected to the ion-bombardments instead of the target. Generally, in-situ sputter etching is preferred than doing it in a separate chamber. During transferring the substrates to the different deposition chamber, substrate surface may get oxidized or at least get covered with foreign particles by physio-adsorption [26]. Sputter etching method, however, is known to have some negative effects on substrates, which include re-deposition, change of surface morphology and some surface contamination due to impacts of sputtering gas ions [39].

In this work, the substrates were sputter-etched by applying negative voltage to them and igniting glow discharge inside the sputtering chamber filled with argon gas at a low pressure. Sputter etching was carried out at 400 V, 220-230 mtorr pressure and for 15 min or 30 min, depending upon the substrate, as described later in Chapter 6. Sputter etching was done after baking and cooling the chamber overnight, but prior to deposition.

#### **4.5 Deposition Procedure**

- 1. Substrates preparation for deposition is done (Section 4.1, 4.2)
- Substrates (aluminum, steel, Si and SiO<sub>2</sub>) are mounted on substrate holders and maximum of 7 holders could be loaded for one process cycle.
- 3. The sputtering system is opened. Parts like substrate platter, shutter, substrate shield, target shield, etc are cleaned to avoid peel off of loosely attached film and drop down on the target. Even condition of target is checked. If target is used for more than 18 hrs, old target is replaced by new target.
- 4. System is pumped overnight with the help of the cryogenic pump to pressure of about  $3 \times 10^{-7}$  torr.
- 5. Next day system is baked at about 300°C for 6-8 hours and then left to cool down overnight to get vacuum of  $7.52 \times 10^{-8}$  torr or lower.
- 6. Cryogenic pump gate valve is fully closed and Turbovac 150 pump is started.
- 7. Sputtering gases are passed in to the chamber at specific flow rate and the gate valve of turbo pump is adjusted to get desired pressure.
- 8. Target is cleaned for 15-20 minutes by sputtering on blank holder to remove native oxide film or other impurities atom adsorbed on the target surface.
- 9. Sputter etching is carried out on selected holder.
- 10. Tantalum nitride films are deposited in some experiments by reactive sputtering in nitrogen and argon atmosphere on selected substrates.

- 11. Sputtering is carried out after step 9 or step 10
- 12. After deposition the samples are allowed to cool in high vacuum overnight. Next day chamber is vented with ultra high pure nitrogen gas (99.999%) and samples are taken out for analysis.

## **CHAPTER 5**

#### **CHARACTERIZATION TECHINIQUES**

Characterization is done to determine characteristic or property of a material in a defined and reproducible way. The characterization of tantalum film was done after the deposition, by using techniques like:

- Dektak Profilometer for thickness measurement.
- X-Ray Diffraction to analyze crystalline structure.
- Four Point-Probe for resistivity measurement.
- Corrosion Test.

#### 5.1 Dektak Profilometer

There are many direct and indirect techniques for measuring the thickness of a deposited thin film. Since films have a low thickness, substrate surface roughness can play a major role in the thickness measurement [40]. The most generally used technique is the surface Profilometer (stylus technique).

In this work, thickness of tantalum film deposited on silicon and oxidized silicon were measured using Sloan Dektak II Profilometer (Veeco Instruments Inc) at NJIT clean room. In this technique, a step in the deposited film is first created, by masking during deposition. Profilometer consists of diamond stylus with a tip radius of 12.5  $\mu$ m, which in turn scan a length of 0.05 mm to 30 mm and measure the step height. The stylus force is adjustable from 1 to 40 mg, and vertical magnifications of a few thousand up to a million times are possible This information is displayed on chart recorder or CRT. In order to
measure thickness without vibration, leveling (nitrogen gas is used) is most important. Periodic calibration of stylus profilometer is required using standard method.



Figure 5.1 Dektak II Profilometer at NJIT.

## 5.2 X-ray Diffraction

X-ray diffraction (XRD) provides a unique and practical means for obtaining crystallographic information like crystal interplanar distance form which lattice constant, phases and even composition can be determined by comparison with the standard data.

X-rays are a form of electromagnetic radiation. As shown in Figure 5.2, a parallel beam (1 and 2) of x-rays of wavelength  $\lambda$  is incident on parallel planes (A-A1 and B-B1) at an angle  $\theta$ . When a beam of x-rays impinges, a portion of this beam (labeled 1 and 2) will be scattered in all directions by the electrons associated with each

atom (P and Q). If the path length difference between diffracted beams 1-P-1a and 2-Q-2a is equal to a whole number, *n*, of wavelength, condition of diffraction is satisfied. This condition is given by Bragg's Law:

# $n\lambda = 2d\sin\theta$

where, n = integral number describing the order of reflection,

 $\lambda$  = wavelength of the x-rays,

d = interplanar spacing for the reflecting plane,

 $\theta$  = Bragg angle where a maximum in the diffracted intensity occurs.



Figure 5.2 Diffraction of x-rays by planes of atoms (A-A1 and B-B1) [41].

The X-ray diffractometer works as shown in Figure 5.3, a specimen S in the form of a flat plate is supported so that rotations about the axis labeled O are possible. The x-ray beam is generated at source (point T), and intensities of diffracted beams from the sample are detected by counter at point C. As the counter moves at constant velocity, a recorder automatically plots the diffracted beam intensity as a function of diffraction angle  $2\theta$  and peaks are obtained [41].

In this work, x-ray analysis of the deposited films was done using Philips Expert MPD instruments with CuK $\alpha$  radiation. The obtained spectrums for alpha tantalum and beta tantalum were compared to standard peaks, which were taken from JCPDS – International Center for Diffraction Data (ICDD).



Figure 5.3 Schematic diagram of an x-ray diffractometer [41].

#### **5.3** Four-Point Probe Technique

The Four Point Probe is used to measure the resistivity of material by contact with it surface [42].

The schematic of the in-line four-point probe is provided below in Figure 5.4. This tool consists of four probes, made up of tungsten carbide, which are put in an in-line configuration with equal spacing. The outer probes are current probe and inner probes are voltage probes. A current source,  $I_s$ , is injected through one of the current probes and extracted form the other, while a voltmeter measures the voltage, V across the inner probes. Due to the separation of the current probes and the voltage probes, the voltage is measured essentially independent of contact resistance While measuring the resistivity, the four point probe head were placed at the center of specimen viz. silicon wafer and oxidized silicon wafer. The resistivity is then calculated from the voltage, current, probe spacing and film thickness. For bulk materials (t >> S) where t is the sample thickness and S is the probe spacing, resistivity is calculated by the following equation [20]:

$$\rho = 2\pi S V/I_S$$

where,  $\rho$  is the volume- resistivity ( $\Omega$ -cm).

For thin layers (t<<S) resistivity is computed in the following manner [20]:

$$\rho = [\pi t/\ln 2] [V_M/I_S]$$

The sheet resistance,  $R_s$  (ohms) can be computed form the resistivity as follow [20]:

$$R_s = \rho/t$$

The above equation apply to samples with diameter d >> S under the assumption that the probe is far from the sample edge.



Figure 5.4 Schematic of the in-line four-point probe.



Figure 5.5 Resistivity meter at NJIT.

As shown in Figure 5.5, an automatic Resistivity Meter FPP-5000 made by Vecco Company was used in this work to measure resistivity at NJIT clean room. Resistivity values for all different specimen were measured based on their film thickness determined by a stylus Profilometer (Section 5.1). XRD measurements were conducted to confirm the validity of the Ta phase, determined by the in line four point probe measurement.

#### **5.4 Corrosion Testing Method**

Potentiodynamic and Potentiostatic are the two techniques used to measure the corrosion behavior of metal. These methods allow the controlled polarization of metal surfaces in electrolytes of interest, in order to directly observe cathodic and anodic behaviors. These techniques control the electrochemical potential and measure the corresponding current.

Potentiodynamic polarization tests have become fully automated with computerbased, menu-selectable programs for establishing test parameters and performing the tests compared to potentiostatic polarization.

The individual components of the test apparatus are described below:

- Working electrode: Electrochemical reactions being studied occur at the working electrode. In corrosion testing, the working electrode is a sample of the corroding metal and it can be bare or coated metal.
- Reference electrode: A reference electrode is used in measuring the working electrode potential. A reference electrode should have a constant electrochemical potential. Two examples are the saturated copper/copper sulfate electrode (CSE) and the saturated calomel electrode (SCE).

- Auxiliary Electrode: The Auxiliary electrode is a conductor that completes the cell circuit. The auxiliary (counter) electrode in electrochemical cells is generally an inert conductor like platinum or graphite.
- Electrochemical cell: Three electrodes are contained in the electrochemical cell, which is filled with required electrolyte e.g. NaCl, H<sub>2</sub>SO<sub>4</sub>, tap water, deionized water, etc.

In this work as shown in Figure 5.6, a constant (Potentiostatic) or a varying DC potential ( $V_C$ ) (Potentiodynamic), was applied to the metal of interest viz. aluminum and steel substrate coated with Ta while it is immersed in the electrolyte. Here, electrolyte used was deionized water with pH of 5. The substrate is referred to as the working electrode (WE). The Saturated calomel electrode (SCE) was used as reference electrode. Reference electrode (RE) is typically selected to be very stable under the selected test conditions, and is used to monitor and maintain potential at the WE surface. Graphite is used as a counter electrode. Now, when process was started, ionic current passes through the electrolyte between the counter electrode (CE) and the WE, and electron current passes between the CE and the WE through a low resistance connection provided and was monitored. Voltage and current test data were automatically uploaded to computer by using Data acquisition system. Evaluation of the current/potential behavior under a variety of conditions helps to understand a range of corrosion phenomena. The experimental set-up used in this work is shown in Figure 5.6.



Figure 5.6 Experimental set-up measurements at NJIT.

#### CHAPTER 6

## **ANALYSIS OF DEPOSITED FILMS**

The main goal of this research was to study the condition of deposition of tantalum coating yielding bcc phase, on steel and aluminum substrate. The corrosion resistance of tantalum films was also investigated. Deposition of tantalum was carried out on:

- Substrate at room temperature.
- Heated substrates.
- Substrate with tantalum nitride interlayer deposited, prior to tantalum deposition.

The detailed deposition conditions are listed in Appendix C.

Sputter etching was done on same substrates prior to deposition of tantalum or tantalum nitride interlayer. In order to determine the usual time required to sputter etched the substrate, sputter-etching current is measured along with time during sputter etching. Substrates were sputter etched using argon as sputtering gas from 220 mtorr to 230 mtorr pressure with flow rate of 18 sccm. The curves of sputter etching current as a function of time at a constant voltage (400 V) for aluminum and steel substrate is shown in Figure 6.1.

As shown in Figure 6.1, sputter-etching current was initially 2 mA. This value does not depend on the type of substrate. Then current increases with time and becomes stable. In case of aluminum the current became stable in nearly 15 min, while in case of steel, it takes about 30 min for current to be stabilize. The saturation plateau for both aluminum and steel substrate is around 5 mA. Thus, the usual sputter etching time for aluminum and steel sample in this work was 15 min and 30 min respectively.

64



**Figure 6.1** Sputter etching current as a function of time at constant voltage for aluminum and steel substrates.

### 6.1 Deposition of the Film

The thickness of films deposited was determined by measuring the height of a step at the film edge using Sloan Dektak II Profilometer (Section 5.1). The surface roughness of substrate plays a major role in the thickness measurement. Since steel and aluminum substrate has higher surface roughness, profilometer did not give valuable results. Hence, thickness of the films deposited was estimated by measuring it on silicon and oxidized silicon substrates mounted on same holder as metal substrates. The step was formed because a part of the substrate was masked by a steel foil. Example of step profile is shown in Figure 6.2. The film was deposited at 0.5 A, 250 V with 5 mtorr pressure on aluminum substrate for 2 hours using Ar sputtering gas at a flow rate of 18 sccm. The

thickness of the film as shown in Figure 6.2 is 66000Å. A deposition rate, calculated, as ratio of film thickness (66000 Å) to deposition time (about 2 hours) was 10 Å/S. This is typical deposition rate form the new target. The deposition rate in the system increases to 14 Å/S when target is eroded. In some experiments Ta was sputtered reactively to deposit TaN, with different concentration of nitrogen in the chamber.



Figure 6.2 Step Profile of a  $SiO_2$  substrate with Ta deposition.

The same method was used in order to determine the deposition rate of the tantalum nitride films deposited on silicon and oxidized silicon substrates with different flow ratio. Tantalum nitride films were deposited on silicon and oxidized silicon substrates by reactive sputtering with a mixture of nitrogen and argon gases. All the samples were sputter etched for 20 min at 220-230 mtorr followed by TaN deposition for 20 min at 5mTorr pressure. The flow rate of the working gases was increased viz. 1/18,

1.5/30, 0.5/30, 2/30, 2/18, 3/18, 4/18, 5/18, 7/18 and 9/18, where, numerator is the value of flow rate of nitrogen gas (in sccm) and denominator is the flow rate of argon gas (in sccm). Deposition rate of the as-deposited films as a function of flow rate ( $N_2/Ar$ ) is shown in Figure 6.3.



Figure 6.3 Deposition rate of the TaN films deposited at various  $N_2$ -Ar ratios.

It was found that deposition rate decreased approximately linearly with an increase in flow rate of  $N_2/Ar$  i.e. increasing the flow rate cuts the deposition rate. The decrease of deposition rate could be attributed to a nitride layer, which is grown on the cathode (target poisoning). This layer decreases the area of metallic sites on the target surface for sputtering [43] as the compound with the lower sputtering rates is formed.

#### **6.2 Resistivity Measurement**

The Four Point Probe technique (section 5.3) was used to measure the resistivity of film deposited on the SiO<sub>2</sub> substrate. The resistivity of tantalum film, with the interlayer of tantalum nitride was measured to be 18-25  $\mu\Omega$ -cm, which indicate that this is the alpha phase (bcc) Ta film [6]. Tantalum deposited without the interlayer of tantalum nitride had a resistivity of 140-200  $\mu\Omega$ -cm indicating that this is the beta phase (tetragonal) Ta film [6]. It was determined that resistivity of Ta film deposited on steel substrate at room temperature decreased when, the interlayer of TaN was present. This indicates that pure alpha phase (bcc) was deposited on substrate with a TaN interlayer.

Resistivity of TaN films was measured on silicon and oxidized silicon for different flow rate (section 6.1), after measuring thickness. Measured value of the as-deposited films as a function of flow rate ( $N_2/Ar$ ) is shown in Figure 6.3.



Figure 6.4 Resistivity of the TaN films deposited at various N<sub>2</sub>-Ar ratios.

As shown in Figure 6.4 by increasing the nitrogen to the sputtering (argon) gas ratio (form 1:18 to 5:18), a very small increase resistivity is observed. However, a clear increase in resistivity can be seen with a flow rate of 7:18. This change in resistivity with flow rate is attributed to change in TaN film stoichiometry with increase in flow rate.

#### 6.3 X-Ray Analysis

6.3.1 Tantalum Deposition on Steel and Aluminum Substrate at Room Temperature The substrates were prepared under the same condition except sputter etching of aluminum sample was done for 10 min compared to steel for 30 min according to the result presented in Figure 6.1. Sputter etching is followed by sputtering of Ta for 30 min at 5mTorr with argon flow rate of 18 sccm. The XRD spectra of 2.6  $\mu$ m and 1.7  $\mu$ m films obtained on steel and aluminum substrate are shown in Figure 6.5(a) and 6.5(b) respectively. Alpha phase was observed in case of aluminum sample, while in case of steel sample beta phase was observed. Peaks are labeled (as shown in Figure 6.5) by crystallographic planes of the two tantalum phases, based on comparison with the standard peaks (Appendix A). Beta phase Ta was observed on both steel and aluminum samples which were not sputter-etched.

For aluminum it is expected that sputter etching remove the natural oxide  $(Al_2O_3)$  exposing aluminum surface, which lead to the formation of alpha tantalum [44]. The natural oxide present on substrates that were not sputter-etched may be responsible for growth of beta phase tantalum films. Thus sputter etching does not affect the tantalum phase on steel substrate, but it affects the Ta phases of films deposited on aluminum substrates.



Figure 6.5 (a) XRD spectrum of Ta deposited on aluminum sample.



Figure 6.5 (b) XRD spectrum of Ta deposited on steel sample.

# **6.3.2 Tantalum Deposition on Heated Substrates**

Tantalum coatings were deposited on aluminum and steel substrates at elevated temperature using Ar sputtering gas. From the experiments carried out on steel substrates, it was found that the temperature above 350°C produces alpha tantalum, while mixed phase was grown on substrate heated below 350°C. The XRD spectra of 6.6  $\mu$ m and 3  $\mu$ m films obtained on aluminum and steel are shown in Figure 6.6. These films were deposited on heated substrates to 400°C and these substrates were not sputter-etched before Ta deposition.



Figure 6.6 XRD spectra of Ta coating deposited on aluminum and steel substrates heated to 400°C.

As shown in Figure 6.6, alpha phase tantalum coating was observed on both aluminum and steel substrate heated to 400°C. In these XRD spectra intensity of alpha Ta (110) peak for aluminum substrate is dominant, while for steel substrate intensity of (211) peak is dominant. The difference in intensity may be due to different preferred orientation of Ta film grown on aluminum and steel substrates. The microscopic images of both coating are shown in Figure 6.7(a) and 6.7 (b). Surface of Ta coating deposited on steel was shiny, smooth with good adhesion while, Ta deposited on aluminum was rough and peel off.



Figure 6.7 (a) Microscopic image of Ta deposited on steel substrate 400°C.



Figure 6.7 (b) Microscopic image of Ta deposited on Al substrate at 400°C.

#### 6.3.3 Tantalum Deposition with Interlayer of Tantalum Nitride

In this part of research interlayer of tantalum nitride was deposited prior to subsequent deposition of tantalum and influence of interlayer was investigated on the phases of tantalum. The minimum thickness of TaN required to yield bcc phase was determined by depositing TaN of various thickness followed by deposition of Ta and XRD measurements. Due to the limitation of profilometer to measure thickness less than  $0.1 \,\mu\text{m}$ , the thickness of the thin nitride interlayer was estimated form the deposition time and deposition rate calculated from thick nitride coatings deposited under similar conditions.

Tantalum nitride interlayer was deposited on both sputter etched and not sputter etched aluminum and steel substrates, followed by tantalum coating on it. The discussion of the result is divided into two parts,

# **Sputter Etched Aluminum and Steel Substrate**

Tantalum nitride interlayer was deposited on aluminum and steel substrates at room temperature by reactive sputtering. As shown in Figure 6.8, the flow rate of  $N_2/Ar$  used for the nitride interlayer in aluminum and steel sample was 3/18. The estimated interlayer thickness was 20 nm in both samples. The XRD spectra revealed only alpha peaks.



Figure 6.8 XRD spectra of tantalum coating deposited on nitride interlayer on sputter etched aluminum and steel substrate.

The XRD spectra for tantalum nitride film deposited on steel substrates with different flow rate are shown in Figure 6.9. The XRD pattern of the film deposited with flow rate 1/18, 1.5/18 and 9/18 reveal one peak at 35.9°, which could be described as (002) of Ta<sub>2</sub>N. The XRD pattern of the film deposited with flow rate above 2/30 reveal two peaks, one of fcc (111) TaN at 35.7° and other cubic (200) TaN at 41.1° [1]. According to Riekkinen et al. [43], (111) orientation becomes dominant at the expense of (200) as the flow rate is increased.



Figure 6.9 Comparison of the XRD spectra of tantalum nitride films  $(1 \ \mu m)$  deposited on sputter-etched steel substrates.

Tantalum coating deposited on interlayer of TaN, produces alpha tantalum for flow rate of 3/18, 4/18, 5/18, 7/18 and 9/18. The minimum thickness of TaN needed to produce alpha tantalum is 20 nm. The flow rate lower than or equal to 2/18 produce mixed phases or alpha phase, even with a 20 nm interlayer thickness.

# Non-Sputter Etched Aluminum and Steel Substrate

The XRD spectra of tantalum coating deposited on aluminum and steel with tantalum nitride interlayer are shown in Figure 6.10. The flow rate of  $N_2/Ar$  used for the nitride interlayer in aluminum and steel sample was 3/18. The deposited interlayer thickness was 20 nm in both samples. The XRD spectrum revealed only alpha peaks.

Thus, it can be said that sputter etching or non-sputter etching surface of the substrate does not influence the phases of tantalum obtained with 20 nm interlayer of tantalum nitride.



Figure 6.10 XRD spectra of tantalum coating deposited on TaN interlayer on non-sputter etched aluminum and steel substrates.

#### 6.4 Corrosion Test

Corrosion test was carried out using potentiodynamic and potentiostatic method to determine the corrosion resistance of tantalum and following discussion is divided in to two parts depending upon the methods used.

### **Potentiodynamic Test**

Potentiodynamic test was carried out at room temperature on alpha Ta coating obtained on aluminum and steel substrate in deionized water with pH 5. Al and steel substrate were sputter etched at 220-230 mtorr followed by sputtering of tantalum at 5 mtorr for 30 min at room temperature. The thickness of Ta coating on aluminum and steel substrate was 2.6  $\mu$ m and 2.5  $\mu$ m respectively. As shown in Figure 6.11, the Tafel plots indicate corrosion current densities are lower than 10<sup>-8</sup> A/cm<sup>2</sup>. This suggests that alpha (bcc) Ta provides a passive protective layer on both steel and aluminum substrates.



**Figure 6.11** Tafel plot of potentiodynamic test performed at room temperature in water at pH 5 for alpha Ta coating deposited on aluminum and steel substrates.

### **Potentiostatic Test**

A potentiostatic test was carried out on beta Ta deposited on aluminum substrate in water with pH 5. As shown in Figure 6.12, the test was conducted over a period of about 6 days at a potential near to the corrosion potential. Data indicate that the initial low corrosion current (~50 pA/cm<sup>2</sup>) has not increased for almost 4 days. After about 80 hours, a sharp increase in the current was observed, followed by a plateau after 110 hours. The plateau current of 20 nA/cm<sup>2</sup> remained constant up to 140 h. The test shows that the beta Ta coating on the aluminum shows some corrosive effects after 4 days of continuous testing.

Under similar conditions as used in Ta coated aluminum, potentiostatic test was carried out on an aluminum sample. As shown in Figure 6.12, it was observed that corrosion current sharply increases initially in a few hours to over  $50 \text{ nA/cm}^2$ . After some flucation the value of the current decreases approximately to  $40 \text{ nA/cm}^2$  at about 80 h and than slowly increases till the end of experiment at 120 h.

Comparison of the two curves in Figure 6.12 reveals, that the current density in case of bare aluminum sample increases rapidly compared to the low value for Ta coated aluminum sample. This indicates good protective properties of Ta films. However, after about 100 h protective properties of tetragonal Ta coating are destroyed. To study the effect of the corrosion test on the Ta coating the sample was examined under an optical microscope.



**Figure 6.12** The corrosion current density vs the time plot measured by potentiostatic test in pH 5 water at room temperature on (a) tetragonal Ta coated aluminum and (b) bare aluminum.

Figure 6.13 and 6.14 shows the microscopic examination of Ta on aluminum substrate both before and after the potentiostatic test respectively. A micrograph in Figure 6.14 reveals a hole of approximately 170  $\mu$ m diameter was created by the corrosive effect. This corrosive effect thus indicates that beta Ta is not good corrosion protective layer. Several smaller holes were also observed in the coating. It is possible that corrosion originates at a specific defect in the coating, which will be investigated in the future study.



**Figure 6.13** Microscopic image of Ta deposited on Al substrate before potentiostatic Test.



**Figure 6.14** Microscopic image of Ta deposited on Al substrate after potentiostatic Test.

### CHAPTER 7

#### CONCLUSIONS

The purpose of this thesis was to study protective tantalum coating deposited by sputtering in argon gas on steel and aluminum substrates Properties of these coating were investigated by X-ray diffraction, resistivity measurement and corrosion resistance test. Of the two phases of tantalum, the tough and ductile bcc (alpha) phase is preferred over the hard and brittle tetragonal (beta) phase for protective coating.

The following conclusion can be drawn from the results of these experiments.

# **Phases of Tantalum**

- Tetragonal (beta) phase of Ta was present in coatings deposited on steel at room temperature. Sputter etching of the substrates prior to deposition does not affect the Ta phase deposited on steel at room temperature.
- Heating of steel above 350°C during sputtering yields alpha (Bcc) phase of Ta while mixed phases were found to grow on steel heated at temperature below 350°C.
- The Bcc phase tantalum coatings were obtained at room temperature on aluminum, sputter-etched prior to deposition. This may be explained by the fact that sputter etching of aluminum removes its native oxide layer, exposing pure metal, which promotes the growth of bcc Ta phase. Non sputter-etched aluminum promotes growth of tetragonal beta phase.
- Alpha phase Ta coatings deposited on aluminum were obtained by heating the substrates at 400°C without sputter etching. The bcc-Ta coating on aluminum had

different crystallographic orientations (texture) than coating deposited on steel at this temperature.

• Tantalum coatings with bcc-phase were deposited at room temperature with TaN interlayer (grown by reactive sputtering) on steel and aluminum substrate prior to Ta deposition. Sputter etching of aluminum and steel does not affect the phase of Ta under these conditions.

### TaN interlayer

- Alpha phase tantalum films grow at room temperature on tantalum nitride interlayers deposited on steel with the flow ratio of nitrogen to argon of 3/18, 4/18, 5/18, 7/18 and 9/18, while mixed phase Ta film grow on interlayer deposited at 2/18 flow ratio.
- Resistivity of TaN interlayer depends on concentration of nitrogen in sputtering gas. The resistivity value increases slowly with nitrogen to argon flow ratio of 1:18 to 5:18 but a sharp increase in resistivity was observed at the flow ratio of 7:18. This change in resistivity is interpreted as due to the change in the nitride film stoichiometry with nitrogen concentration in the sputtering gas. Based on the resistivity measurements and XRD spectra, it was concluded that stoichiometric TaN grow with N<sub>2</sub>/Ar flow ratio of 3/18 and above.
- The minimum thickness of the nitride layer on sputter-etched steel, necessary to produce alpha phase of Ta at room temperature, is 20 nm. The minimum thickness of TaN on not sputter etched steel, was found to be as low as 4 nm.

# **Corrosion of Tantalum Coating**

Corrosion test was carried out using potentiodynamic and potentiostatic methods in water with pH 5.

- A potentiodynamic measurements reveals that corrosion current density for bcc Ta films on aluminum and steel was lower than 10<sup>-8</sup> amps/cm<sup>2</sup>, which indicate that alpha Ta coatings may provide good corrosion protection.
- Potentiostatic test revealed that the beta Ta films on aluminum starts to show some corrosive effects after 4 days of constant testing at the corrosion potential. Increased current and etched holes in the coating, seen in microscopic examination, indicate that the deposited beta Ta coating gives only limited corrosion protection to aluminum. Potentiostatic tests of alpha phase coatings are planned as on extension of this work.

# **APPENDIX A**

# STANDARD POWDER DIFFRACTION PATTERNS

X-ray diffraction (XRD) provides a unique and practical means for obtaining crystallographic information like crystal interplanar distance form which lattice constant, phases and even composition can be determined by comparison with the standard data for  $\alpha$ -tantalum and  $\beta$ -tantalum as shown below:



**Figure A1** Standard powder diffraction spectrum of bcc-tantalum (JCPDS Ref. Card No. 04-788)



Figure A2 Standard powder diffraction spectrum of  $\beta$ -tantalum (JCPDS Ref. Card No. 25-1280)

#### **APPENDIX B**

# SPUTTERING DEPOSITION DETAILS OF SAMPLES REPRESENTING THE DATA POINTS IN FIGURE 6.2, 6.3 AND 6.7.

The following table describes the sputter deposition details of the experimental procedure used during the course of research. As shown in table below, SE- row refers to conditions during sputter etching; RS- row refers to deposition conditions during reactive sputtering.

**Table B** Sputtering Deposition Details of Samples Representing the Data Points in Figure 6.2,6.3 and 6.7.

Sample	Conditions	Pressure (mtorr)	Gas Flow (sccm) N <sub>2</sub> /Ar	Temp (°C)	Time (min)	Thickness (Å)	Resistivity (μΩ-cm)
080102-PTa04c	SE	220-230	18	RT	20		
	RS	5	1/18	RT	20	10528	295
082002-PTa01c	SE	220-230	18	RT	20		
	RS	5	1.5/18	RT	20	10077	309
061102-PTa04c	SE	220-230	18	RT	20		
	RS	5	2/18	RT	20	9914	180.3
082002-PTa05c	SE	220-230	18	RT	20		
	RS	5	2/30	RT	20	9781	266
090402-PTa04c	SE	220-230	18	RT	20		
	RS	5	1.5/30	RT	20	10500	239
090402-PTa05c	SE	220-230	18Ar	RT	20		
	RS	5	0.5/30	RT	20	10545	323
082002-PTa03c	SE	220-230	18	RT	20		
	RS	5	2.5/18	RT	20	8109	334
071702-PTa06c	SE	220-230	18	RT	20		
	RS	5	3/18	RT	20	8396	392
080102-PTa05c	SE	220-230	18	RT	20		
	RS	5	4/18	RT	20	7565	843.6
072302-PTa04c	SE	220-230	18	RT	20		
	RS	5	5/18	RT	20	7351	957
080702-PTao5c	SE	220-230	18	RT	20		
	RS	5	7/18	RT	20	6998	2974
080702-PTao6c	SE	220-230	18	RT	20		
	RS	5	918	RT	20	6246	5870

## **APPENDIX C**

# SPUTTERING DEPOSITION DETAILS

The following table describes the sputter deposition details of the experimental procedure used during the course of research. As shown in table below, SE- row refers to conditions during sputter etching; RS- row refers to deposition conditions during reactive sputtering

 Table C
 Sputtering Deposition Details

							T
Sample	Conditions	Pressure (mtorr)	Gas Flow (sccm) N <sub>2</sub> /Ar	Temp (°C)	Time (min)	Thickness (Å)	Resistivity (μΩ-cm)
050202-PTa02Al	SE	220-230	18	RT	10		
	TS	5	18	RT	30	26833	22
053102-PTa03a3	SE	220-230	18	RT	20		
	TS	5	18	RT	30	173444	128.5
070902-PTa06a	TS	5	18	RT	20	11460	
050202-PTa01A1	TS	5	18	RT	30	35095	106.7
111802-PTa07Al	TS	5	18	400	60	25291	15.3
082102-PTa07a2	TS	5	18	400	60	26519	18.4
092402-PTa05Al	SE	220-230	18	RT	20		
	RS	5	3/18	RT	0.33		
	TS	5	18	RT	30	14208	17.6
080702-PTa03a	SE	220-230	18	RT	20		
	RS	5	3/18	RT	0.33		
	TS	5	18	RT	20	10714	19.9
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092402-PTa06Al	RS	5	3/18	RT	0.33		
	TS	5	18	RT	30	17297	18.3
020502-PTao3a	RS	5	3/18	RT	0.33		
	TS	5	18	RT	20	15775	20.6

## **APPENDIX C**

# **SPUTTERING DEPOSITION DETAILS**

The following table describes the sputter deposition details of the experimental procedure used during the course of research. As shown in table below, SE- row refers to conditions during sputter etching; RS- row refers to deposition conditions during reactive sputtering

**Table C** Sputtering Deposition Details

111401-PTao5a2	RS	220-230	3/18	RT	2.5		
	TS	5	18	RT	30	25980	23
100802-PTao1A11	SE	220-230	15	RT	20		
	TS	5	18	RT	30	19526	67.2
111102-PTao3Al3	SE	220-230	18	RT	20		
	TS	5	18	RT	120	66468	187.4
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