INVESTIGATION ON PLASMA PROPERTIES FOR DEPOSITION OF TITANIUM NITRIDE FILMS USING REACTIVE MAGNETRON SPUTTERING SYSTEM

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Special dedicated to my beloved my parents, siblings and friends who have encouraged, guided and inspired me throughout my journey of education….

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ABSTRACT

Deposition of thin film using plasma sputtering system had been widely discovered and developed extensively for many years in technological and industrial process especially formation of titanium nitride (TiN) films due to its high hardness, good wear resistance, low friction coeffcient and chemical stability. These TiN films have been commonly used in microelectronics and coatings area. However, formation of TiN thin flms in nano size device using the plasma sometimes is not stable and hard to achived with optimum level. As a result, fundamental of understanding on the sputter mechanism of atom in reactive magnetron sputtering plasma is very important in order to implement the plasma sputtering for the formation of conformal TiN thin film in a very fine hole in integrated circuit device. In this work, the working power and nitrogen gas flow rate were varied during the deposition process and spectrocopic measurement. Plasma diagnostics such as optical emission spectrocopy and Langmuir probe were used for characterizing plasmas and for better understanding of physical and chemical processes occur during the deposition of TiN films in the plasma sputtering. On the other hand, the formation of TiN films using reactive magnetron sputtering system also have been conducted. The thickness and roughness of TiN films were examined using surface profiler and atomic force microscope respectively. Thus, correlation of relative depostion of TiN films and plasma diagnostics have been successfully obtained to improve the understanding of sputter mechansim process for TiN films. More quantitative analysis also had been done throughout the findings to confirm the effect of different parameters used significantly change the properties of TiN films.

ABSTRAK

Pemendapan filem nipis menggunakan sistem sputtering plasma telah banyak ditemui dan dibangunkan secara meluas selama bertahun-tahun dalam proses teknologi dan perindustrian terutamanya pembentukan filem titanium nitrida (TiN) disebabkan oleh kekerasan yang tinggi, rintangan haus yang baik, keseimbangan geseran rendah dan kestabilan terhadap kimia. Filem-filem TiN ini juga telah biasa digunakan dalam bidang mikroelektronik dan lapisan. Walau bagaimanapun, pembentukan TiN nipis dalam peranti saiz nano menggunakan plasma kadang kala tidak stabil dan sukar dicapai dalam tahap optimum. Akibatnya, asas pemahaman mengenai mekanisma sputter atom dalam sistem reaktif magnetron sputtering adalah sangat penting untuk melaksanakan plasma sputtering dalam pembentukan filem conformal tipis TiN di dalam lubang yang terlalu halus untuk peranti litar bersepadu. Dalam konteks ini, pelepasan kuasa dan kadar aliran gas nitrogen telah berubah semasa proses pemendapan dan pengukuran spektroskopik. Diagnostik plasma seperti spektrokopi pelepasan optik dan Langmuir probe telah digunakan untuk mencirikan plasma dan meningkatkan lagi pemahaman mengenai proses fizikal dan kimia berlaku semasa pemendapan filem TiN dalam sputtering plasma. Sebaliknya, pembentukan filem TiN menggunakan sistem reaktif magnetron sputtering juga telah dijalankan. Ketebalan dan kekasaran TiN filem diperiksa dan diuji dengan menggunakan *surface profiler* dan mikroskopi tenaga atom masing-masing. Oleh itu, korelasi antara relatif pemendapan TiN filem dengan diagnostik plasma telah berjaya diperolehi untuk meningkatkan pemahaman proses mekanisme sputter untuk filem TiN. Lebih banyak analisis kuantitatif juga telah dilakukan sepanjang penemuan untuk mengesahkan kesan parameter yang berbeza yang digunakan telah menyebabkan pengubahan yang ketara berlaku dalam ciri-ciri filem TiN.

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LIST OF SYMBOLS & ABBREVIATIONS

AFM	Atomic force microspcopy
Ar	Argon gas
DC	Direct current
FESEM	Field electron scanning electron microscopy
MFC	Mass flow controlled
n_i	Ion denisty
n_e	Electron density
N_2	Nitrogen gas
OES	Optical emission spectrocopy
RF	Radio frequency
sccm	Standard cubic centimeter per minute
T_e	Electron temperature
TiN	Titanium nitride
UTHM	Universiti Tun Hussein Onn Malaysia

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CHAPTER 1

INTRODUCTION

In this chapter, the research background and problem statement for this project are discussed. Besides that, there are several objectives and scope of research have been listed and presented at following section.

1.1 Research background

Deposition of the thin thin film using plasma sputtering system had been widely discovered and developed extensively for many years.Sputtering method has been well eastablished for wide range of industrial that manufacturing the coatings area. One of the deposition technique commonly used was magnetron sputtering system [1-2]. Magnetron sputtering plasma was a technique that used for layer deposition of a thin film with various materials and it is one of the standard processes of industrial thin film technology such as production of optical coatings, magnetic tapes, decorative coatings and wear-resistant coatings [3]. The interactions of a solid with its surrounding are mainly defined by the physico-chemical properties of its surface. So, it is not surprising that many of the researchers still continues doing research and develop on material science for past decades.

Thin films with transition of metal nitrides has been attracted interest of researchers in community for a few years. These metal nitrides had been applied in several applications due to its high hardness, good wear resistance, low friction coeffcient and chemical stability. For instance, formation of titanium nitride (TiN) coating is one of the most used thin film in various of engineering industrial area. In microelectronics area, TiN thin film was employed as barrier diffusion layers in ultra-large scale integrated (ULSI) circuit. Besides than that, TiN also has been reported successfully implemented as protective coatings against wear and corrosion to increase the life expectancy of surgical implants and prosthesis [4–6]. Previously, there were various methods had been discovered for purpose of deposition of TiN thin film which including physical vapour depostion (PVD) and chemical vapour depostion (CVD). Some of the researchers were also using electrochemical and chemical nitridation of metallic Ti (pure/ alloy) or compounds as depostion techniques for preparation of TiN film. However, deposition of TiN thin film using reactive magnetron sputtering system plasma has been used by many researchers over the years.

There were some issues had been arise where the size of trench of integrated circuit chips had been scale down year-to-year in microelectronic field. This phenomenon quite hard to achive in the formation of comformal thin film in nano-scale patterned wafer. One of the technique that proposed used to grow the thin film in nano-scale patterned wafer was ionized physical vapor deposition (IPVD). The sputtered metal atoms were ionized in the plasma and thus used for the directional deposition by using this method. As a result, it has proven that deposition of thin film using magnetron sputtering plasma at high pressure condition had able to improved the ionization of the titanium atoms in pure argon plasma enviroment [7-8]. Furthermore, there were experimental works have been reported which regarding to the studied of the ionization process of titanium atom in reactive mixture of nitrogen and argon plasma environment. This reactive process was employed for the growth of TiN film for an integrated circuit chips. In fact, there are still many researchers around the world are working hard to investigate the ionization mechanism of sputtered atoms that obtained in the reactive plasma sputtering during the deposition of metal nitride. Fundamental of understanding on the ionization of Ti atom in reactive magnetron sputtering plasma is very important in order to implement the IPVD method for the formation of conformal TiN thin film in a very fine hole in microelectronics device. The throughput of this experimental works is useful and able to contribute for deeply understanding of the ionization mechanism of titanium atom during depostion of TiN films. It is expected that the most basic ionization and excitation mechanism such as electron impact ionization and penning ionization would be the dominant in plasma sputtering [8- 9].

In order to deeply understand the ionization and excitation process that occur during the deposition of thin film in IPVD, studied of plasma diagnostics is one of the simple way that applied in analysis of the deposition mechanism in plasma sputtering system. It is very important to describe and understand the specific transition emission of various plasma. The most popular diagnostics methods employed for probing the species constituting the plasma are described and namely as mass spectrometry, gas phase Fourier transform infrared spectroscopy, optical emission spectroscopy and etc. For this research, optical emission spectroscopy (OES) would be used as plasma diagnostics tool to investigate the ionization mechanism of sputtered atoms in reactive sputtering plasma. OES is helpful in analyzing the light emitted by neutral or ionized atoms, radicals or molecules which have been electronically excited by collisions with energetic electrons. As mentioned earlier, the intensity of spectral lines is observed with spectrometers and the ratio between the intensities is calculated. From these ratios, the temperature of the gas can be evaluated and calculated. However, not all spectral lines are equally suitable for this method. A new approach to better understand how the sputtering parameters affects the TiN thin film properties is to determine the type of reactive species formed in the plasma during the reactive magnetron sputtering. Identification of the type and concentration of reactive species in correlation with main plasma parameters including the plasma density, n_e, electron temperature, T_e, and plasma potential, V_p during the sputtering process could contribute to the understanding of the film growth mechanism process.

The aim of this research was carried out to investigate the ionization mechanism of titanium atoms in reactive high pressure magnetron sputtering plasma and correlated with the plasma diagnostics's properties with the deposited TiN thin film in magnetron sputtering plasma system. It is shown how theoretical calculations based upon the density functional theory method have proven to be a powerful tool for assisting in the interpretation of the complex diagnostic data. Furthermore, there is a related issue that has been reported and published. The ionization mechanism of Ti in high pressure magnetron sputtering plasma would be intensively studied using advanced optical emission spectroscopy method that will provide an in-situ distributions of atoms an ions in reactive magnetron sputtering plasma [10–12].

1.2 Problem Statement

Deposition of TiN films as barrier diffusion layer onto an extremely fine trenches of the integrated circuit by using a conventional magnetron sputtering system had become more challenging and difficult to been achieved. Therefore, concept of ionized physical vapor deposition (IPVD) technique has been proposed to overcome this problem. Therefore, studied on the deposition sputter mechanism of TiN films in the reactive magnetron sputtering system is very essential for research and development purpose on the TiN layer in the microelectronic industry. However, the fundamental of the ionization mechanism of the plasma still not well study and understood. In fact, there are only a few reports have considered the relation between the film deposition and plasma properties during the growth of TiN layers using reactive magnetron sputtering. As a result, the investigation on the plasma characteristics of the TiN films in plasma still not sufficient in order to improve the film quality. Different corresponding parameters can affect the intensities of sputter deposited atom and film properties of TiN films.

1.3 Objectives

The objectives of this project are:

i. To study the intensities of atom and ion of the plasma using OES during the growth of the TiN films.

ii. To investigate the ion and electron density of the plasma using Langmuir probe.

iii. To investigate the deposition rate, thickness and roughness of TiN films using characterization tools.

1.4 Scope of Research

In order to meet above objectives, this project is carried out as below:

i. To construct the plasma diagnostics experiment using Ocean Optics HR4000 to collect the optical emission of Ar, Ti and N_2 in reactive magnetron sputtering system as plasma diagnostics tool.

ii. Langmuir probe used to characterize the plasma such as ion, electron density and electron temperature in the chamber.

iii. Evaluate the relative wavelength of spectrum for each species spectral line based on the National Institute Standard and Technology (NIST) database.

iv. Working pressure of chamber was varying from 100 to 113.7 mTorr in the mixture of Ar/N_2 throughout the experiment.

v. Determine the gas temperature using data that have been collected from OES and formula that proposed by other researchers.

vi. Studied the effect of the radio frequency (RF) discharge power and N_2 gas low rate during the deposition of TiN films using reactive magnetron sputtering system.

vii. TiN films were deposited at different RF discharge power (100, 150 & 200 W) and flow rate of N_2 gas (10, 20 & 40 sccm).

viii. Thickness and roughness of TiN film were measured using surface profiler and AFM respectively.

CHAPTER 2

LITERATURE REVIEW

This chapter is explaining about the fundamental of plasma sputtering process and type of plasma sputtering system. Besides that, fundamental of plasma diagnostics and characterization techniques also been discussed. Application of using TiN thin films in a variety industry are presented at below.

2.1 Fundamental of plasma sputtering system process

Plasmas are partially ionized gases that contain approximately equal numbers of positively and negatively charged species [13]. By averaging the plasma, density of the neutral species would be more dominant than charged particles. Unbalance of the any carries charged definitely would create the electric field and thus they will tend to move in such a way to eliminate the unbalance reaction. Therefore, the density of the electrons and the negative charged ions will be equal to the density of the positive charged ions [14-15].

While plasmas are a common state of matter in the universe, they are rarely a natural occurrence on earth. Their unique properties make them a powerful tool used in the modification of materials and ranging from material removal (etching) to the deposition of thin films or coatings as well as analytical techniques. Plasmas are significantly different from non-ionized gases which is a consequence of the mass difference between the positively charged ions and negatively charged electrons as well as the energy of these species. Although a number of plasmas have been used in materials processing including arcs, flames, and electron beam-generated plasmas, the most common types are discharge plasmas generated by applying an electric field to a volume of gas [1], [15-16].

When an electric field is applied to an ionized gas, energy is transferred more rapidly to the electrons than to the ions. The transfer of kinetic energy from an electron to a heavy particle including atom, molecule or ion in an elastic collision is proportional to the mass ratio of electrons and heavy particles. Electron collisions are not as common at low pressures. These electrons would accumulate sufficient kinetic energy to achieve a high probability of exciting, dissociating or ionizing the heavier gas atoms and molecules during inelastic collisions. The production of these species and their interactions with surfaces and growing films is one of the reasons for low-pressure discharge plasmas have assumed a dominant role in materials processing. The processing application that utilize plasmas include sputter deposition, reactive sputter deposition, activated reactive evaporation, ion plating, plasma-assisted chemical vapor deposition (PACVD), plasma-assisted physical vapor deposition (PAPVD), plasma-assisted etching, and plasma polymerization. In the plasma physics, study of degree of ionization mechanism is an important key point that attributed to the fraction of the original neutral species that have become ionized. The importance of study on degree of ionization is to sustain a plasma that requires some energy source to produce the minimum energy that required by atoms or molecules.

In the manufacturing of semiconductor industries, sputtering method has been introduced for many years. Basically it is involving of the ion bombardment concept whereby atoms are ejected from the surface of solid metal target resulting from bombardment of the energetic particles. In addition, sputtering method purely considered as physical process that uses glow discharge to remove material from a target. During the bombardment of target atoms, it causes the ions ejection of target atoms and then condense on a substrate to form thin film. The amount of target atoms leaving from the surface target depends on the number of the bombarding ions[17]. However, the incoming particle usually have much higher kinetic energy than conventional thermal energies which is more than 1 eV. There have other by-product particle produced during the process of ions bombardment such as secondary electrons, ions reflection at the target surface and ion implantation with the particles that permanently confined into target.

In the configuration of sputtering system, solid metal as target source of the sputtering mainly placed at cathode while substrate would be placed at the anode.

Figure 2.1 has shown the bombardment mechanism of sputtering by the high impact energetic particle on the surface of target. There are various advantages and disadvantages of using this technique in deposition thin film that been reported. One of the main advantage of using this technique is able to produce better step coverage of the thin film [75]. Thus, large surface area of the thin film could be formed. Besides that, it is suitable used for sputtering of any metal and alloys and able to form highly intrinsic thin film. There are wide range of metal materials could be choose. In contrast, sputtering technique also have its disadvantage such as the cost of equipment of sputtering machine very high and high contamination in plasma [1], [16], [18-19].

Basically evaporation is one of the method that used for formation thin film for past time. It is a thermally technique where the metal is heated to its vaporization point and thus evaporate to the wafer to form the thin film. However, this technique have some weakness point during the formation of thin film. In the evaporated process, evaporated materials have to be directional resulting thermal evaporation provides poor coverage. Table 2.1 have discussed about pros and cons between evaporation and sputtering technique used for formation thin film. Positive ions from the discharge are attracted to the cathode and bombard it with elevated energy. Transfer of momentum from the bombarding ions to the molecules of the cathode causes collision cascades that end with the ejection of molecules from the cathode with considerable kinetic energy. Although it is not always possible, for best results the atomic weight of the bombarding species should be similar to that of the target material maximizing the momentum transfer. There is only quite small ionization of the sputtered material and ideally these molecules travel in straight lines to impinge on the anode, or substrate, and form there a thin solid film. The momentum transfer from the arriving material promotes a dense microstructure in the film.

Table 2. 1: The comparison properties of the evaporation and sputtering techniques

Evaporation	Properties	Sputtering
Melt/ Solid	Target phase	Solid
Thermal	Removal mechanism	Ion bombardment
Evaporant atoms, compound fragments and residual gases	Composition	Sputtered atoms, ionized species, reactive gas, ions, electrons and residual gases
Poor	Coverage area	Good
High	Deposition rate	Low
Low	Cost of equipment	High

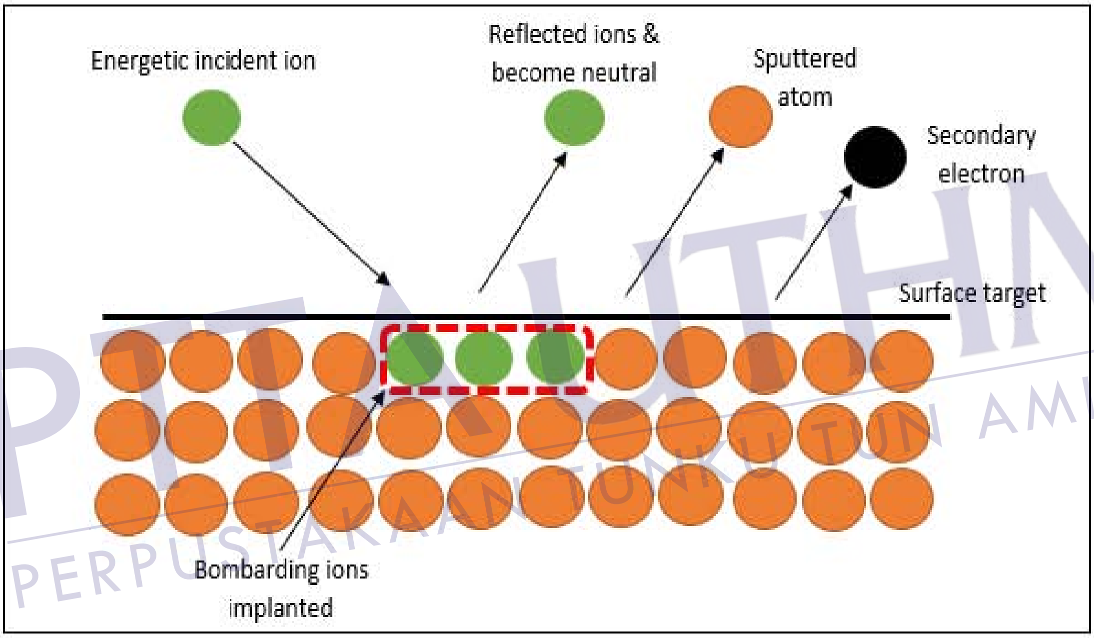

Figure 2. 1: The overview of mechanism of sputtering by energetic particles on surface target

2.2 Type of plasma sputtering system

2.2.1 Magnetron sputtering plasma system

Magnetron sputtering system had been developed rapidly over the last decade. Thus, it finally become established as the process of choice for the deposition. So it has been widely used and efficient tool in the formation of important coatings in wide range of industrial area. In fact, sputtering process implement the concept of ion bombardment process where the ions been ejected from its surface solid when collide onto a surface target material. Sputter deposition categorized as physical vapor deposition process for depositing thin films. The target is the source material. Substrates are placed in a vacuum chamber and evacuated to a prescribed process pressure. When a negative charge is applied to the target material, it could produce a plasma or glow discharge. However, positive charged gas ions that generated in the plasma region are attracted to the negatively biased target plate at a very high speed. Consequently, a momentum transfer was formed due to this collision and thus ejects atomic size particles form the target. Therefore, these particles are deposited as a thin film into the surface of the substrates. In general, there are two type of sputtering power in magnetron sputtering system technique could be implemented which is radio frequency (RF) and direct current (DC). Radio frequency power is more suitable for most of the target material while direct current source is more suitable for metal target material.[20]. For RF power supply, the power will go to auto matching box before reach the target material. While the DC source power supply, the power will directly go to target material without any auto matching box. The purpose of auto matching box was to control the power supply source constantly in the process of deposition.

The most common approach for growing thin films by sputter deposition from the basic method is magnetron sputtering plasma system. It involves placing a magnet behind the target, thus during the sputter process a magnetic field can be used to trap secondary electrons close to the target. The recombination of electric and magnetic fields let the electrons follow helical paths around the magnetic field lines undergoing more ionizing collisions with neutral gaseous near the target than would otherwise occur. This enhances the ionization of the plasma near the target leading to a higher sputter rate. It also means that the plasma can be sustained at a lower pressure. The sputtered atoms are neutrally charged and so are unaffected by the magnetic trap. In many cases, magnetron sputtered films now outperform films deposited by other physical vapor deposition (PVD) processes. Consequently, magnetron sputtering had implemented in many application including hard, wear-resistant coatings, decorative coatings and coatings with specific optical or electrical properties. Moreover, magnetron sputtering is a versatile technique for the deposition of thin films [21].

Magnetron sputtering could be operated either in direct current (DC) or radio frequency (RF) modes. When dealing with the conducting target materials, DC sputtering is one most preferred. On the other hands, RF sputtering able to be done with the both conducting and non-conducting materials. As briefly described earlier,

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