FABRICATION AND TESTING OF APPARATUS FOR ELECTROCHEMICAL MECHANICAL POLISHING (ECMP) OF COPPER FOR SEMICONDUCTOR APPLICATIONS

By

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CHAPTER I

INTRODUCTION

1.1 Background of the Process

The electrochemical mechanical polishing (ECMP) process is a new approach to planarize substrates in the microelectronics manufacturing. Substrate planarization is the key to achieve adequate depth of focus (DOF) which is patterned by lithography [1]. Damascene process is mainly used to make interconnects in a semiconductor device. In this process a substrate is taken and an insulating film made of low-k material is formed on it. Interconnect recesses which are usually trenches and via holes are formed on this insulating film by dry etching [2].

A barrier film made of titanium, tungsten or tantalum is formed on the entire surface by processes, such as physical vapor deposition (PVD) or chemical vapor deposition (CVD). Now interconnect metal film made of aluminum, copper, silver, or gold is embedded on the recesses to fill them completely. This sometimes leads to extra interconnect metal film to spread over the low-k film so, this extra metal layer is subsequently removed by planarization processes, such as chemical mechanical polishing, electrochemical polishing or electrochemical mechanical polishing [2].

In chemical mechanical polishing, the material removal is mainly due to the down force of the pad on the film. In Damascene process, CMP usually damages the low-k film because of the mechanical force. Thus there is a need for a process which can remove the excess conductive interconnect metal layer without damaging the insulating film. Figure 1.1 shows a schematic of the Damascene process [2].

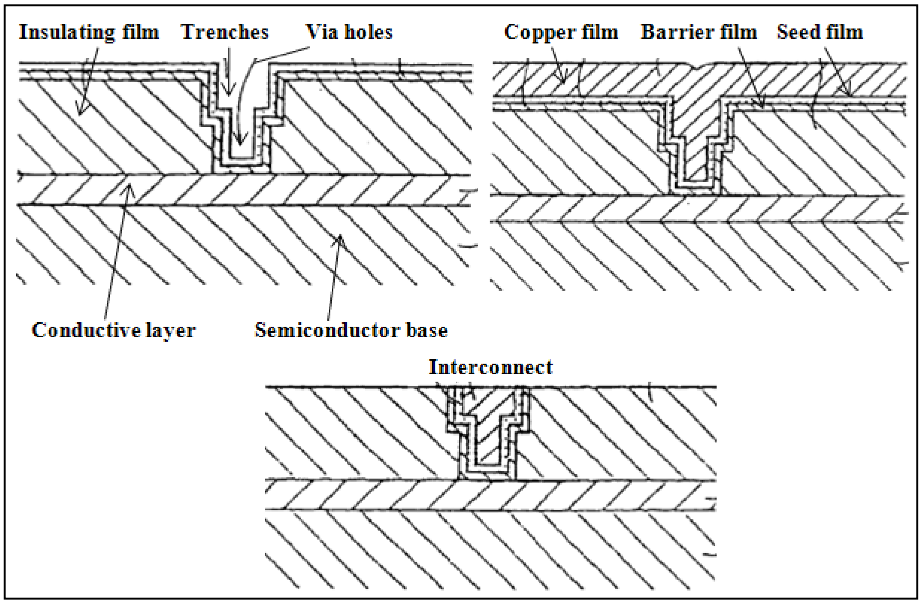


Figure 1.1: Schematic of the damascene process, after Kobata *et al.* [2]

Electrochemical mechanical polishing is very suitable in such processes because there is very little or minimal down force as most of the material is removed by electro dissolution. The mechanical pad just removes the passive film which is formed on the surface. Thus, the surface is not damaged and efficient planarization is achieved. Defects such as dishing, erosion and delamination are considerably reduced when electrochemical mechanical polishing is used. ECMP technology has been instrumental in meeting the technology node requirements of 45 nm and 32 nm technologies. It is capable of ultra low-k compatibility, lithography DOF budget and topography behavior [3].

1.2 Electrochemical Mechanical Polishing Process

In ECMP, the surface layer on the substrate is polished by a combination of three factors:

1. Electrochemical reactions,
2. Chemical reactions, and
3. Mechanical forces.

The electrochemical reactions or dissolution occurs by applying an electrical bias between a cathode and the substrate surface which is positively charged through external means, which acts as an anode. The conductive material is removed from the substrate surface into the electrolyte solution. The polishing composition can be of three types, namely, an electrolyte solution, polishing slurry, or a combination of both [4]. Chemical reactions occur on the surface of the substrate during the process forming a passive film which is subsequently removed by the mechanical component, namely, a polishing pad or an abrasive disk. The schematic of an ECMP system is shown in Figure 1.1. [5].

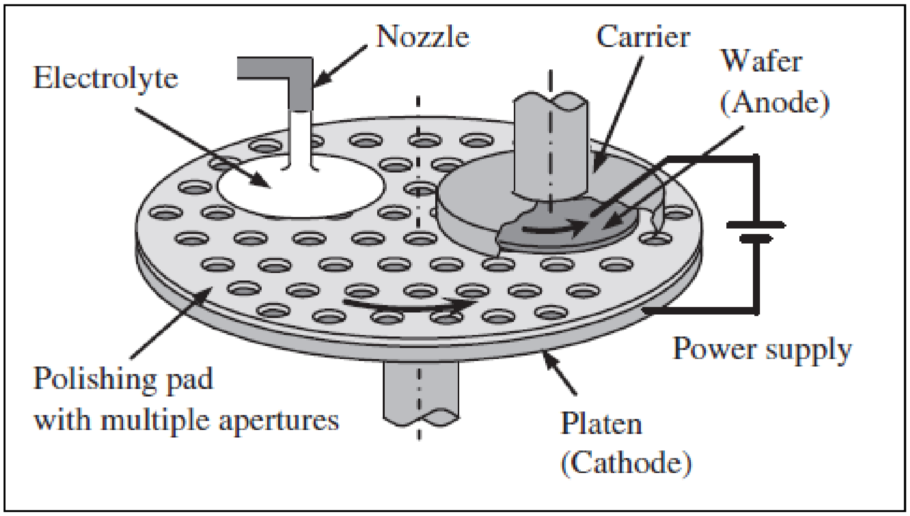


Figure 1.2: Schematics of an ECMP Process, after Fukuda *et al.* [5]

1.3 Advantages of Electrochemical Mechanical Polishing

The main advantage of ECMP is that it can planarize porous low-k materials which would be damaged in a CMP polishing system due to high load or down force. Excess copper which is left over from the formation of interconnects is removed from the low-k film without ripping the insulating layer. This is possible in this process because very less pressure is applied to the wafer by the polishing pad. Applied Materials built a low-k polishing system which is able to achieve this in three separate polishing steps [6].

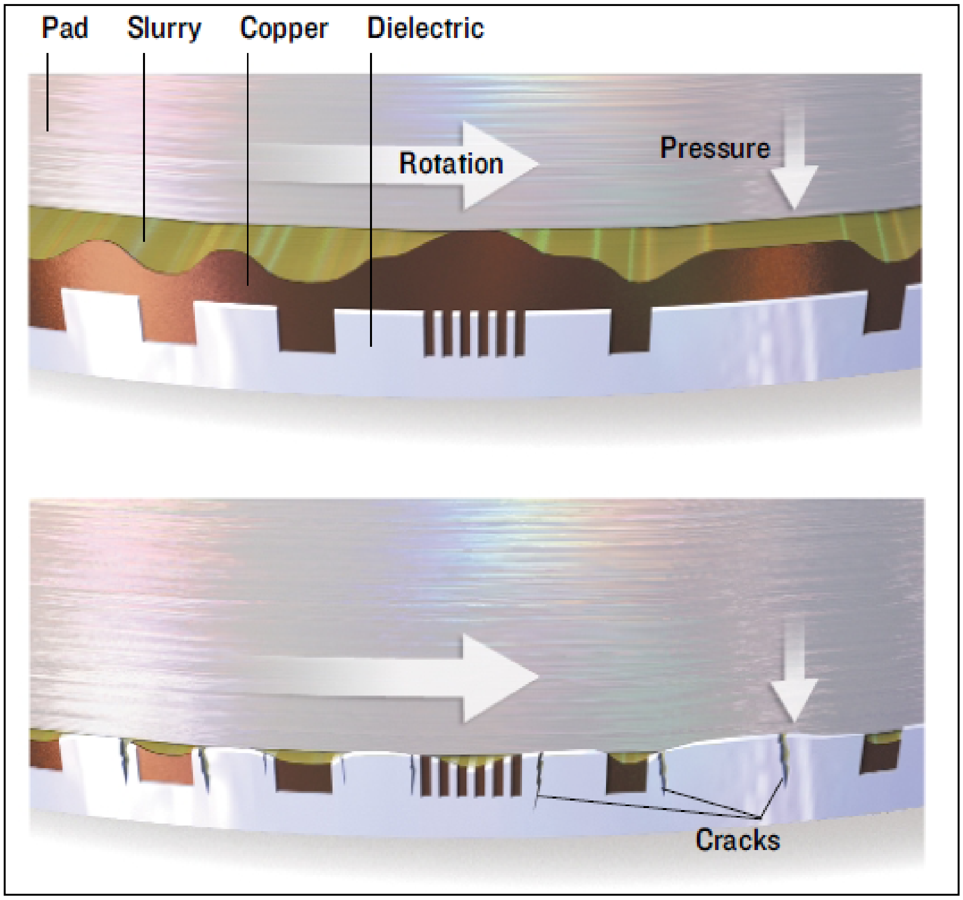


Figure 1.3: Cracks observed in the dielectric layer in chemical mechanical polishing, after Brown [6]

The polishing speed is one more advantage in ECMP. The standard CMP systems cannot achieve a high polishing speed unless and until they increase the pad pressure on the wafer. But if they increase the pad pressure, it will crack and peel away the low-k film [6]. So they will have to reduce the pad pressure which will take long time for the CMP systems to achieve the planarization. ECMP, on the other hand can get the same planarization in minimal time.

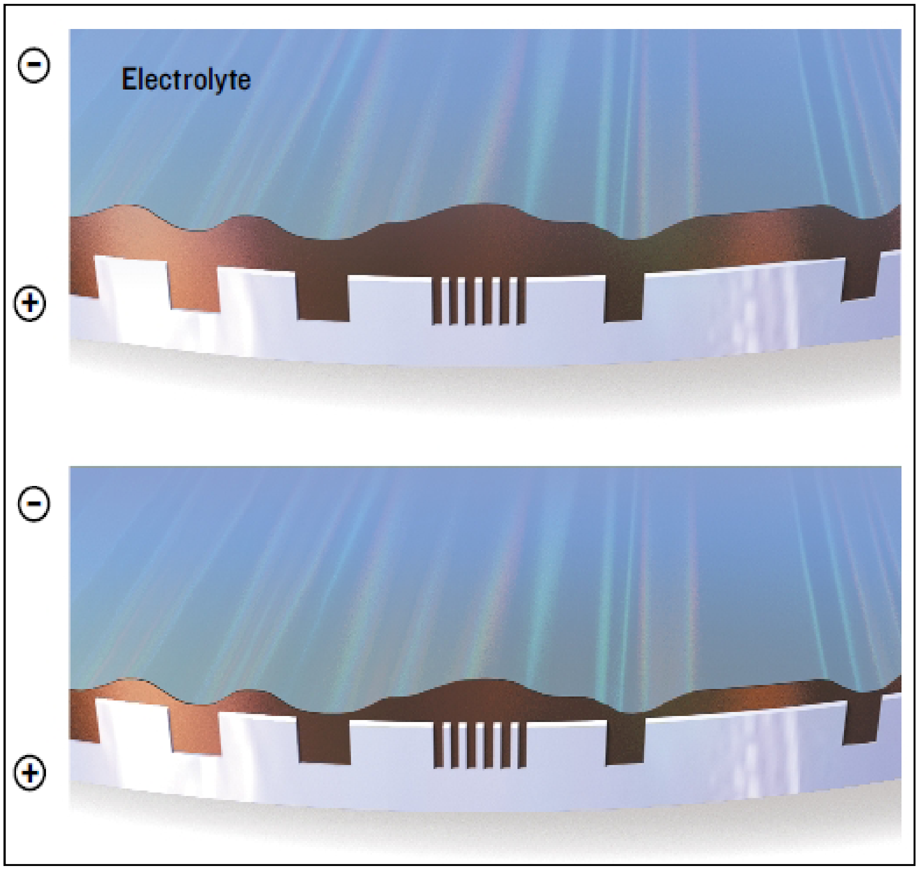


Figure 1.4: Indentations and hills remaining on the surface in electro-polishing, after Brown [6]

The abrasive slurry and polishing pad are important parameters in CMP process. Figure 1.2 shows how cracks are formed in the insulating layer because of the pressure of the polishing pad. Another disadvantage is the slurry gets trapped near the interconnects and can remove more copper than required. This leads to an increase in the interconnect's resistance which will slow its signal transmission capability.

Electro-polishing on the other hand does not use a pad (see Figure 1.3). Hence, it does not damage the dielectric layer. But the surface does not flatten completely because of the uneven distribution of the copper layer. So, further layering of the wafer is not possible [6].

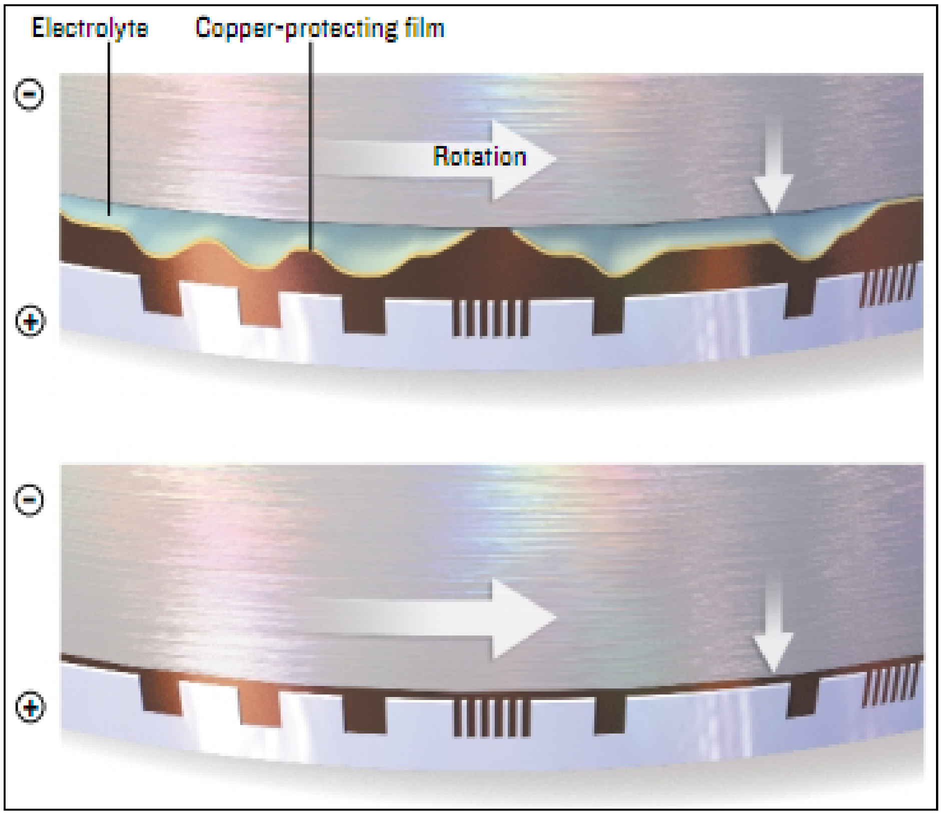


Figure 1.5: ECMP with a flattened wafer and no damage to the dielectric layer, after Brown [6]

ECMP resolves the problems observed in the other two processes as shown in Figure 1.4. Voltage is applied to remove copper by dissolution. The material removal rate is directly proportional to the charge applied. The wafer achieves perfect smoothness and the dielectric layer does not undergo any delamination. The slurry used for ECMP is inexpensive. For example, the cost for the slurry in CMP is \$15 to \$20 for a single wafer while that of ECMP is about \$4.5 to \$6 less. Thus costs 30% less than the abrasive slurries used for the CMP process. This is mainly because of the electrolyte-based slurry used in ECMP which costs less to make [6]. Fang *et al.* [7] studied the method to recycle ECMP slurries and electrolytes to reduce the cost of consumables.

Economikos *et. al.* [8] compared CMP process with ECMP process and showed that ECMP exhibits low dishing. Table 1.1 shows the dishing data for both processes. They also conducted some experiments to identify defects in ECMP using a "defect inspection measurement system" which has the capability to detect defects greater than 600A. The total defect density was found out to be 0.1 defects/cm². Also they reported that different failure modes, such as delamination, copper pull-out and dielectric cracking were not observed in ECMP.

Table 1.1: Dishing data for copper in ECMP and CMP [8]

Process	Left edge	Left middle	Center	Right middle	Right edge
ECMP	300	300	270	250	280
Conventional CMP	730	460	440	590	830

Tiley *et al.* [9] reported higher material removal rates in ECMP than CMP in the case of titanium and nickel alloys. They observed the oxide layer on the surface of the film to be twice the thickness when current was applied.

Various advantages of ECMP can be summarized as follows:

1. Ability to polish low-k materials
2. Low mechanical down force
3. Less polishing time
4. Good within wafer uniformity
5. Low dishing
6. Less surface defects such as delamination and erosion
7. Lower cost of consumables
8. Higher material removal rates
9. Efficient slurry handling and waste disposal systems
10. The extent of planarization can be controlled by the charge applied.

1.4 Parameters that affect Electrochemical Mechanical Polishing process

ECMP is affected by mechanical parameters, such as pad speed, wafer carrier speed, and electrochemical parameters, including electrolyte, slurry, and applied voltage. Various input parameters of this process are:

1. Operating voltage
2. Current density
3. Polishing pad (material used)
4. Pad speed

5. Wafer carrier speed
6. Slurry composition (electrolyte, pH, abrasives and inhibitors)
7. Polishing time

Some of the output parameters, but not limited to, are:

1. Material Removal Rate (MRR)
2. Surface characteristics

1.5 Electrochemical Mechanical Polishing of different materials

ECMP has been developed to planarize different materials used in microchip fabrication and tooling. The materials which ECMP can polish, but not limited to, are:

1. Silicon carbide,
2. Steel,
3. Copper,
4. Tantalum,
5. NiP substrates,
6. Titanium, and
7. Ni based superalloys.

Silicon carbide (SiC) substrate surfaces are polished using ECMP. Colloidal silica slurry is used to remove the oxide layer while hydrogen peroxide and potassium nitrate are used as electrolytes. The current density for the process is operated in the range of 10 $\mu A/cm^2$ to 20 $\mu A/cm^2$. ECMP process is performed in two steps in order to control the oxidation of the anode and removal of the oxide layers [10].

ECMP is also used to polish different kinds of steels. A mixture of sodium nitrate and sodium sulfate is used to prepare the slurry. Higher efficiency, better quality, and low surface roughness are observed in steel polishing. An abrasive tool made of sponge rubber or PVA sponge was used instead of the regular polishing pad [11]. Recently ECMP was performed on tooling steel (SKD11). The I-V curves for the process shows the electrochemical characteristics, such as active, passive, trans-passive states for the steel material. Scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS) were conducted to investigate the surface profile and its metallurgical compositions [12].

Stainless Steel which is used in some of the semiconductor and biomedical industries can also be polished by ECMP. Residual stress and microcracks were rarely observed when stainless steel (AISI 316L) was polished. The formation of passive film also helped increase the corrosion resistance of the workpiece. Phosphoric acid and hydrogen peroxide were used to prepare the slurry compositions [13].

Copper has been widely used in metallization for device structures in semiconductor processing since the late 1990’s. It is used instead of aluminum and tungsten as the interconnect material in silicon-based semiconductor devices because it has better resistance to electromigration. Plasma etching proved to be bad for copper and this led to the subtractive damascene and dual damascene methods for copper planarization. When porous, low-k dielectric materials were introduced, chemical mechanical polishing had to face many challenges because of the mechanical fragility of these materials. Copper electropolishing has many advantages but pattern sensitivity is a major concern. ECMP has proven to be less pattern dependant and has been applied to these low-k materials without damaging them [14]. The electric potential applied is the driving force to oxidize copper to copper ions rather than the oxidizer present in the slurry. These ions later form a passivation layer with other components of the electrolyte which is subsequently removed by the pad [15]. Also, ECMP is excellent for bulk copper planarization as it has high copper removal rates and excellent planarization efficiency [16]. In this thesis, ECMP is performed on 4 inch copper wafers.

Tantalum is mostly used as a diffusion barrier for copper in integrated circuit interconnects. Device structures which are less than 65 nm will continue to use tantalum in the future as they contain porous mechanically fragile dielectric materials. So, in order to process these materials, low pressure of less than 1 psi has to be used. ECMP is the best process for such applications. Alkaline KIO_3 solutions have been used to make the slurry for Ta ECMP. These slurry solutions are able to form the soft surface film which can be easily removed by applying minimum mechanical pressure. Also, dihydroxy benzene sulfonic acid solutions maintained at various pH values were used in Ta ECMP. Recently, some examinations were made to analyze the anodic corrosion of tantalum. This was done by the electro-oxidation of tantalum with NO_3^- ions so that weak surface oxide films are formed. Voltammetry techniques, SEM, and single frequency impedance spectroscopy are generally used to study the corrosion behavior and material removal mechanisms in ECMP of tantalum [17-20].

Recently, ECMP has been used to polish NiP substrates which are magnetic media substrates used in magnetic storage medium. ECMP provides a controlled surface finish to these substrates. In conventional CMP, the polishing is done in two steps using mechanically aggressive slurry in the first step and a mechanically soft slurry in the second step. Even though the second step gives an overall good finish, the scratches produced in the first step of polishing remain due to the left over colloidal abrasives and debris. In order to rectify such surface defects, ECMP has been found to be useful to polish magnetic substrates. Electrolytes are uniquely designed which enhances the effect of electrical current in step height reduction efficiency and nano asperity reduction. Also a shear sensitive supramolecular structure for the delivery of electrolytes has been developed to give a better surface finish [21]. Micron Inc. used ECMP to prepare titanium samples (Ti-6Al-4V) and nickel-based super alloys (IN718) for SEM imaging [9].

1.6 Thesis organization

Chapter 1 gives an introduction to the ECMP process. The background of the process is elucidated showing the need for a process like ECMP for polishing. The schematic of the process is given followed by its advantages over other planarization processes. The parameters affecting the process as well as different materials which can be polished by ECMP are given.

Chapter 2 provides a detailed review of literature for the ECMP process. Five different methods and apparatuses for ECMP are presented. The mechanism of ECMP is explained in which the electrochemical characteristics and voltage induced material removal is shown. The material removal in Cu ECMP is studied. The slurry composition for ECMP is presented describing the essential components to produce a better surface finish. Acid based slurries, phosphate based electrolytes and KOH based electrolytes are discussed in detail. The role of the polishing pad is also described.

Chapter 3 presents the problem statement of the thesis. Various objectives for this thesis are listed in this chapter. Chapter 4 provides a detailed explanation of the fabrication of the apparatus for ECMP. The apparatus without the planetary motion was initially built which did not produce the desired results. So, ECMP apparatus with planetary motion was developed using Pro/E software. The manufacturing process and the materials used for each individual part of the apparatus are described. The final experimental set up used to polish the copper wafers is illustrated.

Chapter 5 provides the methodology and experimental procedure used to polish 4 inch copper wafers. Five different slurry compositions for copper ECMP are investigated to produce a good surface finish. The process conditions and post polishing treatment procedures are discussed. Multi-stage polishing of copper wafers is described. The influence of process parameters, such as polishing time, operating potential, pad speed, and wafer speed are investigated. Surface characterization of the copper wafers is studied using optical microscope and a laser optical interference microscope (MicroXAM).

Chapter 6 presents the results and discussion of the thesis. The effect of slurry composition and pH, polishing time, operating potential, pad speed, and wafer carrier speed are discussed. The material removal rates and surface roughness are calculated for each study. The optimal process condition to achieve a good surface finish is also discussed. Chapter 7 summarizes the findings of this experimental study and scope for future work is outlined.

CHAPTER II

LITERATURE REVIEW

2.1 Apparatus for Electrochemical Mechanical Polishing

ECMP is a relatively new process which is still being explored in different areas. Several new methods and systems are being developed for ECMP to achieve better surface planarization, higher material removal rate, less cost of consumables etc. Some of the researchers have built ECMP apparatuses which do not have planetary motion i.e. there is rotation of only the polishing pad or the rotating abrasive disk while most of them have planetary motion i.e. the polishing pad and the wafer carrier rotate simultaneously.

2.1.1 Apparatus with Planetary Motion

Sharan [1] designed an ECMP apparatus with a planetary motion. Figure 2.1 shows an ECMP apparatus with a platen, polishing pad located over the platen which is connected to a cathode, and a wafer which is held by a wafer carrier. Different motions can be achieved by the platen, such as lateral and vertical translation. The temperature of the platen is maintained by circulating a fluid by means of a chiller or heater. Figure 2.1 shows the ECMP apparatus with planetary motion.

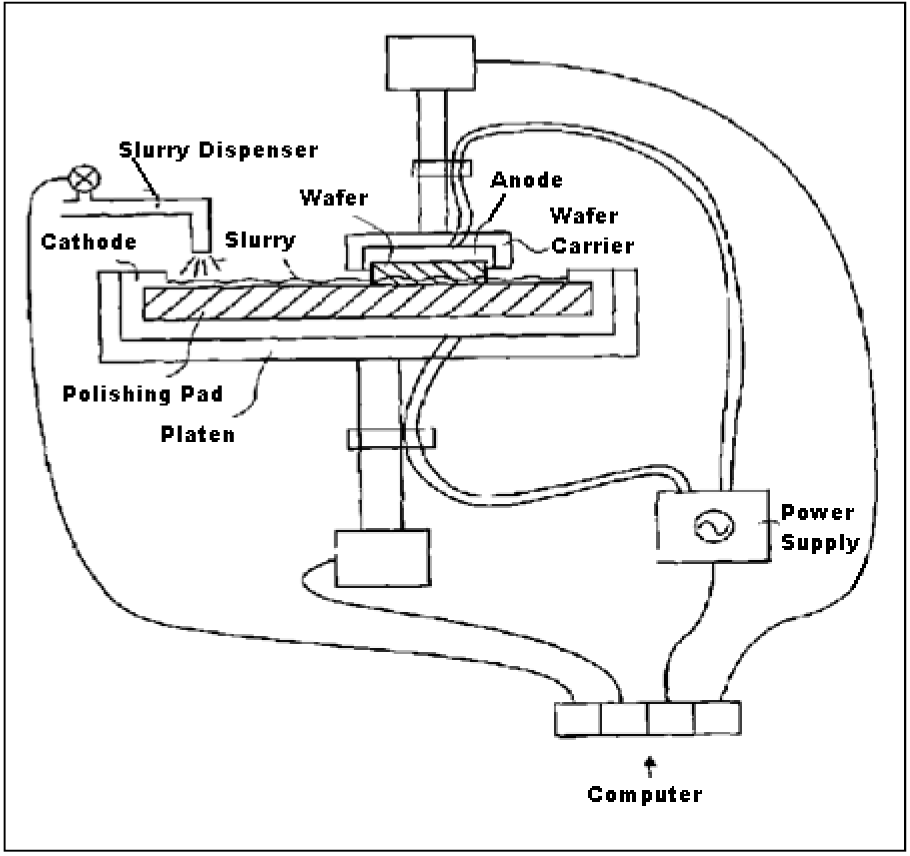


Figure 2.1 Apparatus for Electrochemical Mechanical Polishing, after Sharan [1]

Polishing pad is fabricated keeping in mind certain properties, such as hardness, stiffness, porosity, abrasiveness, and absorbance. Channels are made across the pad and the wafer to enable slurry movement. A cathode is directly connected to the polishing pad. Small segments on the cathode are performed so that current distribution will be uniform across the pad. A slurry dispenser is used to dispose the slurry in different ways. Abrasives, such as alumina or silica are used in the slurry. A pH of 2-3 was maintained for the slurry composition [1].

Anode is connected to the wafer and is segmented to provide uniform distribution of current to the wafer. The wafer is enclosed in a wafer carrier. Different methods are used to hold the wafer, such as vacuum, friction, surface tension and electrostatic forces. Mass transfer of the slurry occurs when the platen is moved in conjunction with the wafer carrier. When the power supply provides a voltage across the pad and the wafer, the slurry completes the electrical circuit for the polishing to take place. A computer is connected to the whole system to study the electrochemical characteristics [1].

2.1.2 Apparatus with Magnetic Slip Ring

Doyle *et al.* [22] used a magnetic slip ring in the platen assembly of the ECMP apparatus. They did this to avoid the drawbacks conventional slip rings have with respect to moving surfaces. The apparatus essentially consists of a drive system which is connected to a planarizing head which holds the wafer or the substrate to be polished. A controller is provided to the drive system so that the rotation and direction of the head can be controlled. A retaining ring made of plastic materials is used to position the substrate so that it does not slip. Figure 2.2 shows an ECMP apparatus utilizing a magnetic slip ring.

A platen assembly is connected to the base of the machine and is supported by a bearing so that it may have rotary motion. A rotary coupler with magnetic slip-ring assembly is connected between the platen assembly and the base so that electrical, mechanical, fluid, and pneumatic control can be achieved effectively. The platen assembly has two plates, the upper one is made of metal or rigid plastic and the lower one is made of aluminum.

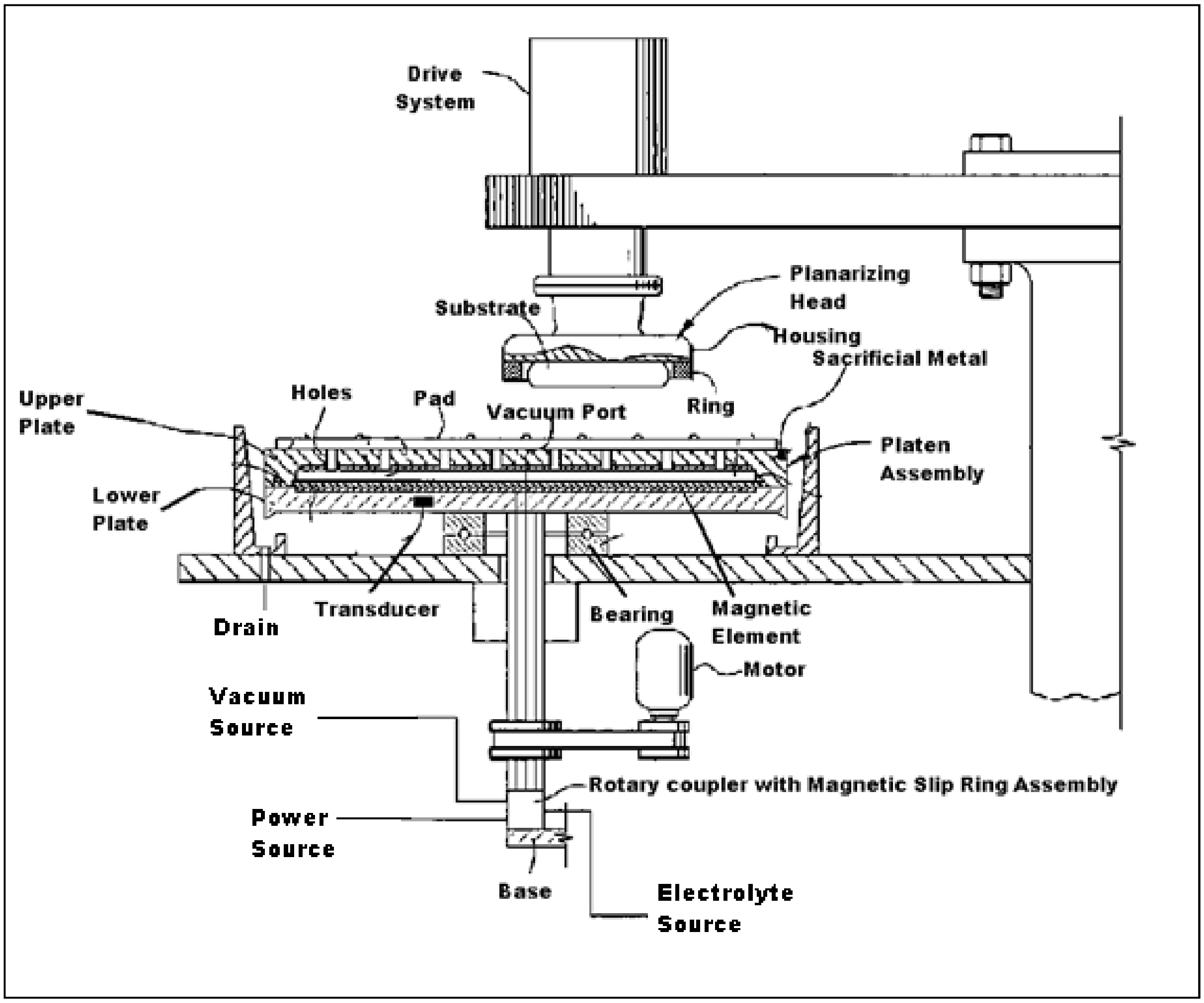


Figure 2.2: ECMP apparatus with platen assembly having a magnetic slip ring, after Doyle *et al.* [22]

A magnetic element is enclosed within the platen assembly such that the pad is attracted to the platen. Also, vacuum ports are coupled to a vacuum source so that the pad is retained against the platen assembly. An electrode is embedded in the pad assembly. Additionally, the platen assembly has a sonic transducer to vibrate the platen assembly to induce rotation of the ball of the contact assembly. A sacrificial metal made of zinc is also place in the platen in order to minimize the chemical attack on the ball by the slurry [22].

2.1.3 Apparatus with Linear Polishing Belt

Du *et al.* [23] built an apparatus for ECMP which gives better surface finish and higher material removal rate. Here, they developed a new method where instead of the regular polishing pad which has rotational motion, a polishing belt is provided so that there is a linear motion. The idea was that the linear motion of the polishing belt will be much faster than the rotating polishing pad and it does not dry out the belt. Figure 2.3 shows an ECMP apparatus, after Du *et al.* [23] using a polishing belt with linear motion.

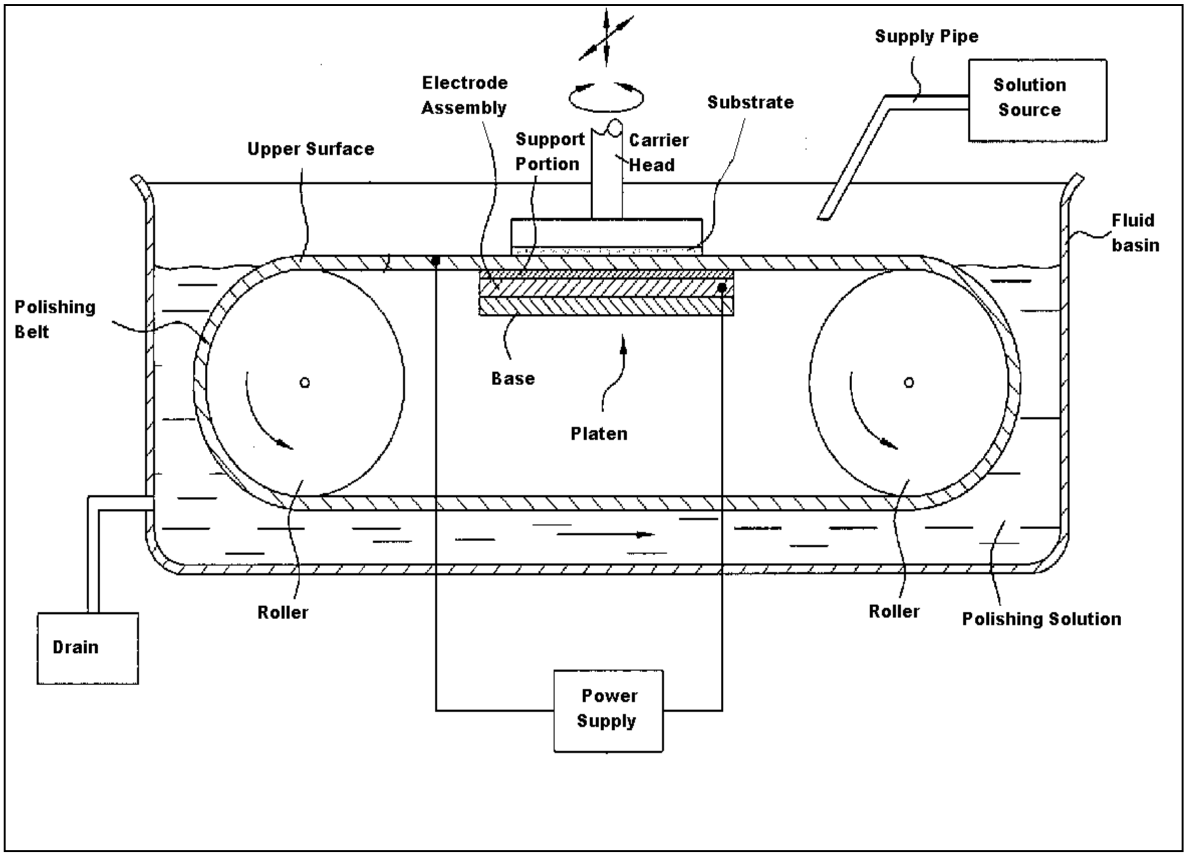


Figure 2.3: ECMP apparatus using a polishing belt with linear motion, after Du *et al.* [23]

A fluid basin is filled with the polishing slurry and two rollers are disposed in this basin. A polishing belt made of a conductive material is made to roll over the rollers such that it has a constant linear motion. Small perforations are also made on the belt so that the slurry flows through it. A platen is built between the rollers and acts as a rigid support for the polishing belt. The electrode assembly is disposed in the platen to provide the negative charge. Polishing takes place when the power supply is adapted between the electrode assembly and the belt [23].

The substrate or the wafer is held firmly using a carrier head which is positioned above the belt. It can move in the vertical direction to position the substrate so that it is in contact with the polishing belt. The slurry is filled in the basin such that the upper surface of the belt is not soaked in the slurry solution. The supply pipe will provide the extra polishing solution to the upper surface, if needed. Relative motion between the rotating substrate and the polishing belt gives a uniform surface finish for the substrate [23].

2.1.4 Multiple Polishing Station Apparatus

Sun *et al.* [24] stated that in automated semiconductor manufacturing, there is a need for an apparatus which is of the multi polishing station-type. Figure 2.4 shows such an ECMP apparatus which has three polishing stations and a transfer station located on the lower machine base. Every polishing station has a platen and a polishing pad. A pad conditioner is also provided for each station in order to maintain the polishing pad.

A multi head carousel located on the upper table surface is positioned above the lower machine base. It is supported by a center post and is rotated about the carousel axis by a power motor and drive shaft. Four carrier heads are mounted on the carousel base plate and they are used to retain the wafer and press it against their respective polishing pad for the automated ECMP polishing [24].

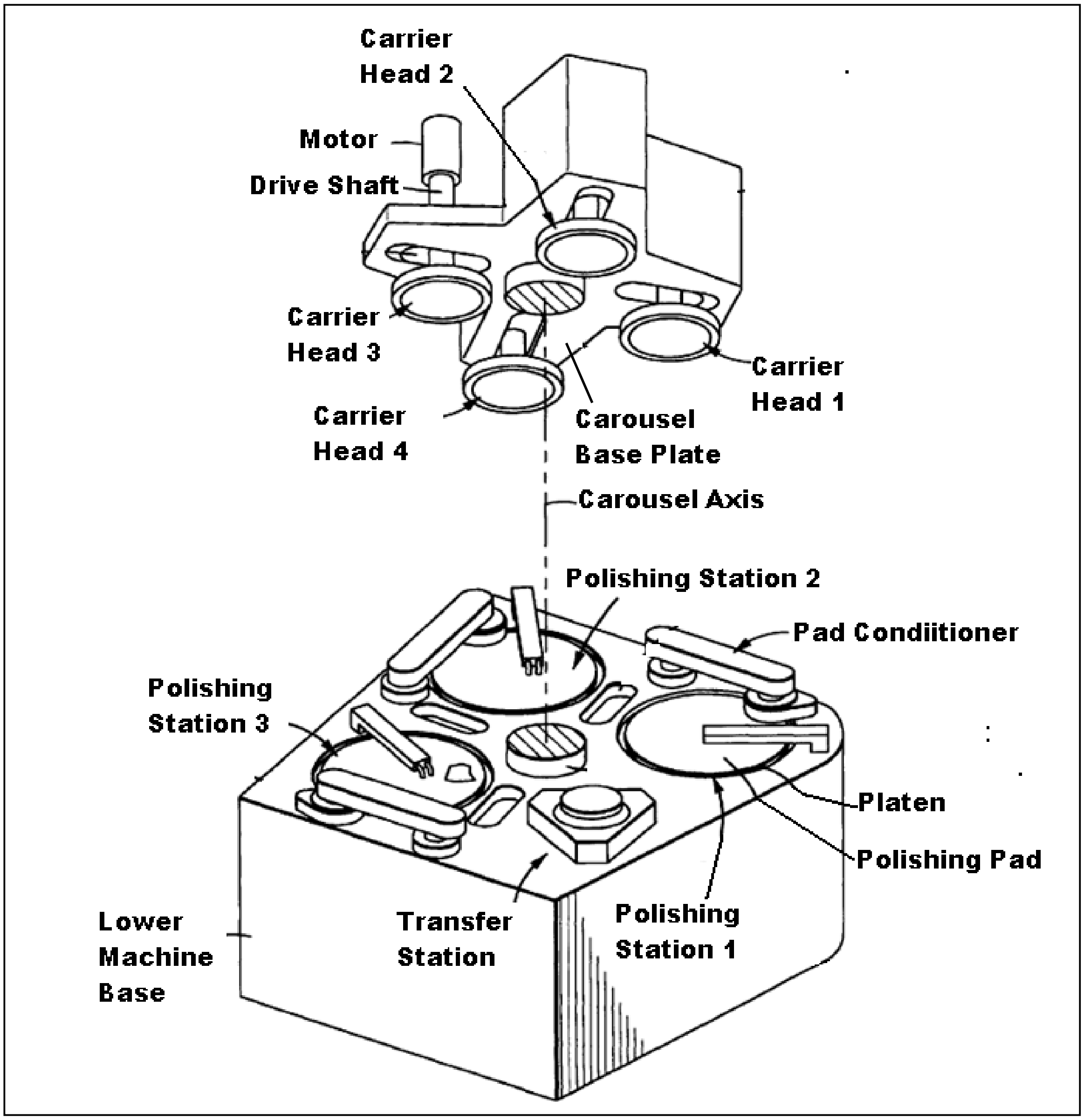


Figure 2.4: Multi-station ECMP apparatus, after Sun *et al.* [24]

2.1.5 Face-up Polishing Apparatus

Duboust *et al.* [25] showed the method and an apparatus for face up electrochemical mechanical polishing. Here, the substrate is polished face-up instead of the usual face-down polishing. The polishing pad is positioned above the wafer carrier and is smaller than the substrate which is to be polished. This reduces the cost of consumables as a smaller conductive pad would be much cheaper than a larger conductive pad. The polishing head which holds the pad also is smaller than the diameter of the substrate.

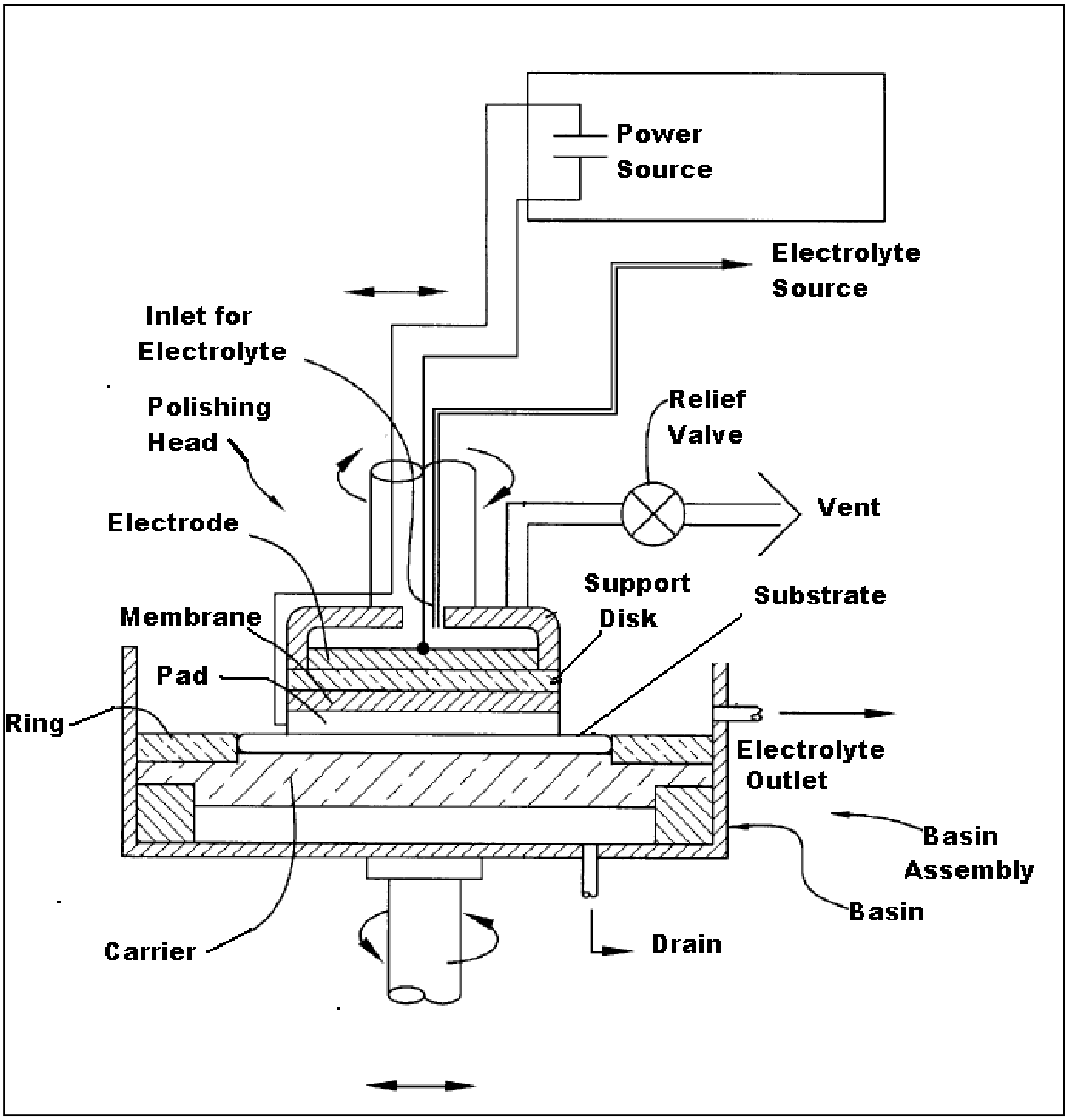


Figure 2.5: ECMP apparatus with face-up substrate polishing, after Duboust *et al.* [25]

The substrate is disposed in a basin assembly of the apparatus. The basin assembly has a basin with a wafer carrier in the middle. A retaining ring is used to hold the substrate in position. The polishing head initially polishes the center of the substrate and then is programmed to move towards the sides. Overall planarization can be attained by an end point detection system. Figure 2.5 shows an ECMP apparatus with face-up substrate polishing. [25]

An inlet is provided in the housing of the polishing head in order for the electrolyte to flow through the pad. The flow of the electrolyte is designed in such a way that it flows from the inlet first to a permeable electrode, then to a membrane, then to a support disk, and finally flowing though the pad onto the surface of the substrate. After the polishing is done, the electrolyte is allowed to exit through the outlet provided in the basin assembly. A vent is provided on the polishing head which allows the hydrogen gas to escape during polishing. A relief valve ensures that the electrolyte will not inadvertently flow out through the vent [25].

Table A in Appendix A gives a list of patents that gives different methods and apparatus for electrochemical mechanical polishing. Some of the systems provide conditioning methods and some of them show some modifications to the slurry flow to make it more effective. Some of the patents show process control and endpoint detection methods for better surface finish and uniformity of the substrate.

2.2 Mechanism of ECMP

Chen *et al.* [11] points out that a very small gap should be provided between the workpiece and the electrode and this gap should be filled with the electrolyte. The electrolyte or the slurry should be able to passivate the surface of the workpiece. The passive film formed is an insulating film which is thin and compact. The surface of the workpiece is protected by this film. When the mechanical abrasives brush the surface, the passive film is removed and the surface is protected. Again the surface is passivated and the mechanical abrasives remove the film. Thus the passivation-brush cycle continues until a uniform polish is obtained.

Wang *et al.* [26] developed a polishing sequence for ECMP. Initially a substrate has to be loaded into the apparatus and has to be retained properly within the polishing head. The polishing head should be positioned above the pad assembly and should be mechanically stabilized. Now the head should be rotated relative to the surface of the polishing pad. An electrochemical removal process should be performed on the substrate. A first voltage should be applied to the substrate for a time period and then a second voltage should be applied which is greater than the first voltage until the desired polish is achieved.

Duboust *et al.* [27] also introduced a method to polish substrates at a high polishing rate using ECMP. Initially the substrate is exposed to the electrolyte solution. A passivation layer is allowed to form on the metal substrate. The substrate is initially applied with a voltage of 1.5 to 3 V for a period of time to increase the passivation strength of the passivation layer. A second voltage of 4.5 to 5.5 V is applied to polish the substrate for another time period. Finally, conductive material is removed from a portion of the substrate by anodic dissolution.

2.2.1 Electrochemical Characteristics

Lee *et al.* [12] studied the electrochemical characteristics of tool steel SKD 11 such as active, passive, and trans-passive dissolution states by observing the current density vs voltage (I-V) curves. The effect of electrolyte concentration was also studied using these curves. Figure 2.6 shows an I-V curve which clearly indicates different electrochemical states of the substrate.

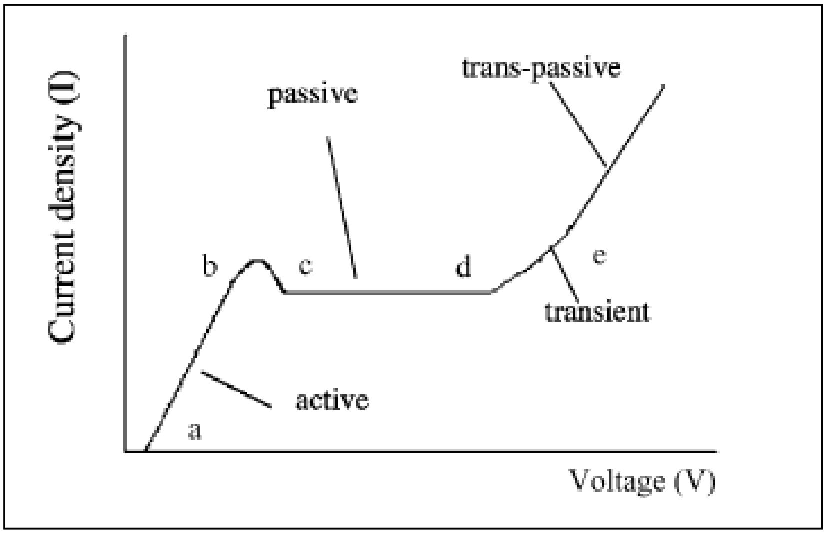


Figure 2.6: I-V curve showing different electrochemical states in ECMP of tool steel (SKD11), after Lee *et al.* [12]

The point ‘a’ depicts the start of the electrochemical reaction in the process. Nernst equation [12] is used to obtain its value as follows:

$$E_d = E_r + \eta_c + \eta_a + IR = (E_c - E_a) + \eta_c + \eta_a + IR$$

Where, E_d is the decomposition potential, E_r is the reversible potential, E_c is the cathode reversible potential, E_a is the anode reversible potential, η_c is the cathode overpotential, η_a is the anode overpotential, and IR = potential drop.

Initially, as observed from Figure 2.6, normal electrochemical dissolution occurs in the region a-b where the curve is linear. At point ‘b’, the dissolution limit starts owing to the concentration of the slurry. The region c-d shows the passive state as metallic hydroxides are formed on the compound generating a passive film. As the voltage increases from ‘c’ to‘d’ the passive state did not change much because the film has very high electrical resistance. At point‘d’ the voltage now is able to remove the metallic ion through the passive film. The passive film thus begins to peel away till the operating potential reached the point ‘e’. The region d-e, where the passive film is removed, is called the transient state. After this region, the electrochemical reactions became very active where the trans-passive state of the substrate begins [12].

2.2.2 Voltage Induced Material Removal

Han *et al.* [28] studied the voltage induced material removal mechanism using the same electrochemical states described above for copper ECMP. The I-V curves employed in this study were obtained from a linear sweep voltammetry (LSV) and cyclic voltammetry (CV). The I-V curves were obtained as a function of the concentration of KNO_3 and HNO_3 electrolytes. Figure 2.7 shows the I-V curves for these two electrolytes. These curves were observed to investigate if the concentration of the electrolyte would affect the I-V curves. Concentrations of the electrolyte were taken as 5%, 10% and 20%.

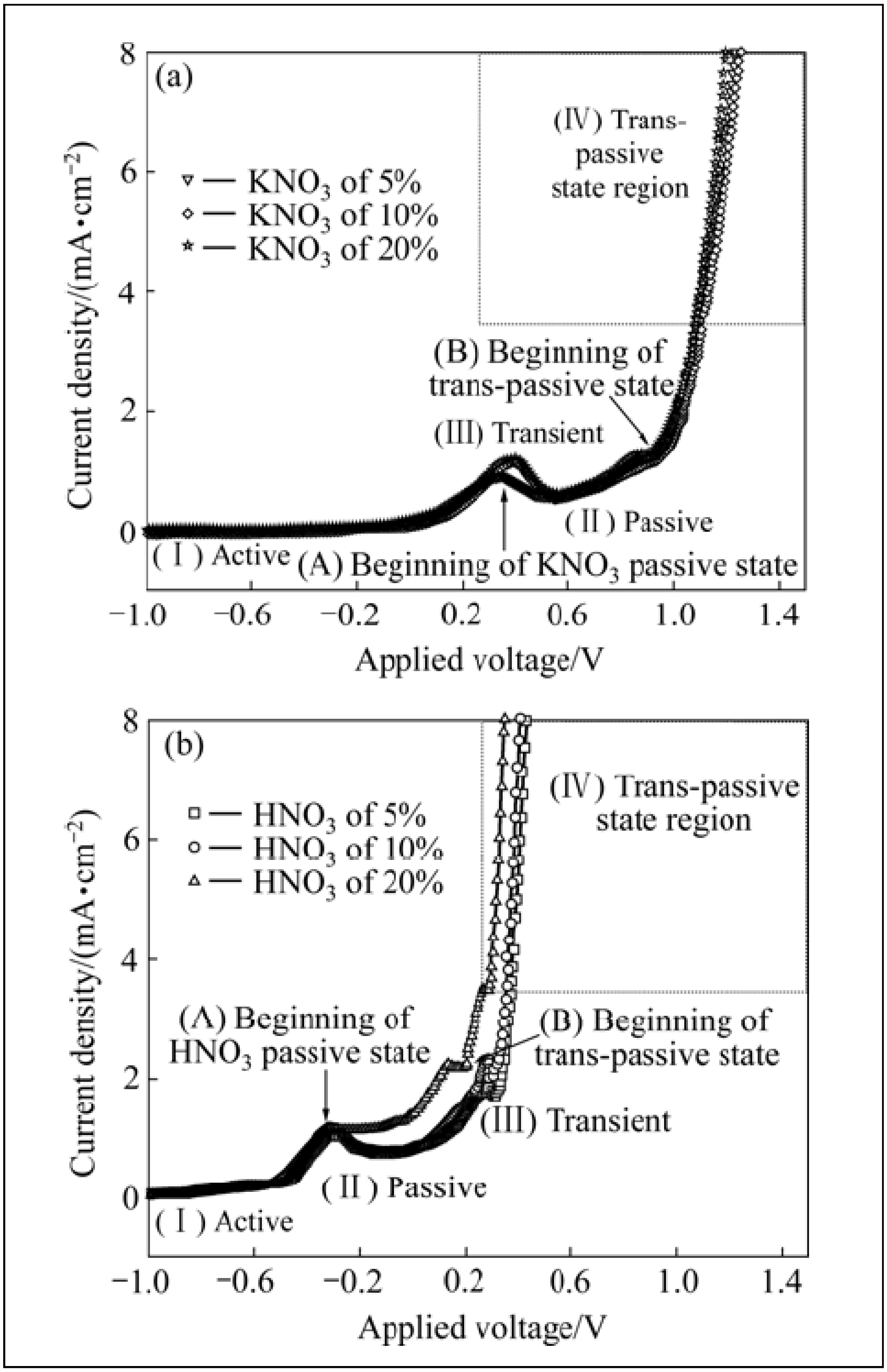


Figure 2.7: I-V curves as a function of electrolyte concentration of (a) KNO_3 and (b) HNO_3, for copper, after Han *et al.* [28]

In the case of KNO_3 electrolyte, when the concentration is increased, current density increases and the trans-passive voltage is decreased. The formation of passive state is not clearly seen owing to the formation of a continuous metallic hydroxide on the surface of the copper wafer. In the case of HNO_3 electrolyte, the transient voltage tends to decrease. Thus electrolyte concentration does affect the I-V curve which indirectly affects the material removal mechanism [28].

Yong-Jin Seo [29] investigated the voltage activated electrochemical reactions of copper for ECMP using different slurry concentrations. He studied different electrochemical states, such as active, passive, transient and trans-passive for copper using the I-V curves. Cu discs of 99.99% purity were used in the ECMP experiments. No mechanical polishing was done to understand the electrochemical behavior only. I-V curves were plotted for different concentrations of nitric acid electrolyte. When the voltage starts to increase from -0.25 V to 0.25 V, a thin passive film begins to form on the surface. This passive film is generally made of metallic hydroxides which are shown in the following chemical reactions.

$Cu + 2H_2O \rightarrow CuOH.H_2O + H^+ + e^-$

$CuOH \rightarrow CuO + H^+ + e^-$

Initially the concentration of the electrolyte was not much of a factor in the active region but in the trans-passive region, as the concentration of the electrolyte was increased, higher current density was observed. Active, passive and trans-passive states were seen at voltage values of -1.0, -0.25, and 0.7 V, respectively [29].

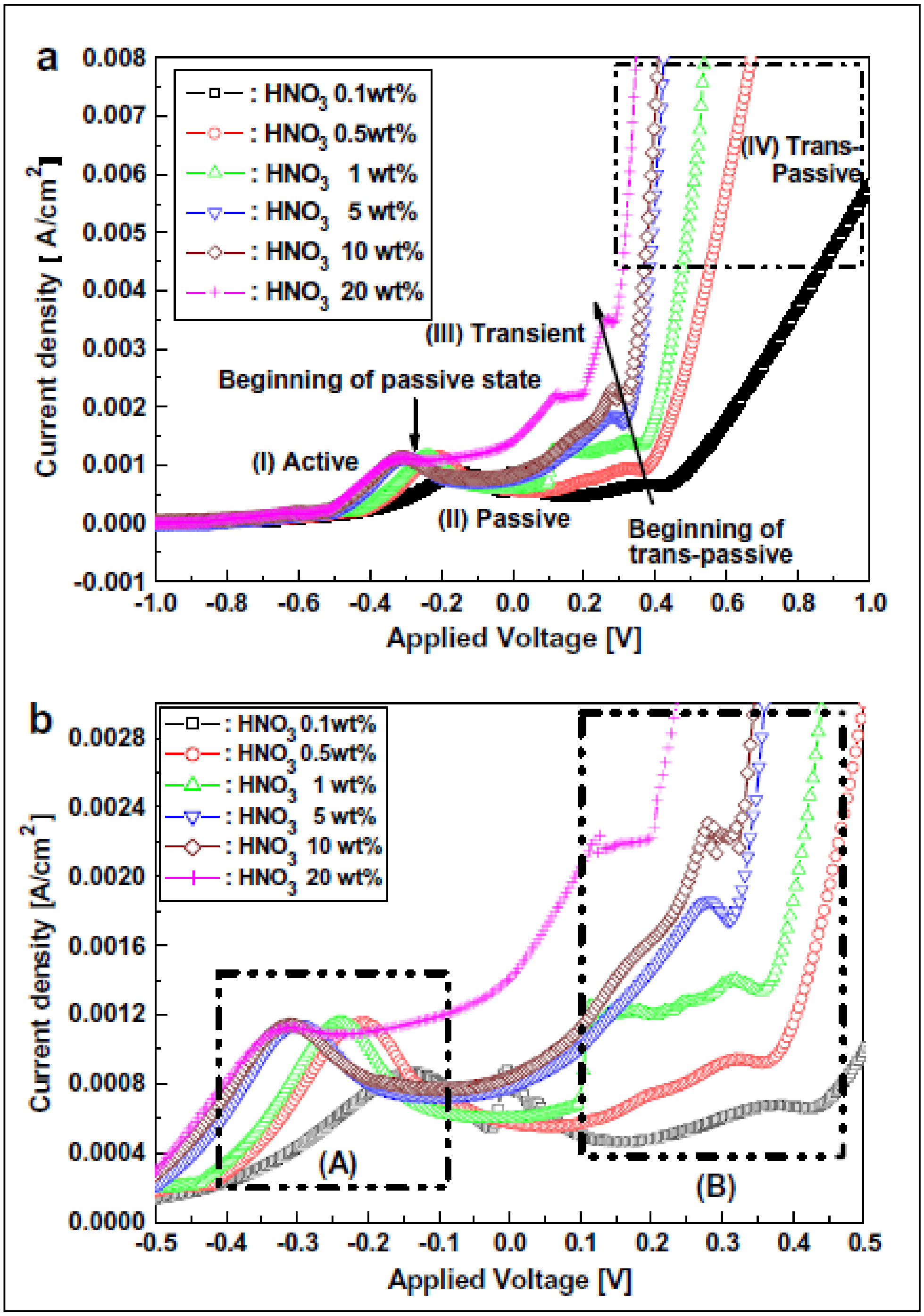


Figure 2.8: I-V Curves to study different electrochemical regions of copper ECMP (a) Voltage applied from -1 to 1 volts (b) Voltage applied from -0.5 to 0.5 volts, after Seo [29]

Figure 2.8 shows the I-V curves with different electrolyte concentrations. The first part of the figure shows the voltage values between -1.0 and 1.0 volts while the second part shows a more detailed picture between -0.5 and 0.5 volts [29].

Region 1 is the active region where normal anodic dissolution occurs and at -0.25 volts, a plateau region (region 2) is formed which is the passive state. The third region is the transient stage and the fourth region is the trans-passive state. The optimal conditions of material removal in ECMP can be evaluated by observing the I-V curves. The second part of Figure 2.8, shows two boxes where voltage drop occurs. Voltage drop in an I-V curve indicates the presence of oxides formed on the copper surface which increases the resistance to voltage applied. The first box indicates the passive state and the second box shows the trans-passive state [29].

Figure 2.9 shows the SEM surface images of the electrochemical states observed in Figure 2.8. The original surface is the initial condition of the copper wafer (as received) having numerous scratches. Active state at -1.0 V had fewer scratches but some pits due to corrosion and bubbles were still observed on the surface. The passive state at -0.25 V had considerable oxidation and corrosion formed on the surface. The trans-passive state showed a very different surface which was spongy and had a non-uniform surface as the copper ions were removed by electrochemical dissolution from the copper surface [29]. These experiments were performed without the mechanical aspect of ECMP. Thus, when the mechanical pad is used it will brush away the passive layer and give a smooth surface finish to the copper wafer [29].

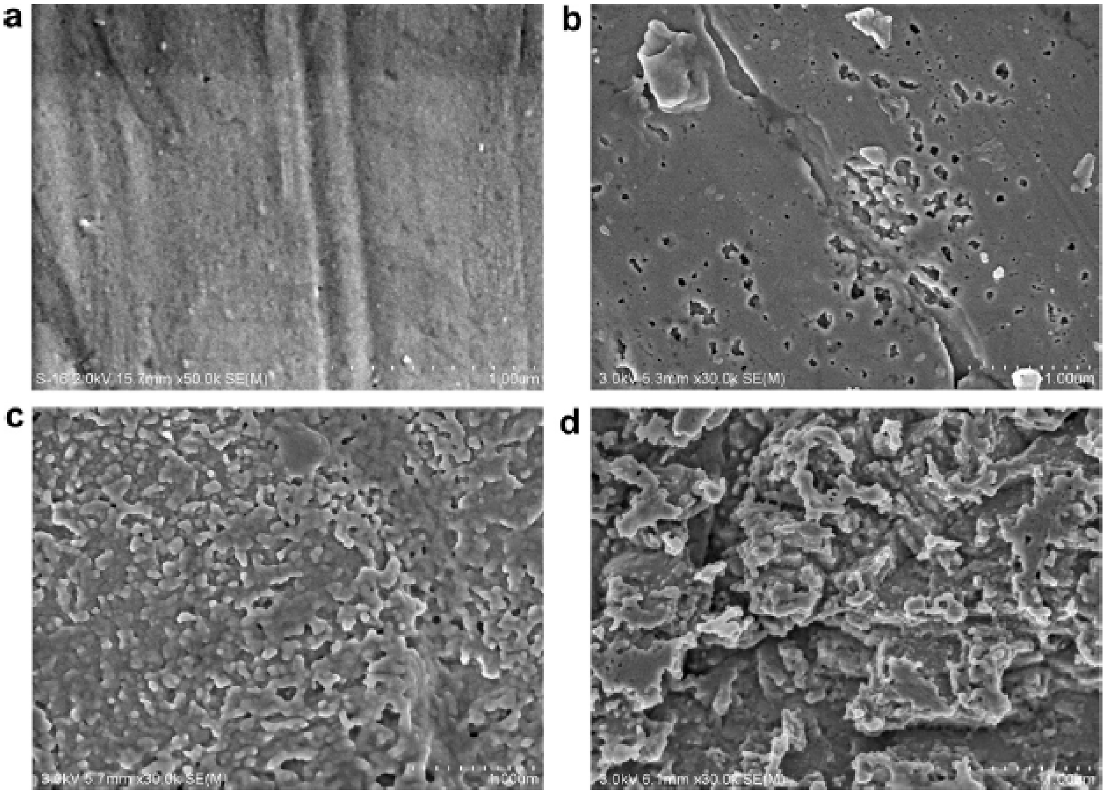


Figure 2.9: SEM micrographs of different electrochemical states on copper (a) Original surface (b) Active state at -1.0 V (c) Passive state at -0.25 V (d) Trans-passive state at 0.7 V, after Seo [29]

2.2.3 Material Removal in Copper ECMP

Ng *et al.* [30] explored the effects of pH and operating potential parameters to study the friction and wear mechanisms in copper ECMP. Figure 2.10 shows the Pourbaix diagram of copper ECMP which has four different regions. Region 1 shows that copper undergoes corrosion. This is because anodic dissolution of copper is very high and no sacrificial surface layer is allowed to form on the copper. Severe pitting occurs on the surface giving a very bad surface finish.

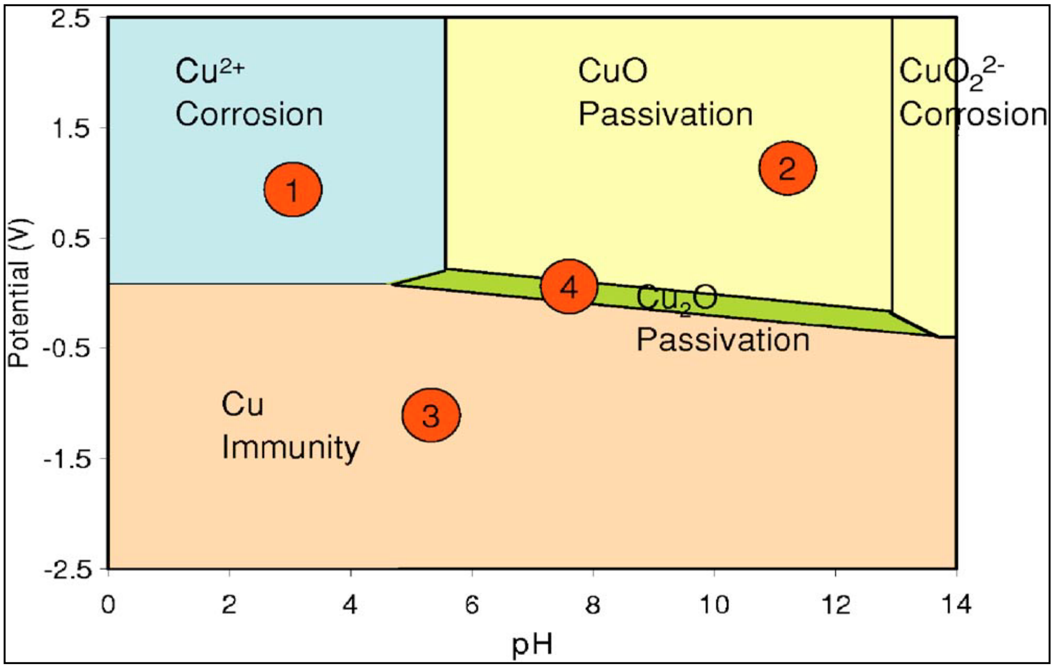


Figure 2.10: Pourbaix diagram of copper ECMP, after Ng *et al.* [30]

Copper dissolution stops at pH above 6. The solubility of the metal interface limits the mass transfer of the metal ions into the solution as the pH is increased. A passive surface layer is formed when the concentrated ions accumulate at the interface. This layer now acts as a sacrificial layer which is removed by the pad during ECMP. Thus this region will give good surface roughness values as shown in Table 2.1. As the pH is increased to higher values, further oxidation of the copper surface occurs which will form a thermodynamically unstable surface layer [30].

Region 3 shows the behavior of copper when cathodic potential is applied. No oxidation occurs on the copper surface and the planarization depends on the mechanical abrasion of the polishing pad. Region 4 shows the application of low anodic and cathodic potentials to the copper wafer with neutral and alkaline pH conditions. Passivation layer is not formed completely because of weak oxidation. Planarity of the surface is not the best because this layer is easily damaged by the mechanical action of the polishing pad [30].

Table 2.1: Surface roughness (Ra) and friction coefficient values of copper ECMP for different pH and potential conditions [30].

Region	Polishing Condition	Surface roughness Ra (nm)	Friction Coefficient
Region 1	pH 2, 1 V	47.55	0.3091 ± 0.0077
Region 2	pH 14, 1 V	4.6	0.1387 ± 0.0095
Region 3	pH 6, 0 V	11	0.2412 ± 0.0066
Region 4	pH 10, 0 V	20.12	0.3028 ± 0.0098

Kung *et al.* [31] investigated the effect of copper ion concentration on the material removal rate and surface planarization in copper ECMP. Various chemical reactions occurring in Cu ECMP are given in the following:

$Cu_{(s)} \rightarrow Cu^{+} + e^{-}$

$Cu_{(s)} \rightarrow Cu^{2+} + 2e^{-}$

$2Cu^{+} + H_2O \rightarrow Cu_2O + 2H^{+}$

$Cu^{+} + 2OH^{-} \rightarrow Cu(OH)_2$

$Cu_2O + H_2O \rightarrow 2CuO + 2H^{+} + 2e^{-}$

$Cu + H_3PO_4 + H_2O \rightarrow [CuOH]^{+}[H_2PO_4]^{-} + 2H^{+} + 2e-$

From these equations, it is quite evident that there are lots of copper ions which are formed in ECMP. Figure 2.11 shows the material removal rate as a function of Cu ion concentration for electrochemical mechanical polishing, chemical mechanical polishing and electrochemical polishing. The removal rate is higher in ECMP than in the other two processes, as can be seen from Figure 2.11. In CMP, as no electric potential was added, passive layer was not formed and the removal rate is very low. Thus, the effect of copper ions in CMP was limited. In ECP, the passive layer begins to form at 0.8 V potential and the material removal is partial due to the copper ions which escape from the passive layer.

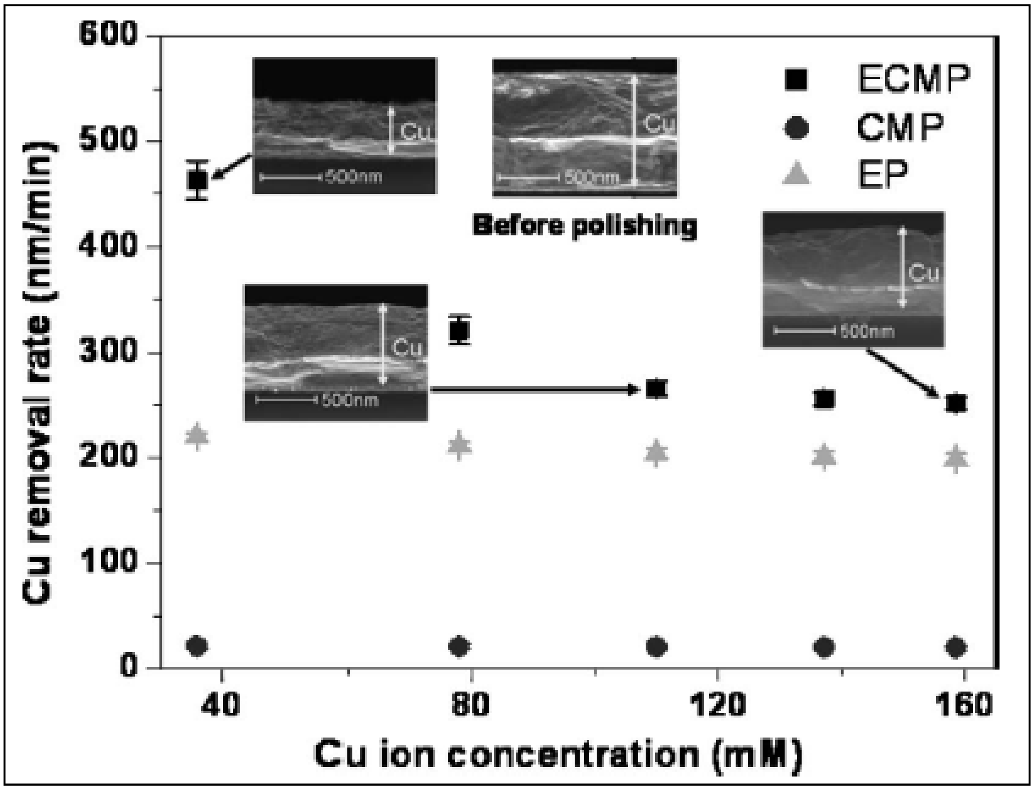


Figure 2.11: Material removal rate of copper in H_3PO_4 electrolyte with respect to Cu ion concentration in ECMP, CMP, and ECP processes, after Kung *et al.* [31]

In ECMP, the mechanical pad removes the passive film as soon as it was generated thereby increasing the removal rate. The passive film has a tendency to recover fast due to the presence of the Cu ions. A diffusion layer is formed eventually as the Cu ion concentration is increased which will significantly reduce the material removal rate. The current density was decreased from 91 to 62 mA/cm^2 when the Cu ion concentration is increased. CuO is the main product formed when the Cu ion concentration is more in ECMP while $Cu(OH)_2$ is formed when the concentration is less. Thus more amount of copper ions in the electrolyte decreases the material removal rate in copper [31].

Hardikar [32] introduced a method of multi-step polishing of copper. First a current density in the range of 5 to 25 mA/cm^2 was used to polish the substrate. In this step, the first portion of the metal layer is removed to planarize the surface with high and low topographies. In the second step, a current density in the range of 20 to 40 mA/cm^2 was applied to the substrate. The material was removed from the bulk layer till a desired predetermined thickness remained on the substrate.

2.3 Slurry Composition for ECMP:

The slurry composition is very important as it should be able to passivate the metal surface in ECMP. The chemical concentration of the slurry should be appropriate so that topographical defects are not formed on the surface. Some of the acidic slurries which have very low pH tend to corrode the metal surface very easily. So there is a need for a corrosion inhibitor in ECMP slurry. There are some components in the slurry which are essential to produce a smooth finish in electrochemical mechanical polishing.

2.3.1 Essential Components of the Slurry

Liu *et al.* [33] introduced a method and a polishing composition for low dishing in copper ECMP. The essential components of the slurry are the following:

a. Acid based electrolyte
b. Chelating agent
c. Corrosion inhibitor
d. Inorganic/organic salt
e. pH adjusting agent
f. Oxidizer
g. Abrasive particulates
h. Solvent

Electrical conductivity is achieved by the acid based electrolyte. The slurry can contain about 1 to 30% (vol.) depending upon the conductivity required for polishing. Phosphoric acid, sulfuric acid, nitric acid, acetic acid, perchloric acid, and citric acids are suitable types of acid based electrolytes [33].

Chelating agents or complexing agents are used to generate a complex compound on the surface of the substrate to add to the anodic dissolution. They bind to the copper ions and increase the material removal rate. Dissolution uniformity is also achieved by these compounds. Some of them can be used as buffers to adjust the pH level in the slurry. The formation of passivation layer is also enhanced by the presence of these chelating agents. Suitable examples of chelating agents are ethylenediamine (EDA) and ammonium citrate. Acetic acid also can be a good chelating agent. The concentration of these compounds can be anywhere between 0.1% to 15% by volume or weight of the total composition [33].

Corrosion inhibitors are very important for ECMP slurry. They form a passivation layer on the surface of the metal substrate which reduces the chemical interaction between the metal surface and the slurry. Thus the oxidation or corrosion of the surface of the substrate is significantly reduced. The passivation layer minimizes the electrochemical current from the surface which reduces the metal dissolution. The concentration of the corrosion inhibitors can be between 0.001% and 5% by weight. Organic compounds such as benzotriazole (BTA) and benzimidazole can be used as corrosion inhibitors. Polymeric inhibitors such as polyalkylaryl ether phosphate can also be used [33].

Inorganic or organic salts are used in the slurry to enhance the formation of complex compounds. They are also used as chelating agents. The concentration of these salts can be between 0.1% and 15% by volume or weight of the total composition. Potassium or ammonium salts are suitable examples for these salts [33].

A pH adjusting agent is used to maintain a desired pH value in the slurry. A pH range of 2 to 10 is used for ECMP. The concentration of the pH adjusting agent can vary depending upon the composition of the other chemicals used in the slurry. Usually 0.2% to 25% by volume is used in the slurry. Common examples of pH adjusting agents are potassium hydroxide, ammonium hydroxide, and sodium hydroxide. They can be added to acidic slurry until the desired pH is obtained [33].

Oxidizers or oxidizing agents are used to enhance the material removal rate of the substrate. Oxidizers form oxides and hydroxides on the surface of the metal. In copper polishing, the copper surface undergoes oxidation to form Cu^{1+} ions and further oxidation will form Cu^{2+} ions. Chemical etching of the surface is enhanced sometimes by using an oxidizing agent. Hydrogen peroxide is a common oxidizing agent used in ECMP slurry [33].

Abrasive particles are used in the slurry to produce a good surface finish and enhance the material removal rate of the metal substrate. When abrasives are used, ECMP can achieve a surface roughness equal to that of a conventional CMP process. The concentration of the abrasives can be anywhere from 0.001% to 5% by weight of the total composition. Silica, alumina, zirconia, titania and ceria are suitable examples for abrasive particles. Finally, a solvent is used as the remainder of the polishing composition. Deionized water is generally used as a solvent for the slurry [33].

In addition to the above components some additive compounds are used to increase the effectiveness of the polishing composition. They are suppressors, leveling agents, surfactants, brighteners, stabilizers, and striping agents. Leveling agents are used to limit electrochemical reactions by forming depolarizing agents. They suppress the dissolution current by attaching themselves to the conductive substrate. One such example of a leveling agent is polyethylene glycol [33].

2.3.2 Corrosion Inhibitors

Klug *et al.* [34] used electrochemical techniques to test the efficiency of corrosion inhibitors on the metal surface. In ECMP, the inhibitor is necessary to form a thin passivating film on the surface. Benzotriazole (BTA) and ammonium dodecyl sulfate (ADS) were investigated as the corrosion inhibitors for Cu ECMP. The complexing agent used in the slurry for ADS was ß-alanine (3-aminopropionic acid). An anonic surfactant was used in the slurry for BTA. Effective inhibition of Cu dissolution is achieved by using 5 mM of BTA alone. The same results were obtained by using 1mM of BTA mixed with 3 mM of ADS. Using 3mM of ADS alone also proved to be a good inhibitor for Cu ECMP.

Lin *et al.* [35] investigated the adsorption-desorption performance of benzotriazole (BTA) as a corrosion inhibitor for Cu ECMP. Phosphate based electrolyte was used in the slurry. Effective inhibition was achieved by BTA because a continuous passive layer was formed adsorbed on the Cu surface. Mass-transfer-controlled adsorption was attained by BTA at lower operating potentials. Figure 2.12 shows the atomic force microscopy images of phosphoric acid based slurry and phosphate based slurry.

Figure 2.12 (a) and (b) show phosphoric acid slurry and phosphoric acid slurry with 0.01M BTA. Very few spots were observed in the solution containing BTA. This indicated that BTA was not adsorbed on the surface adequately. Figure 2.12 (c) and (d) show phosphate based slurry and phosphate based slurry with 0.01M BTA. Continuous cotton-like structure was observed on the solution with the BTA indicating the adsorption of BTA on the surface. Thus effective inhibition can be achieved by using BTA as a corrosion inhibitor. When the concentration of BTA was lowered, the time taken to form the passive layer increased. Desorption time of BTA increased by decreasing the operating potential. It also increased with the BTA concentration originally present in the film. Thus higher concentration of BTA was recommended at lower operating potentials to observe a stable passivation film [35].

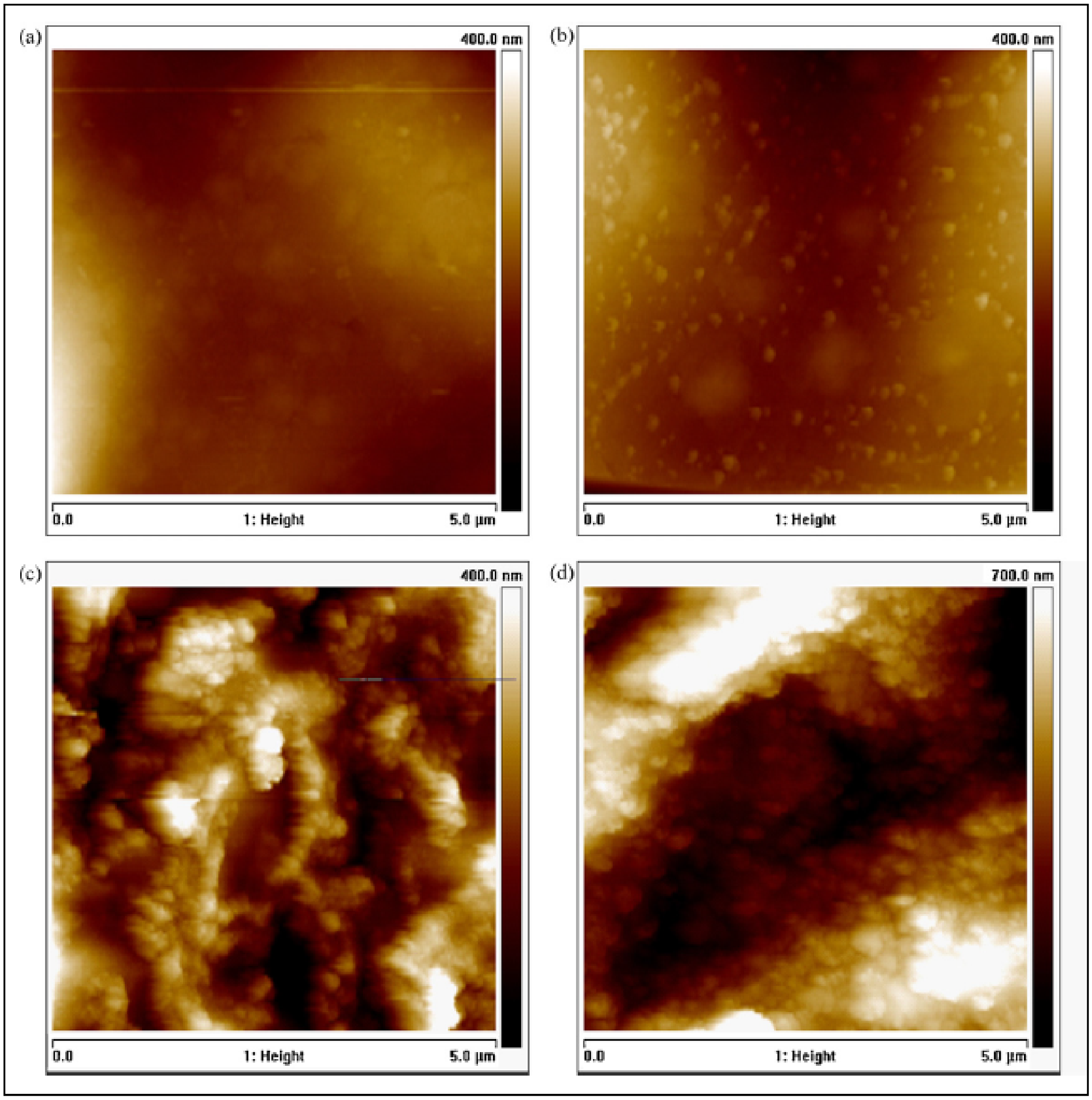


Figure 2.12: Atomic Force Microscopy images of copper using (a) phosphoric acid solution (b) phosphoric acid solution with 0.01 M BTA (c) phosphate based electrolyte (d) phosphate based electrolyte with 0.01 M BTA, after Lin *et al.* [35]

2.3.3 Acid Based Slurries

Wang *et al.* [36] provided a phosphoric acid based slurry for conductive material removal in ECMP. REFLEXION system available from Applied Materials, Inc. was used to polish a copper substrate of 300 mm diameter in two steps. The polishing composition for the first step was 6 vol. % H_3PO_4, 2 vol. % ethylenediamine, 2 wt. % ammonium citrate, 0.3 wt. % BTA, 1.5 vol. % H_2O_2, 0.15 wt. % silica abrasives and de-ionized water was used as the solvent. A contact pressure of about 0.3 psi was applied by the pad and the operating potential was about 3 volts.

The polishing composition for the second step was 5.1 vol. % $H_3PO_{4,}$ 2 wt. % ammonium citrate, 0.3 wt. % BTA, 0.5 vol. % polymeric inhibitor XP-1296, 0.025 vol. % polyethylenimine (PEI) and rest deionized water. KOH was added till the slurry had a pH of about 5.75. After the second step, the excess copper layer on the substrate surface was effectively removed [36].

Goonetilleke *et al.* [37] studied the effect of acetic acid as a complexing agent, hydrogen peroxide as an oxidizer and BTA or ADS as a corrosion inhibitor for ECMP of copper. Acetic acid provides good resistance against pH drift. Acetic acid has high planarization efficiency and is used to remove the oxides and hydroxides formed on the surface. It is also cost effective and easy to handle. The need for a pH lowering additive is eliminated when acetic acid is used.

Tripathi *et al.* [38] used hydroxyethylidenediphosphonic acid (HEDP) and oxalic acid for Cu ECMP slurry. PTA (5-phenyl-1-H-tetrazole) was used as the inhibitor in the slurry. Silica abrasives were used to achieve high planarization efficiency. The RMS surface roughness was about 7 to 10 nm and the within wafer non uniformity was close to 10%.

2.3.4 Phosphate based electrolytes

Shattuck *et al.* [39] explored phosphate electrolytes for Cu electrochemical mechanical polishing. The chemicals used to prepare the slurry were ortho-phosphoric acid, potassium phosphate, BTA and de-ionized water. The ratio of KH_2PO_4/K_2HPO_4 was used to maintain the pH of the slurry. Phosphoric acid was added whenever the pH of the solution had to be decreased. Tests were conducted with pH in the range of 0 to 10, BTA concentration from 0 to 0.1 M and the potassium phosphate salt concentration from 0.1 to 1.6 M. The optimal slurry composition was found at 1 M potassium phosphate concentration. The material removal rates were observed to be from 750 to 2500 nm/min.

Lin *et al.* [40] investigated the synergetic effect of BTA and chloride ion on the passivation layer formed in Cu ECMP using phosphate electrolytes. The composition of the slurry was 1 M potassium phosphate, pure ortho-phosphoric acid, potassium chloride, BTA and de-ionized water. The thickness of the passive film was increased in the presence of chloride ions.

Figure 2.13 shows the AFM images of the copper foils with BTA alone and BTA with chloride ion in the solution. The average thickness of the passive film with BTA alone was 52 ± 7 nm while that of BTA with chloride ion was approximately 104 ± 18 nm, respectively. Thus the passivation capability of the slurry increased when chloride ion was present [40].

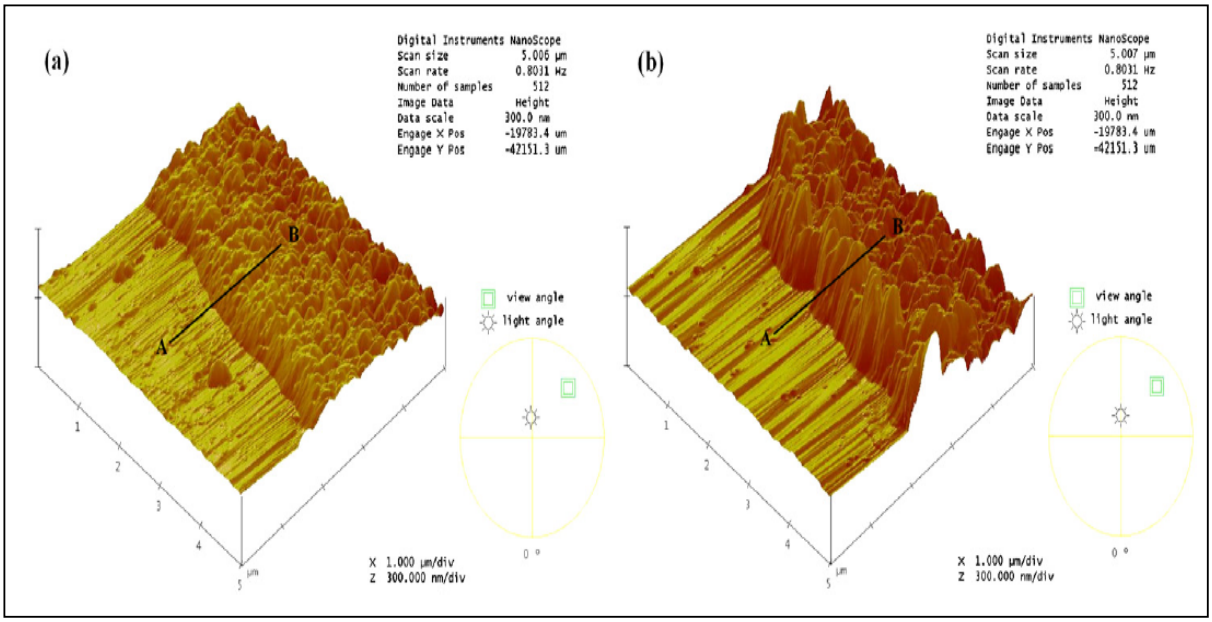


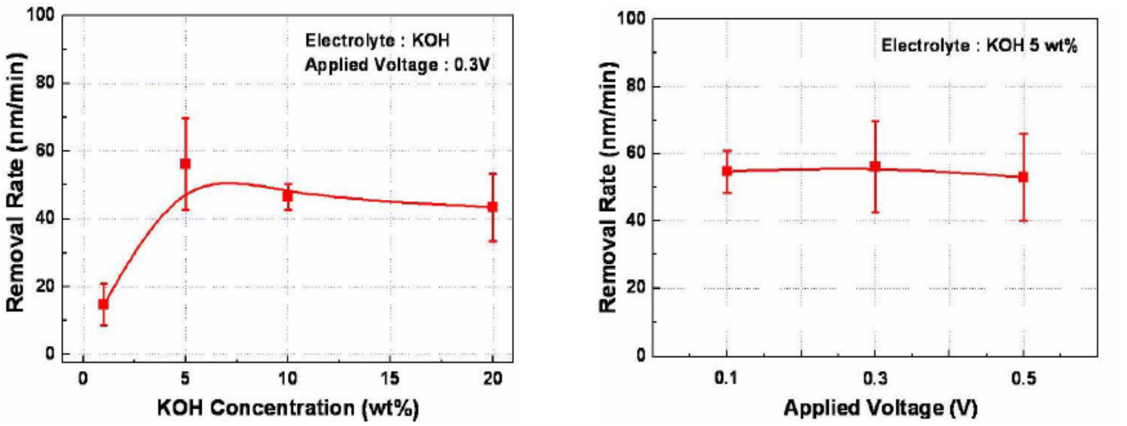
Figure 2.13: Atomic Force Microscopy 3D images of Cu foil in phosphate based electrolytes: (a) solution with 0.01 M BTA (b) solution with 0.01 M BTA and 500 ppm Cl^-, after Lin *et al.* [40]

2.3.5 Potassium hydroxide based Slurry

Kwon *et* al. [41] used KOH^- based electrolytes for Cu ECMP. The electrolyte in the slurry was KOH and H_2O_2 and citric acid were also added. In this study, it was observed that the removal rate increased when 5% by weight KOH, 5% by volume H_2O_2 and 0.3 M citric acid was used. A conventional desktop polisher was modified and used for ECMP of copper. The electrochemical removal rate of Cu wafer and disk were measured. For evaluation of the ECMP system and Cu etch and removal rates, electroplated Cu wafers (1.5 µm thickness) and Cu disk (99% purity in 50 mm diameter) were used. To remove organic contaminations and oxides on the Cu surfaces, acetone, isopropyl alcohol and dilute HF (DHF, 0.5%) were used.

Electrolytes at different concentrations from 1 to 20 wt% were prepared using potassium hydroxide (85% by weight). The etching and polishing behaviors were evaluated by adding an oxidant, hydrogen peroxide. Citric acid was used as the complexing agent. Cu samples were investigated as a function of KOH, H_2O_2 and citric acid concentrations. Surface planarity was achieved at a down pressure of 1 psi and 30 rpm head and platen speeds for a polishing time of 1 min [41].

The material removal rate of Cu during ECMP process was studied as a function of KOH concentration and applied voltage as shown in Figure 2.14 (a). The copper removal rate was saturated at 60 nm/min when the concentration of the KOH electrolyte was 5 wt% in the slurry. Figure 2.14 (b) shows the removal rate of copper as a function of applied voltage from a removal rate of 60 nm/min. This curve is nearly a constant and is independent of the voltage as it is in passivation region [41].



(a) (b)

Figure 2.14: Material removal rate of copper with respect to (a) concentration of KOH in the slurry and (b) voltage applied, after Kwon *et al.* [41]

The effect of the additives H_2O_2 and citric acid in the KOH electrolyte was also studied. In 0.3 M citric acid concentration, the static etch rate was observed up to 90 nm/

min and the maximum material removal rate was 240 nm/min. When the concentration of citric acid was lower than 0.2 M, a low removal rate of 50 nm/min was recorded. When the citric acid concentration was increased from 0.2 M to 0.3 M, the material removal rate was increased by 5 times at 250 nm/min. This was because the citrates enhance the complexation of the dissolved copper from the copper surface. Figure 2.15 (a) shows the static etch rate and Figure 2.15 (b) shows the material removal rate as a function of citric acid concentration [41].

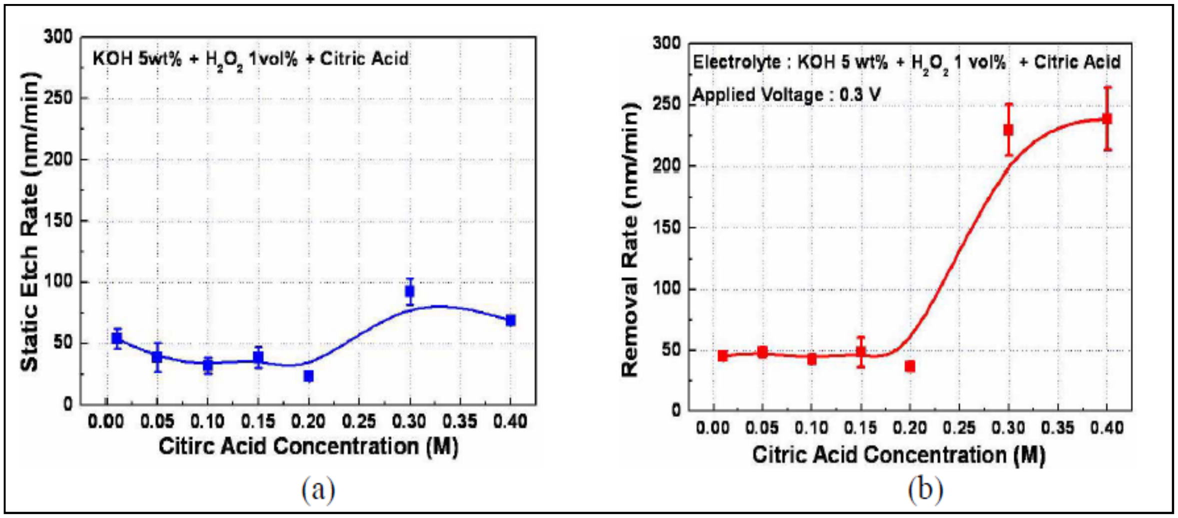


Figure 2.15 (a) Static etch rate and (b) Material removal rate as a function of citric acid concentration, after Kwon *et al.* [41]

The effect of H_2O_2 concentration on the material removal rate and the thickness of copper oxide formed in the slurry was investigated. When the concentration of H_2O_2 was 5% by volume, copper removal rate was highest at 350 nm/min, as shown in the Figure 2.16 (a). Decrease in the removal rates was observed at concentrations higher than 5% by volume. With increase in H_2O_2 concentration, the Cu oxide thickness increased as shown in the Figure 2.16 (b). At 10% by volume H_2O_2 the removal rate decreased due to the formation of a thick and dense Cu oxide which may have prevented the electrochemical reaction to occur [41].

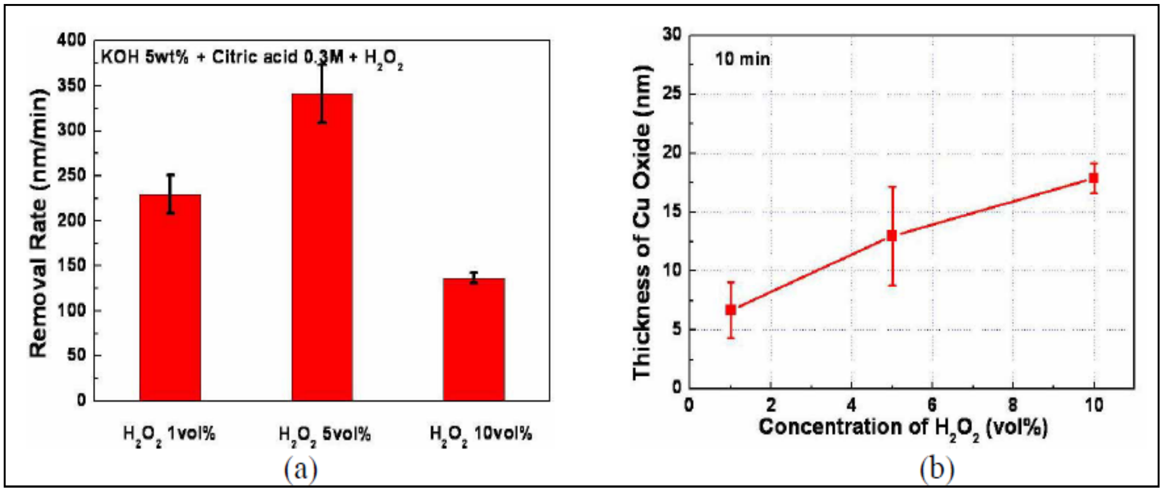


Figure 2.16: (a) Removal rate of Cu and (b) thickness of Cu oxide as a function of H_2O_2 concentration, after Kwon *et al.* [41]

2.3.6 Recycling and Foam removal of ECMP slurry

In ECMP, the cost of consumables is decreased because the slurry can be recycled and is cost effective. Golden *et al.* [42] devised a method for recycling of the ECMP fluids. A recycling unit is developed where the selected portion of the used ECMP fluid is delivered. Here the concentration of the slurry is carefully measured. Depending upon the measurements, individual components of the slurry are added to ensure that the used slurry has the same concentration as before. In some cases, virgin ECMP slurry is also be added to achieve the desired concentration. Then the fluid is delivered from the recycling unit to an ECMP system for further polishing.

Jia *et al.* [43] provided a method to remove foam in an ECMP process. Foam formation can increase the defects in an ECMP system. A foam removal assembly is positioned above the polishing pad using a shaft which is attached to the fluid delivery system. It is placed in such a way that a gap is provided between the foam generated on the metal surface and the bottom edge of the foam removal assembly. It will skim the foam off the surface of the electrolyte without generating any turbulence in the slurry.

Table B in Appendix B gives a list of patents on polishing compositions for ECMP. Most of the slurry compositions are given for electrochemical mechanical polishing of copper. The chemicals used in the slurry are for one application for each patent mentioned in the table.

2.4 Polishing Pad for ECMP

The mechanical aspect of ECMP is the polishing pad. Very low pressures of up to 0.3 psi are applied on the surface of the substrate by the polishing pad. The polishing pad is used to remove the passivation layer formed in the process to provide the substrate a clean smooth finish. The type of polishing pad used is important for ECMP. Harder pads are used for bulk material removal and softer pads are used for fine material removal of the metal surface.

2.4.1 Role of the Polishing Pad

Jeong *et al.* [44] studied the effect of the mechanical aspect of ECMP. They explained the importance of polishing pad for ECMP as it is both a mechanical and electrochemical process. Polymeric pad is used to polish in Cu ECMP. Mechanical integrity and resistance to the slurry chemicals are a necessity for a polishing pad. The pad should also have enough hardness and modulus and should not undergo mechanical abrasion easily. The viscoelasticity of the pad should also be stable during the experiments. In ECMP, the slurry chemistries are very rigorous, which can be highly acidic or highly alkaline. The polishing pad should be able to withstand these conditions. Figure 2.17 shows the schematic of a polishing pad used for Cu ECMP.

Polyurethane pad has stable viscoelastic behavior and is resistant to high chemical attacks in the slurry. It also has high hardness which will enable high material removal rates. Global uniformity is also achieved because it does not wear out easily. Silica abrasives are important in the slurry as they are useful in removing the passivation film formed due to the electrochemical reaction. When the concentration of the abrasives is more than 10% by volume in the total composition of the slurry, effective planarization is achieved. The surface roughness values are also improved [44].

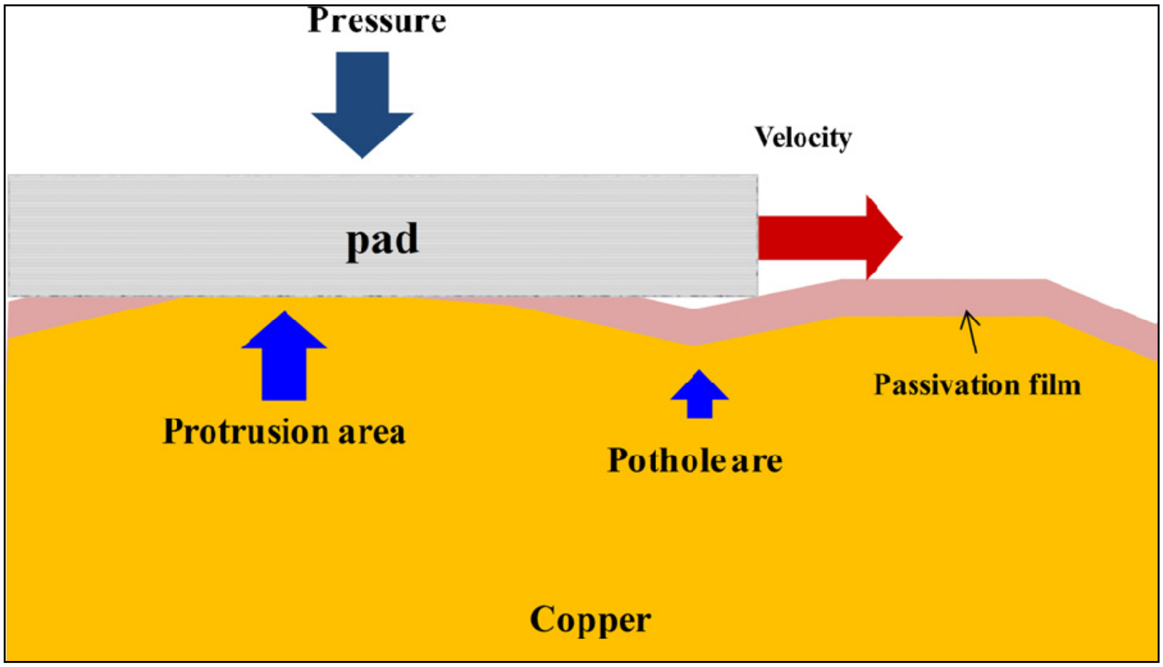


Figure 2.17: Schematic of the polishing pad for Cu ECMP, after Jeong *et al.* [44]

2.4.2 Different types of Polishing Pads

Jeong *et al.* [45] used a polishing pad with holes for ECMP of copper. IC 1400 K-groove pad, a conventional closed type pad with holes was used for the polishing. The slurry is supplied to the surface of the copper through these holes. The pad also removes the passivation layer formed due to electrochemical reactions. Holes are made on the pad so that conductivity is reserved. Wafer overhang distance (WOD) is an important factor as it influences the material removal rate (MRR) and the within wafer non uniformity (WIWNU). Figure 2.18 shows a ECMP system which has a polishing pad with holes in it.

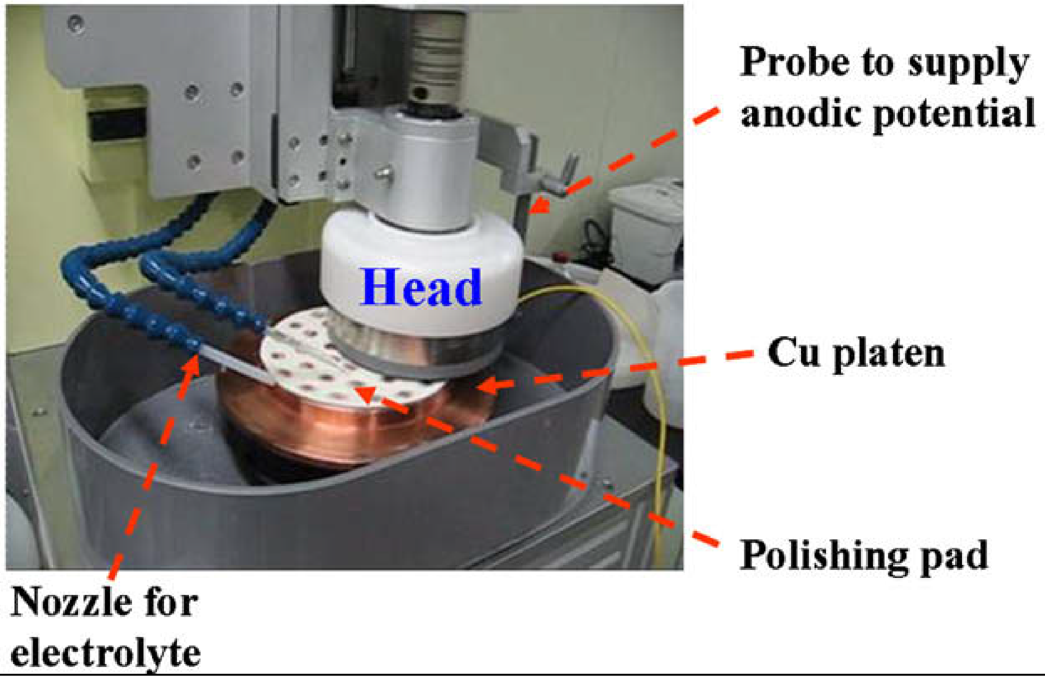


Figure 2.18: Polishing pad with holes for a Cu ECMP system, after Jeong *et al.* [45]

Tominaga *et al.* [46] developed a hybrid ECMP process for copper with a noncontact electrode pad in two steps. In the first step, the bulk copper was polished by applying a constant electric current. Here, ECMP mode was used where the pad was applied at a low down force on the copper wafer. Bulk of the material was removed at a removal rate of 3.5 µm/min till the endpoint was detected. The power supply was turned off and the copper was now polished using the same pad in CMP mode. The dishing on the surface of the copper was reduced by using this hybrid process.

Kondo *et al.* [47] designed a novel carbon polishing pad for ECMP. Its diameter is 16 inches and it can be used in a 300 mm CMP machine. It has 3 layers, the first layer is made of a surface carbon layer, the second is a intermediate insulating layer and the third is a cathode sheet. Several small electro cells were fabricated inside the tri-layered polishing pad. It had a thickness of about 5 mm. The intermediate insulating layer is made of soft carbon material so that it does not damage the copper surface.

The insulating layer behaves like a cushion layer and improves the within wafer non-uniformity (WIWNU). At the edge of the pad, power supply was given both to that cathode and anode. The carbon pad can be used to modify a CMP apparatus into an ECMP by sticking it to the CMP platen by an adhesive. It can also be removed easily so that it does not affect the CMP system [47]. Table C in Appendix C gives a list of patents on polishing pads for ECMP.

CHAPTER III

PROBLEM STATEMENT

Electrochemical mechanical polishing is a relatively new process employed for planarization of low-k dielectric films. Copper is widely used for metallization in these films. Electrochemical mechanical polishing is excellent for bulk copper planarization because it has higher material removal rates and better planarization efficiency at low down force. Surface defects, such as dishing, erosion, and delamination are reduced in this process. Different methods and systems are currently being developed for ECMP. These systems have different ways of providing electric charge to the anode and the cathode. The objectives of this study are as follows:

1. Fabricate and test a face-up electrochemical mechanical polishing (ECMP) apparatus to polish a 4 inch copper wafer. To build the apparatus with a planetary motion where both the polishing pad and the wafer carrier rotate relative to each other. To investigate a method to positively charge the copper wafer while it is rotating inside the wafer carrier.

2. To identify the optimal conditions in the process that will achieve a mirror-like finish on the surface of the copper wafer without any defects, such as scratches, pits and marks left by oxidation.
3. To investigate different slurry compositions for polishing copper wafers that will produce a good surface finish. To identify the necessary components in the slurry that will form a passivation layer and prevent the surface from damage due to corrosion from the electrochemical reactions.
4. To study the effect of process parameters, such as slurry pH, polishing time, voltage applied, and pad and wafer carrier speeds on the material removal rate and surface roughness.
5. To study surface characterization of copper wafers using optical microscope and MicroXAM, a laser interference surface mapping microscope.

CHAPTER IV

FABRICATION OF THE ECMP APPARATUS

This chapter gives a description of the method and fabrication of the ECMP apparatus. Initially ECMP apparatus without planetary motion, where only the polishing pad rotates over the copper wafer, was used. This apparatus did not give the desired results. So, an ECMP apparatus with planetary motion (where both the polishing pad and the wafer carrier rotate with respect to each other) was built. Pro/E CAD software was used to develop this apparatus. The processing and the materials used to manufacture the apparatus are given in detail in this chapter. Finally, the experimental set-up used to polish 4 inch copper wafers is also shown.

4.1 Initial Face-up ECMP Apparatus without the Planetary Motion:

An already existing face-up CMP apparatus was modified to build an ECMP apparatus. The copper wafer placed in the wafer carrier rotates relative to the polishing pad in the CMP process. But for ECMP, the wafer had to be positively charged using an anode so that electrochemical reactions also take place. So, a wafer carrier which has an aluminum tank where the wafer is placed was given a positive charge by an alligator clip as shown in the Figure 4.1. The aluminum tank thus was positively charged and the wafer which was placed in it also becomes positively charged.

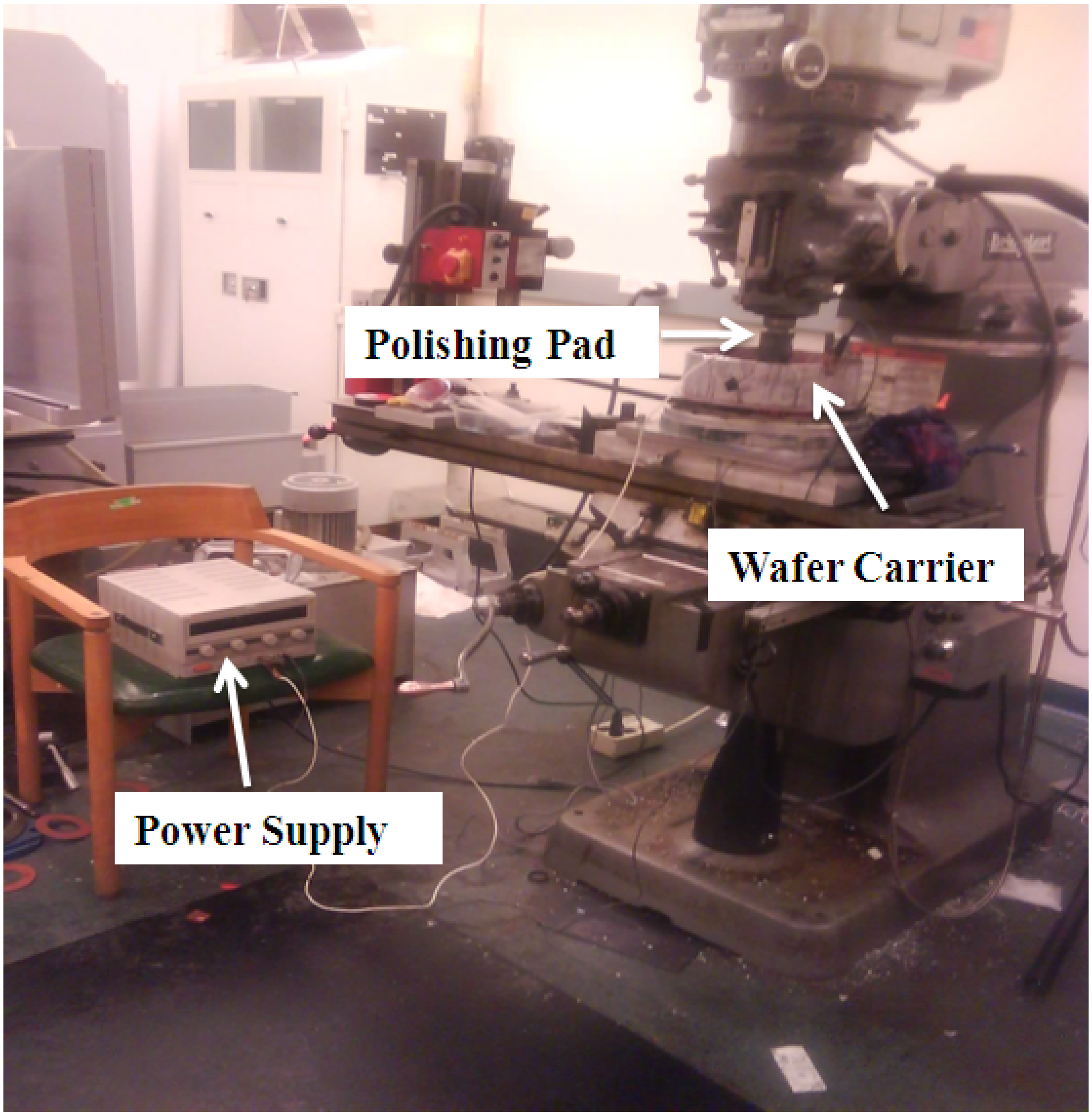


Figure 4.1: Face-up ECMP apparatus without planetary motion

Negative charge was given to a small copper piece which acted as a cathode and was inserted in the slurry. It can be seen from the figure, two different wires were used to give the positive and negative charge, so the wafer carrier could not be rotated as the wires will get entangled. Therefore, only the polishing pad rotated above the wafer carrier. Copper wafers of 4 inch diameter were polished in this apparatus. During the experiments, a reddish color appeared in the slurry because the aluminum tank which was positively charged began to undergo electrochemical reactions. This was possibly because of the acidic nature of the slurry which will be explained in Chapter 5. So, a plastic or a corrosion resistant wafer carrier was required for face-up electrochemical mechanical polishing.

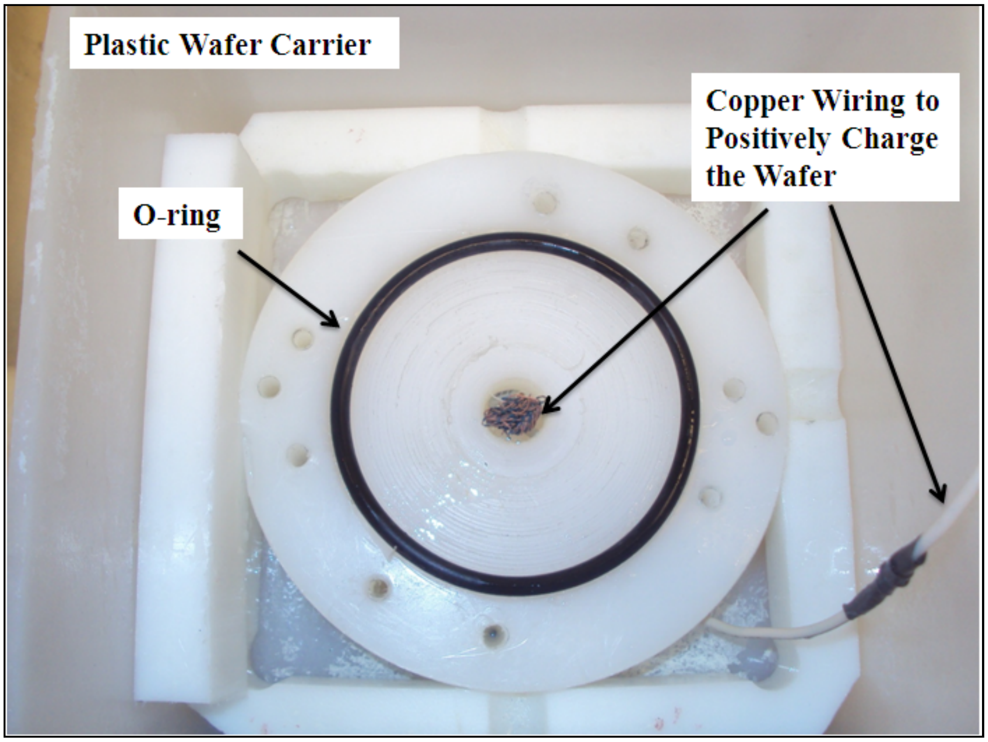


Figure 4.2: A plastic wafer carrier with copper wiring to give positive charge to the wafer

Since a metal wafer carrier proved to be disadvantageous, high density polyethylene (HDPE) plastic was used to make the wafer carrier. In this apparatus, the copper wafer was submerged in the slurry inside the wafer carrier. A slot was made in the side of the wafer carrier through which copper wires were inserted so that they come out of the center as shown in the Figure 4.2. These copper wires acted as the anode. An O-ring was used to tightly retain the copper wafer in the carrier. A wafer holder was made such that the inner diameter exposed the copper wafer which was to be polished. This arrangement is shown in Figure 4.3.

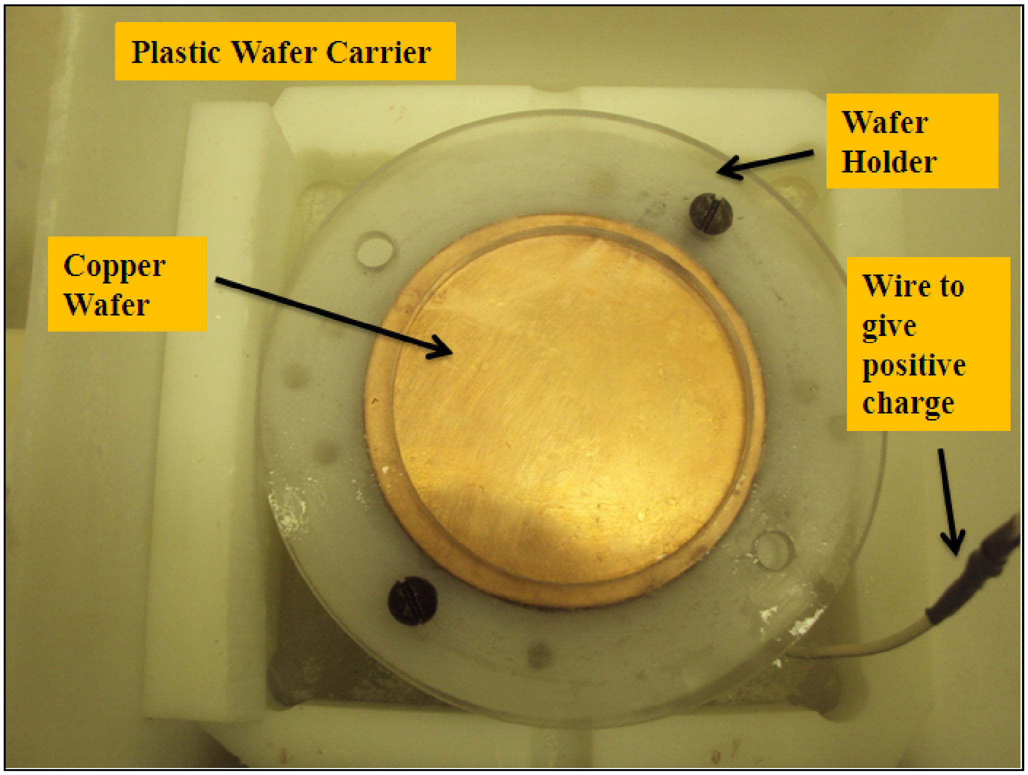


Figure 4.3: Wafer holder to retain the copper wafer before polishing

A mini milling machine was used to give the rotation to the polishing pad. Polishing pad was adhered to a plastic pad holder. A thin copper square rod was inserted in the wafer carrier and was negatively charged, which acted as a cathode. The slurry was filled up to two thirds of the carrier. Power supply was used to give the positive charge to the wafer and the negative charge to the cathode. The apparatus is shown in Figure 4.4.

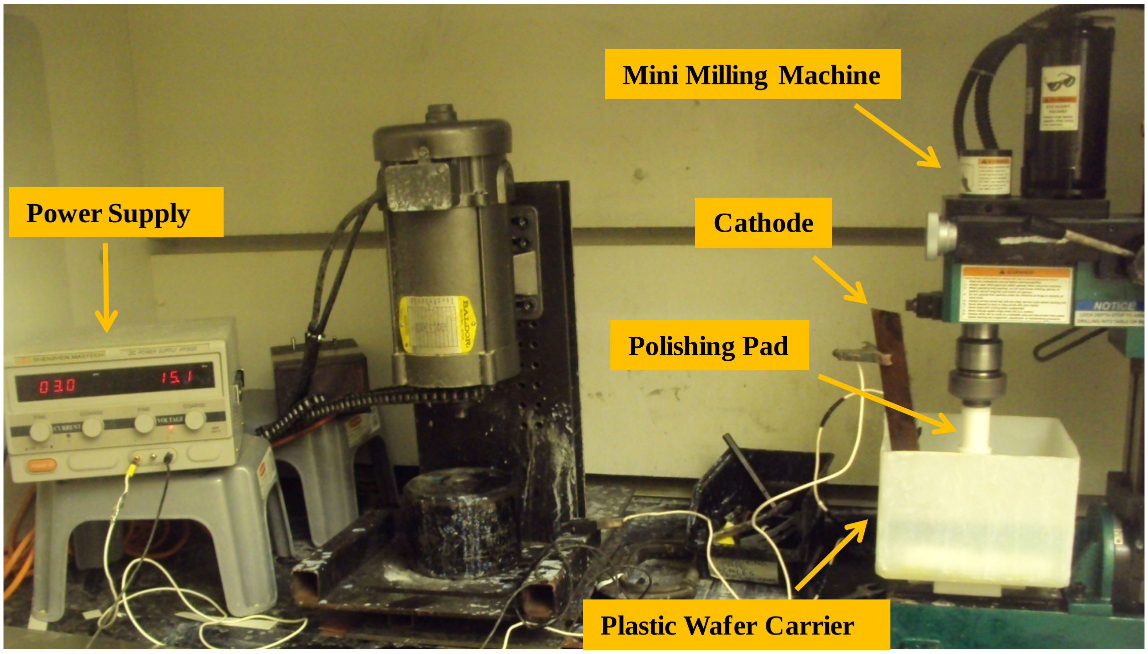


Figure 4.4: Submerged face-up ECMP without planetary motion

Experiments were conducted on copper wafers with H_3PO_4−based slurry. The copper wafer had some scratches and concentric rings formed on the surface because of the polishing pad. The entire copper surface was not being polished because the wafer holder had to press the copper wafer on the edges so that it has contact with the copper wiring. Some pits were also observed because the slurry flow was not uniform on the copper surface. Thus there was a need to rotate the wafer carrier as well as the polishing pad, so that there is a planetary motion.

4.2 Face-up ECMP Apparatus with Planetary Motion:

As discussed in the literature review, several methods have been used to provide charge to the rotating pad or the rotating wafer. Some of them used magnetic slip rings while others used vacuum based systems to hold the wafer in the wafer carrier which was connected to the anode. In this investigation, we develop a new method to build a face-up

ECMP apparatus. In order to give planetary motion, a completely new apparatus was designed and built where a ball bearing was used to transmit positive charge to the rotating copper wafer.

4.2.1 Wafer Carrier Assembly:

The wafer carrier assembly of the apparatus was developed using Pro/E Wildfire 4.0, parametric integrated 3D CAD software. Individual parts were designed separately and later were assembled to complete the design of the apparatus.

The base of the wafer carrier has a length of 11 inch, width of 8 inch, and thickness of 1 inch. A groove of 1 inch is made on the base for the alligator clip to be connected to the bearing holder in order to pass current to the bearing. Four holes are made on the base so that it can be fastened to the bearing holder using bolts and nuts. The holes are of 0.25 inch in diameter. Each of the two holes is separated by a distance of 3.5 inch. Figure 4.5 (a) shows a close up view of the base of the carrier with a groove.

The bearing holder also has four holes aligned to the holes on the base of the apparatus. The diameter of the bearing holder is 7 inch and its thickness is 1.1 inch. A 2.5 inch diameter hole is made in the center. This hole is further increased to a diameter of 3.5 inch from the top surface to a thickness of 0.4 inch within the bearing holder. This is done so that there is a seat like arrangement for the ball bearing in the bearing holder. The specifications of a commercially available ball bearing were used to design the ball bearing. Figure 4.5 (b) and (c) show the bearing holder and the ball bearings respectively.

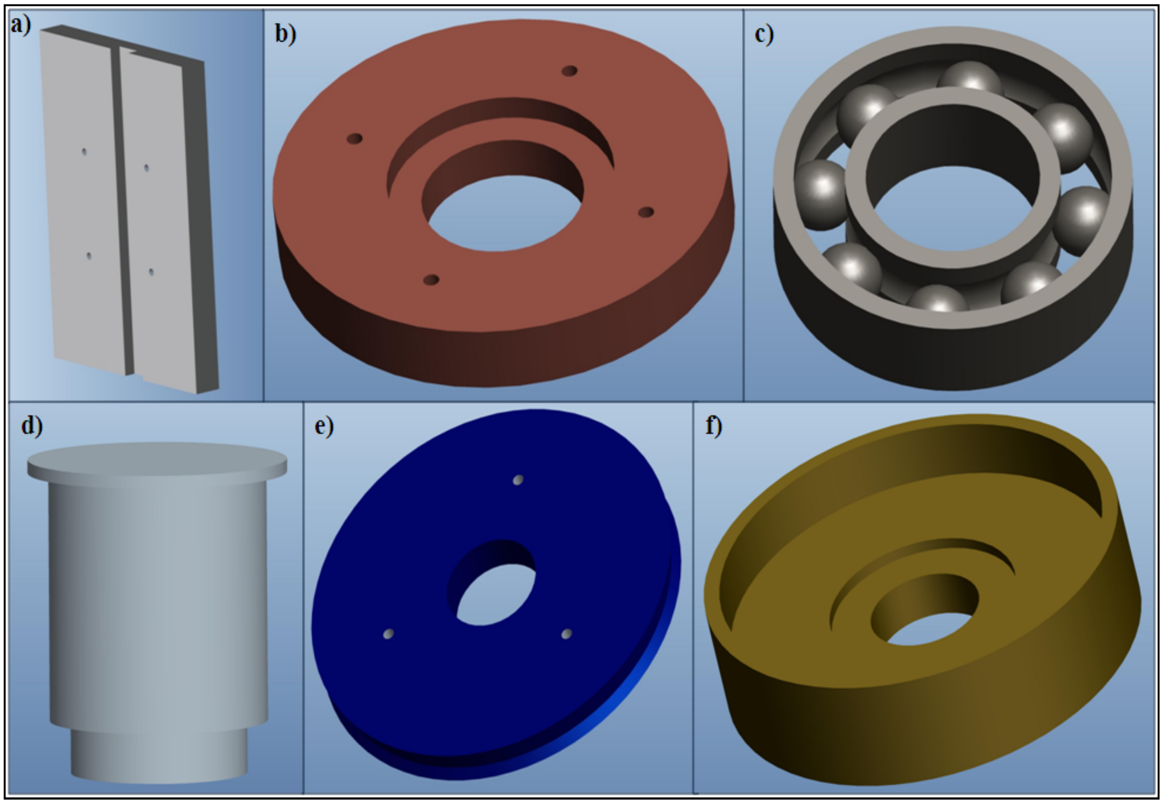


Figure 4.5: CAD models of different individual parts (a) Base of the carrier (b) Bearing holder (c) Ball bearing (d) Anode shaft (e) V-belt pulley and (f) Wafer carrier

A metallic shaft is designed such that it is fitted securely in the bearing so that current passes though it while it is still rotating. This shaft acts as the anode of the apparatus and it has three different segments. The middle segment is 2.375 inch long and a 2.1 inch diameter. The wafer carrier and the pulley attached to it are fitted to this segment. The bottom segment of the shaft is 0.5 inch long and has the same diameter as that of the inner diameter of the bearing. This is because it has to be fixed firmly inside the bearing. The top segment of the shaft is 0.125 inch thick and has a diameter of 2.45 inch. It appears like a thin head and it is disposed in the base of the wafer carrier in the middle so that it is in contact with the copper wafer. In this apparatus, the current carrying anode and the wafer carrier are separate entities because the wafer carrier should be made of plastic so that it does not corrode by the slurry used in ECMP. Figure 4.5 (c) shows the ball bearing which acts as the anode.

A V-Belt pulley is used in the belt transmission for the rotation of the wafer carrier. It has an outer diameter of 8.45 inch and has an X-dimension of 3/4 inch. The bore size is made exactly the same size of the middle portion of the aluminum shaft. The pitch diameter of this belt is 8.2 inch. Three equally spaced holes are made on the base of the pulley so that it is attached to the wafer carrier using bolts. Figure 4.5 (e) shows the V-belt pulley.

The wafer carrier is used to hold the copper wafer during polishing. Figure 4.5 (f) shows the wafer carrier. It can be filled up to two thirds with the slurry such that the wafer is submerged in it. It has an outside diameter of 8 inch and an inside diameter of 7 inch. It has a height of 2 inch and the thickness of its base is about 0.8 inch. Three holes are made on the lower side of the base of the wafer carrier so that they are aligned exactly with the holes on the pulley.

A hole is made in the center of the carrier such that the top portion of the anode shaft is fitted to its base. A circular groove of 4.2 inch diameter and 0.2 inch thickness is made on the base of the carrier for the copper wafer to be placed on top of this shaft. Figure 4.6 shows the assembly of the individual parts to complete the assembly of the ECMP apparatus.

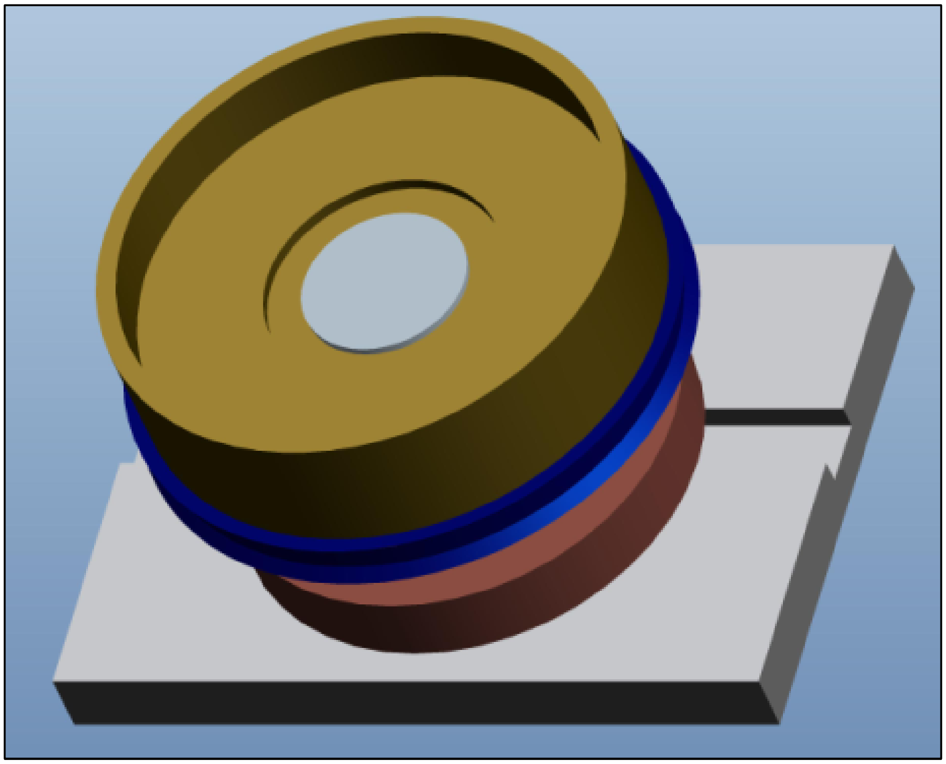


Figure 4.6: Final assembly (CAD model) of the ECMP apparatus showing the anode shaft disposed in the wafer carrier

4.2.2 Machining Process and Materials used:

Conventional lathe and milling machines were used to machine the apparatus. A press fit machine was used to fit the parts of the machine with close interferences. Dial indicators were used to locate the centers of the parts whenever necessary.

High density polyethylene (HDPE) plastic was used to make the base of the apparatus so that the apparatus is insulated from the rest of the experimental set up. A milling machine was used to machine the base of the apparatus. The bearing holder was made of aluminum and was machined using a conventional lathe. Four bolts, nuts, and washers were used to fasten the bearing holder to the base of the apparatus. Commercially available ball bearing (Model no. 3308) was used in this apparatus. The ball bearing was press fitted to the hole made in the bearing holder with an allowance of 0.002 inch using a press fit machine. Figure 4.7 shows the ball bearing fixed to the bearing holder attached to the base of the apparatus.

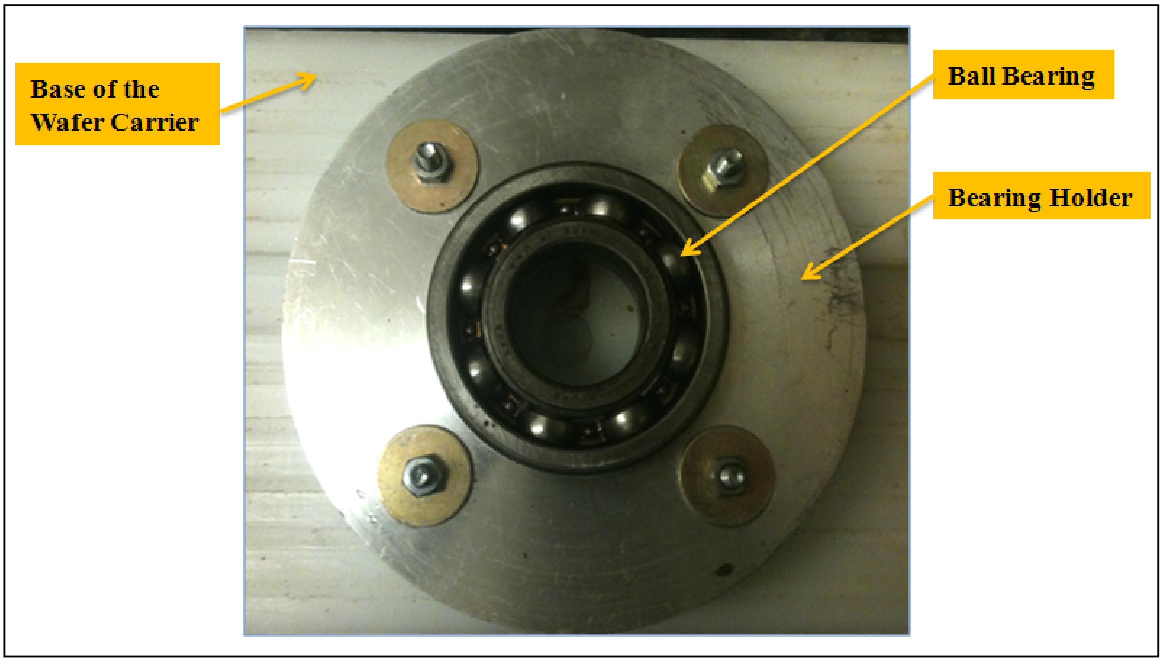


Figure 4.7: Ball bearing arrangement for ECMP apparatus

Polyvinyl chloride (PVC) plastic was used to construct the wafer carrier as it is chemically resistant to the slurry used in ECMP. Conventional lathe was used to machine the shape of the carrier and the vertical milling machine was used to drill the necessary holes. A circular groove was made inside the wafer carrier for the copper wafer to be place in it. A small chamfer was provided so that a retaining ring can be placed to hold the wafer.

Ultra high molecular weight (UHMW) polyethylene was used for the V-belt pulley as it is a very tough material and has very high impact strength. It was machined using a lathe and a milling machine to drill holes. Dial indicators were used to locate the centers for both the wafer carrier and the V-belt pulley.

An aluminum shaft was machined to the desired dimensions using a conventional lathe. The bottom portion of the shaft was machined first to fit the inner diameter of the ball bearing. Next, the top portion of the shaft was made with extreme precaution because of its small thickness. Finally, the middle portion of the shaft was precisely machined to fit both the wafer carrier and the pulley. An interference of 0.007 inch was given so that the shaft would be very securely fixed within the wafer carrier and the pulley. The rotation of the wafer carrier and the top segment of the shaft depended on this particular press fit.

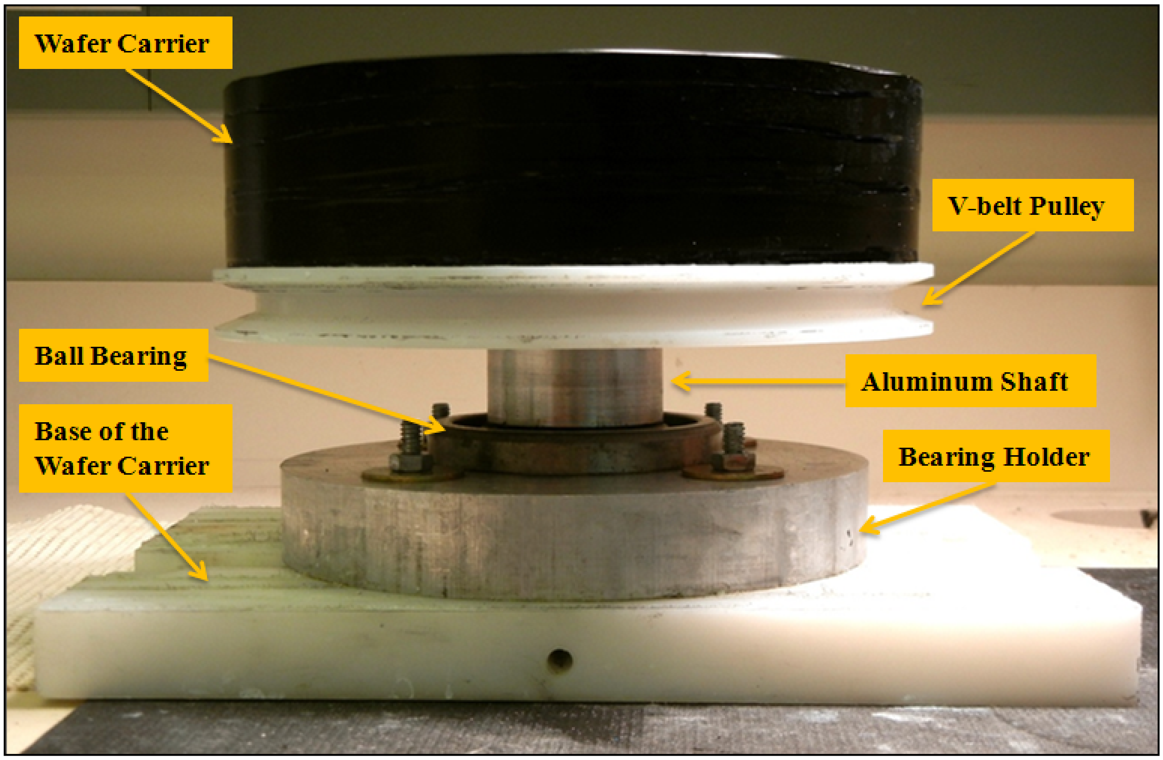


Figure 4.8: ECMP apparatus showing the wafer carrier assembly after machining

Emery sand paper was used to achieve a good finish on the surface. A heavy duty press fit machine was used to push the aluminum shaft through the wafer carrier and the pulley. Water was injected into the wafer carrier to ensure no leakage occurred. Now the bottom portion of the shaft was press fitted to the ball bearing to complete the apparatus. Figure 4.8 shows all the parts of the wafer carrier assembly after machining.

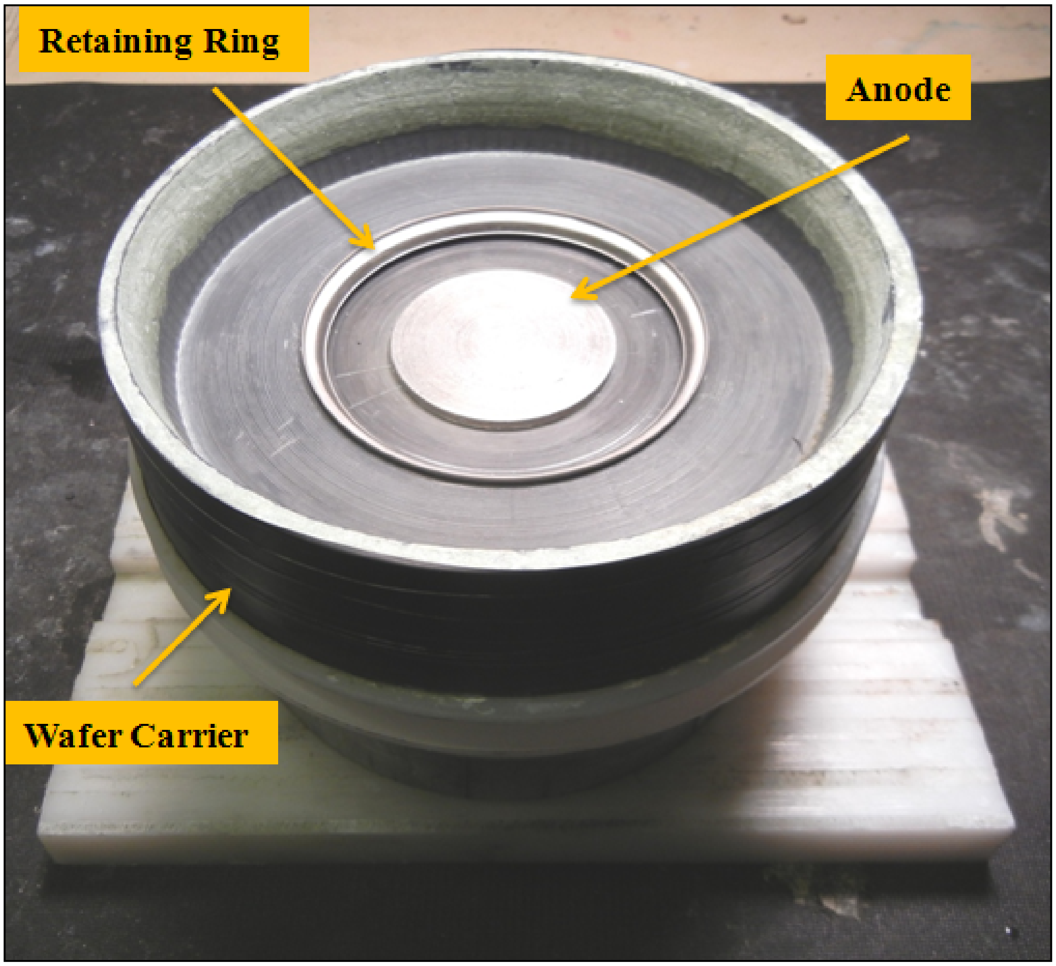


Figure 4.9: Top view of the wafer carrier showing the anode and retaining ring to hold the wafer

A metallic ring was made to retain the copper wafer from falling out during polishing, as shown in Figure 4.9. Copper wafers were placed on this ring and they were positively charged as they had contact with the anode i.e. the head of the aluminum shaft. Pad holders were manufactured to hold different types of pads in the mini milling machines used in the multi-stage polishing. As explained in the literature review, the size of the pad is smaller than the size of the wafer being polished in face up substrate polishing. Different types of plastic materials, such as HDPE and PVC were used to fabricate them so that they are insulated from the current in the apparatus. Figure 4.10 shows four different pad holders of different pad sizes used for electrochemical mechanical polishing.

Figure 4.10: Pad holders for different polishing pad sizes used in the multi-stage ECMP

4.2.3 Experimental Set-up:

A mini vertical milling/drilling machine (Model no. 44991) is used to give rotation to the polishing pad which was positioned above the wafer carrier. The working table was moved with the cross feed handle wheel and the longitudinal feed hand wheel to adjust the position of the wafer carrier with respect to the polishing pad. The pad was offset so that the complete wafer is polished as both of them rotate relative to each other.

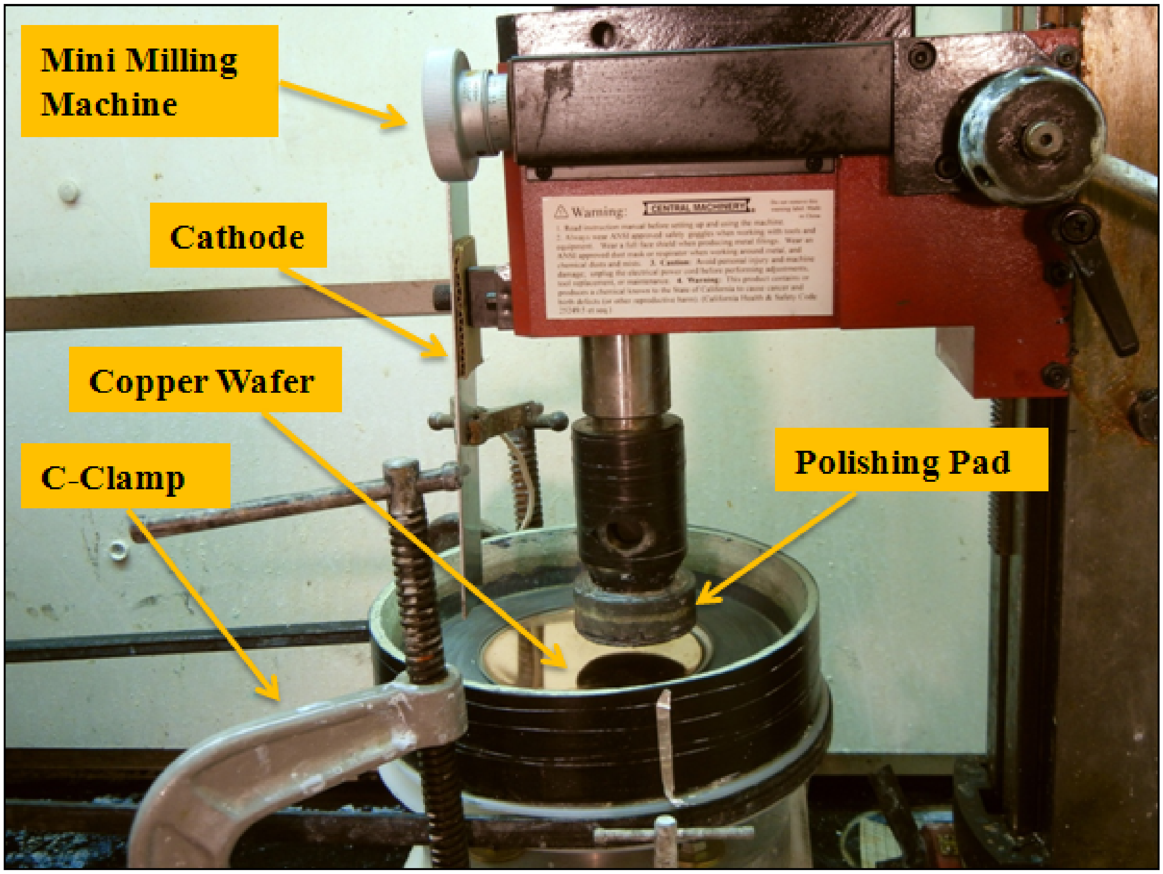


Figure 4.11: Cathode and polishing pad of the ECMP apparatus

The cathode for the apparatus is a thin aluminum bar (9 inch long and 1.5 inch wide and 0.1 inch thick). The dust guard was removed and the clamp bolt was used to fix the cathode to the milling machine. Negative charge is given using an alligator clip. The cathode was electrically insulated from the rest of the apparatus. C Clamps were used to fix the wafer carrier to the working table. Figure 4.11 shows the arrangement of the cathode and the offsetting of the polishing pad for the planetary motion.

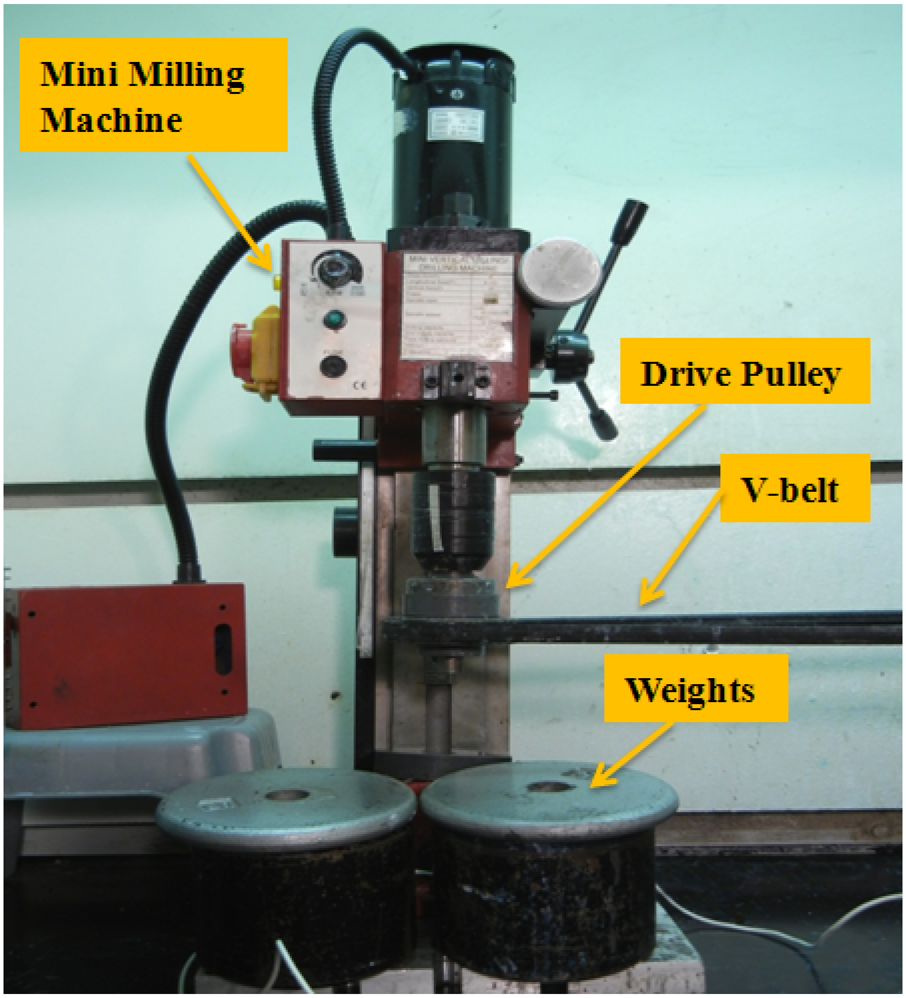


Figure 4.12: Drive pulley for the rotation of the wafer carrier

A second mini milling machine of the same type as the first one is used to provide rotation to the wafer carrier by means of a drive pulley and a V-belt, as shown in Figure 4.12. A V-belt (Model no. A-66) was used and a knob in the milling machine was used to control the speed of the rotation of the carrier. Different weights were used to secure the milling machine to the base. Shenzhen Mastech Power Supply with a digital LED display was used to give the current to the wafer and the cathode. Its specifications are 600 W Power, 30 V Voltage and 20 A Current. Figure 4.13 shows the power supply unit used for ECMP.

Figure 4.13: Digital power supply unit

Figure 4.14 shows the final set-up used for electrochemical mechanical polishing of copper. The polishing pad, wafer carrier assembly, drive system for wafer carrier, cathode and the power supply are shown. Proper care was taken to ensure that the whole system was electrically insulated from the cathode and the anode. A wooden base was used to insulate the first mini milling machine form the positively charged anode in the wafer carrier assembly. The apparatus was placed in a fume hood to exhaust any chemicals formed during the process.

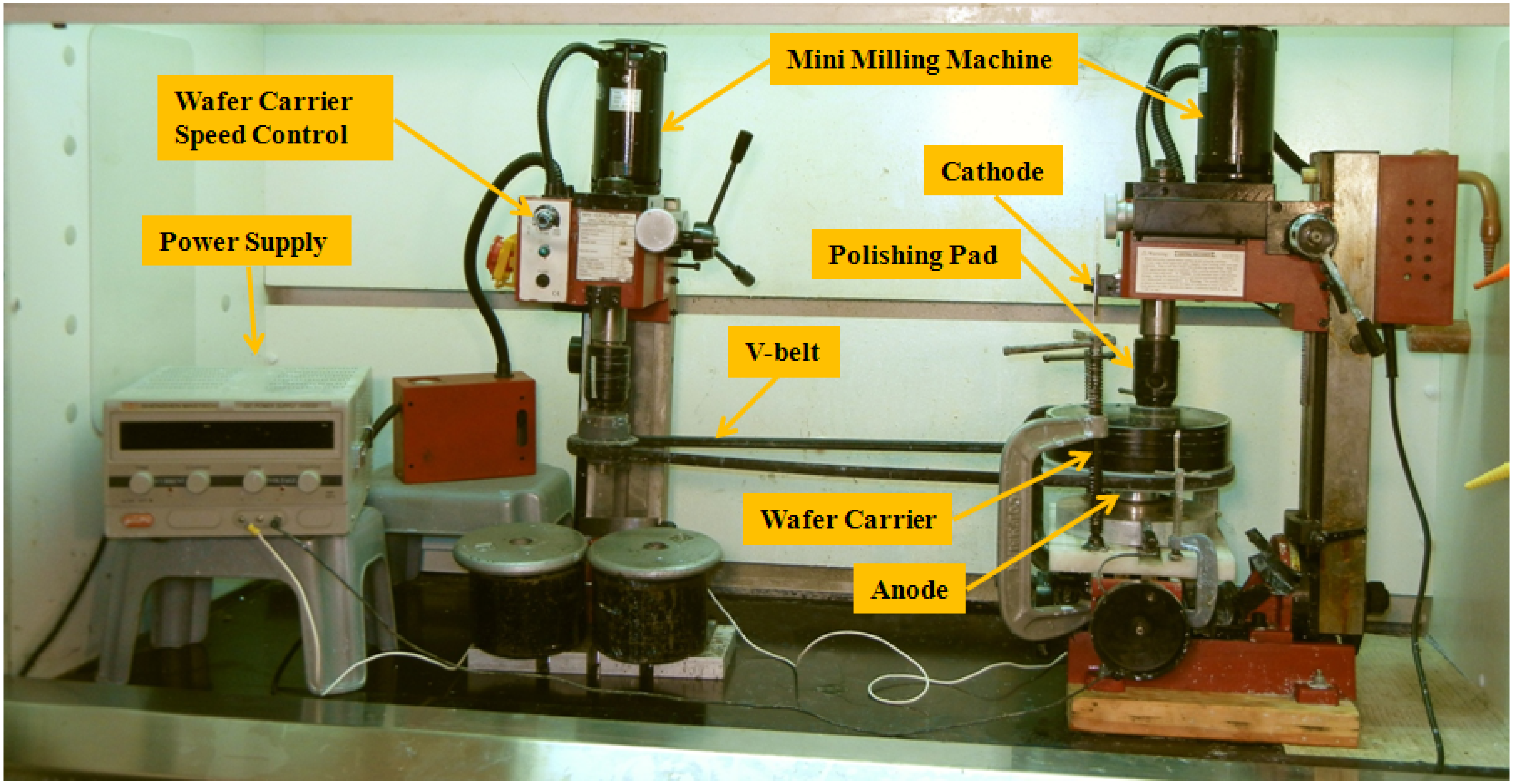


Figure 4.14: ECMP experimental set up for polishing of copper wafers

CHAPTER V

EXPERIMENTAL PROCEDURE

This Chapter provides the methodology and experimental procedure of electrochemical mechanical polishing of copper for semiconductor industry applications. The experimental set up described in the previous chapter is used to polish these wafers. Five slurry compositions were prepared for ECMP of copper. Experiments were performed to observe which slurry composition produced the best surface finish. Multi-stage polishing of the wafers was conducted depending on the initial condition of the wafer. Post polishing treatment is also presented in this chapter. Process parameters were identified and experiments were performed to investigate the optimal conditions which produce the best surface finish. Optical microscope and MicroXAM were used to characterize the surface of the copper wafers.

5.1 Wafer Preparation

Copper wafers of 4 inch (100 mm) diameter and 0.05 inch thick were used in this study. They were initially cleaned with distilled water and acetone to remove coarse particles from the surface. Some of the wafers undergo oxidation in air and bluish/green marks are left on the surface. These marks were removed by fine abrasive paper of grit size 15.3 μm. The abrasive paper was smoothly rubbed with very light pressure so that it does not scratch the surface. Again the wafers were cleaned with distilled water before they were used in the experiments.

5.2 Investigation of Slurry Composition for ECMP

As discussed in the literature, different compositions of slurry for ECMP have been used. The pH of the slurry is in the range of 2 to 10. The purpose of this study was to investigate the slurry composition and pH for Copper ECMP which will achieve the following results:

a. Nanometric surface finish
b. Fewer scratches on the surface
c. Corrosion-free surface
d. Uniform polishing of the complete wafer
e. The slurry should be less pungent and re-usable

Five different slurry compositions were prepared based on the chemicals used previously for Cu ECMP and reported in the literature. Each slurry composition had different chemicals. This was done to study how copper behaved with each of these chemicals. The pH was different for each of the slurry composition in order to study the effect of pH on the surface finish. The pH was tested using a water-proof Oakton 35634-20 pH tester from EUTECH Instruments. Politex pad was used for polishing all the wafers. The wafer carrier speed was 15 rpm and the pad speed was 325 rpm were kept constant for all the experiments.

5.2.1 Sodium Nitrate-based slurry

Composition of this slurry:

1. 1 M Sodium Nitrate ($NaNO_3$)
2. 2% (vol.) Sodium Sulfate (Na_2SO_4)
3. 2% (vol.) Ethylene Glycol ($C_2H_6O_2$)
4. 1% (vol.) Glycerol ($C_3H_8O_3$)
5. Deionized Water

Sodium nitrate was the electrolyte used in the slurry [11]. Sodium sulfate is the inorganic salt used to perform as a chelating agent. Ethylene glycol is the leveling agent for the inhibition of electrochemical reactions to prevent corrosion. Glycerol was the stabilizing agent in the slurry. De-ionized water was the solvent. The pH of the slurry was 6.19 before polishing.

The experiments were conducted at an operating voltage of 10-10.7 V. The current obtained in the process was in the range of 1.7- 2.6 A. The polishing time was 10 minutes. The pH after polishing was observed to be 10.25. The slurry turned form colorless to darkish green. Polish was obtained only in the centre of the wafer. The rest of the wafer was corroded and a brown layer was observed on the surface.

5.2.2 Potassium Phosphate-based slurry:

Composition of this slurry:

1. 1 M Potassium Phosphate (K_3PO_4)
2. 0.01 M Benzotriazole (BTA) ($C_6H_5N_3$)

3. 0.01 M Potassium Chloride (KCl)
4. Ortho-phosphoric was added till the pH became 2
5. 0.15% (wt.) Alumina abrasives (0.05 micron)
6. Deionized water

Potassium phosphate was the electrolyte used in the slurry [39]. BTA was used as the corrosion inhibitor to prevent corrosion which occurred on the surface using the previous slurry. Potassium chloride was added to increase the passivation layer thickness so that electrochemical dissolution will be low [40]. The surface will not be greatly affected as the pad will remove only the passive layer. Phosphoric acid was added in small quantities till the pH became 2.04. Fine alumina abrasive was added in the slurry to get a good finish. Deionized water was used as the solvent.

Experiments were conducted with an operating voltage of 9.7- 10.5 V. The current obtained in the process was 2- 2.5 A. The polishing time was 10 minutes. The pH of the slurry did not change after the polishing process. Some amount of polish was observed on the surface but there were still some areas which were not polished.

5.2.3 Acetic Acid-based Slurry

Composition of this slurry:

1. 1 M Acetic Acid (CH_3COOH)
2. 1% (vol.) Hydrogen Peroxide (H_2O_2)
3. 1mM Benzotriazole (BTA) ($C_6H_5N_3$)
4. 2% Ethylene Glycol ($C_2H_6O_2$)

5. 0.15% (wt) Alumina abrasives (0.05 micron)
6. Ammonium Hydroxide (NH_4OH) was added until the pH was 4.
7. Deionized Water

Acetic acid was the electrolyte used in the slurry [37]. Hydrogen peroxide was the oxidizer which forms the oxides and hydroxides on the copper surface. BTA was the corrosion inhibitor. Ethylene glycol is the leveling agent to slow down the electrochemical reactions. Alumina abrasives are present to improve the surface finish. Ammonium hydroxide was the pH adjusting agent. De-ionized water was the solvent. The initial pH of the slurry was 4.18.

Experiments were conducted with an operating voltage of 9.9-10.6 V. The current obtained in the process was 0.1 to 0.4 A. The polishing time was 10 minutes. The pH in the slurry did not change after polishing. Polishing occurred at few places on the wafer but good finish was not obtained.

5.2.4 Phosphoric Acid-based Slurry

Composition of this slurry:

1. 6% (vol.) Phosphoric Acid (H_3PO_4)
2. 2% (vol.) Ethylene Glycol ($C_2H_6O_2$)
3. 0.3% (wt.) Benzotriazole (BTA) ($C_6H_5N_3$)
4. 4% (vol.) Potassium Hydroxide (KOH)

5. 0.45% (vol.) Hydrogen Peroxide (H_2O_2)
6. 0.15% (wt.) Alumina abrasives (0.05 micron)
7. Deionized Water

Phosphoric acid was the electrolyte used in the slurry [36]. Ethylene glycol is the leveling agent used for the suppression of the dissolution current on the surface of the copper [33]. BTA is the corrosion inhibitor used in the slurry. Potassium hydroxide is the pH adjusting agent. Hydrogen peroxide is the oxidizer in the slurry. Alumina abrasives are used to produce good surface finish. The solvent was de-ionized water. The pH of the slurry before polishing was 6.50.

Experiments were conducted at an operating voltage of 10.1- 10.3 V. The current obtained in the process was 1- 1.4 A. The polishing time was 10 minutes. There was no change in the pH after polishing. Very good polish was obtained everywhere on the wafer. The surface planarization was uniform. The surface roughness was obtained in the range of 12 to 20 nm.

5.2.5 Buehler Alumina-based Slurry

MasterPrep alumina polishing suspension from Buehler was also used to polish copper wafers. The slurry was diluted with de-ionized water in the ratio 1:5. The size of the alumina abrasive in the slurry is 0.05 micron. The experiments were conducted at an operating voltage of 9.2- 9.9 V. The current obtained in the process as 0.1-1 A. The polishing time was 10 minutes. The pH of the slurry before polishing was 9.03 and it did not change after the polishing. As in the case of previous slurry, very good finish was obtained on the surface of the copper wafer.

5.3 Multi-Stage Polishing

Since phosphoric acid based slurry and Buehler alumina based slurry gave good results, these slurries were used to polish the copper wafers. Multi-stage polishing of copper was done in two stages:

5.3.1 Bulk Material Removal Process

Harder pads such as TextMet from Buehler and Suba IV were used in the bulk material removal process. TextMet is a hard perforated non-woven cloth. It is used to remove bulk material and retain flatness and uniformity on the copper surface. The slurry composition was the same as the one used in the phosphoric acid-based slurry. Buehler alumina based slurry was also used sometimes.

The operating voltage was in the range of 10.5- 12.5 V. Higher voltage was applied so that the current obtained in the process was high. Thus high material removal rates were achieved in this stage. The wafers were polished for 5 to 10 minutes in this stage depending upon the initial condition of the copper wafer. Sometimes 15 minutes of polishing was required to remove the oxidation marks left on the wafer since they were exposed to air for a long time.

5.3.2 Fine Material Removal Process

In order to achieve a good surface finish, fine material removal process was performed on the wafers after the bulk material removal process. Softer pads, such as

Politex and ChemoMet were used. MicroCloth from Buehler was also used sometimes. ChemoMet is a soft porous, chemically resistant synthetic cloth form Buehler. It is used to remove smear material on the copper surface left form the bulk material process. The slurry was diluted in the ratio 1:4 using deionized water so as to slow down the electrochemical reactions formed in the process.

The operating voltage was in the range of 8.5- 9.5 V. It was lower compared to the previous step so that the material removal would be low and precise. The wafers were polished for 7 to 10 minutes. Good surface finish was obtained after this step. The surface roughness (Ra) was in the range of 12 to 25 nm. For some wafers which did not achieve a mirror like finish, an additional precise material removal process was performed for additional 7 minutes. Here, the slurry was diluted further in the ratio 1:8. Table 5.1 summarizes the multi-stage polishing in ECMP of copper wafer.

Table 5.1: Multi-Stage Electrochemical Mechanical Polishing of Copper

S. No.	Stage	Pads Used	Voltage Applied (volts)	Slurry Used	Polishing Time (minutes)	Material Removal Rate
1.	Bulk material removal	TextMet, Suba IV	10.5-12.5	Phosphoric acid-based slurry or Buehler alumina-based slurry	5 to 10	High
2.	Fine material removal	ChemoMet, PoliTex, MicroCloth	8.5- 9.5	Same slurry diluted to 1:4 or 1:8 with DIW	7 to 10	Low

5.4 Post Polishing Treatment

The copper wafers were cleaned immediately using de-ionized water after polishing to remove the slurry contents from the surface. Then they were put in an ultrasonic cleaner (Figure 5.1) for 2 to 5 minutes.

Figure 5.1: Ultrasonic cleaner to clean the copper wafers

Then the wafers were washed with acetone followed by methanol to remove some of the abrasive particles and the slurry sticking on the surface. Then they were again rinsed with deionized water and a dryer was used to dry the surface.

5.5 Process Parameters

Different process parameters of the ECMP process were investigated in order to investigate how they can affect the material removal rate and surface finish of the copper wafer. The process parameters, such as polishing time, voltage applied, pad speed and wafer carrier speed were identified for the ECMP process. Various experiments were performed to study the role of each of these parameters while keeping the others constant.

5.5.1 Polishing Time

Polishing time is an important factor that governs the ECMP process. The passivation-brush cycles [11] in the process are very important to produce a good surface finish. Experiments were conducted to examine the surface of the wafers after 2, 5, 7, and 10 minutes. ChemoMet pad and phosphoric acid based slurry was used in the experiments. The pad speed was 325 rpm and the wafer carrier speed was 15 rpm. The voltage applied was between 10- 10.5 V and the current obtained was in the range of 0.5 to 1.9 A. Optical micrographs were taken to observe the changes in the surface of the wafer after each polishing time.

To investigate the material removal rate in the ECMP process with respect to the polishing time, different wafers were polished for 5, 10, and 15 minutes. Suba IV pad and Buehler alumina-based slurry was used for these experiments. The voltage applied was in the range of 8.5 -11.9 V. The pad speed was 250 rpm and the wafer carrier speed was 20 rpm. The initial and final weights of the wafers were measured and material removal rate was calculated in each case. From the qualitative measurements taken after polishing, the polishing time of 10 minutes formed to be optimum. Scratches were observed when the polishing time was increased to 15 minutes.

5.5.2 Applied Voltage

The operating voltage is crucial to the ECMP process as the material removal rate is directly proportional to the voltage applied. Sharan [1] found that the final finish of surface of the copper wafer is affected by the voltage in ECMP. Under static conditions, the ‘cutoff’ voltage was found to be ~3.2 V for the phosphoric acid-based slurry. Based on the cutoff and the maximum voltage that can be applied, three different ranges for voltages were considered:

a. Low range (3.5 V to 4.5 V)
b. Medium range (6.5 V to 7.5 V)
c. High range (9.5 V to 10.5 V)

Experiments were conducted for each voltage range to determine the material removal rate and surface finish. The constant parameters were:

1) Pad used: ChemoMet Pad
2) Polishing time: 10 min
3) Slurry used: Phosphoric acid-based slurry
4) Wafer Carrier Speed: 15 rpm
5) Pad speed: 325 rpm

From post polishing analysis, the voltage applied in the high range produced a good surface finish for the copper wafer.

5.5.3 Pad Speed and Wafer Carrier Speed

Experiments were performed to investigate how the pad speed and wafer carrier speed influences the material removal rate and surface finish of the copper wafers. Here the constant parameters used are:

1. Applied Voltage: 9.5- 10.7 V

2. Polishing Pad: PoliTex Pad
3. Slurry used: Buehler Alumina based-slurry
4. Polishing Time: 10 min

For the wafer carrier and for the polishing pad three different speeds of 15, 20 and 25 rpm and three different speeds of 275, 300 and 325 rpm were chosen. Buehler alumina based-slurry was used in these experiments. This is because it is easier to handle as the slurry may spill out when the wafer carrier speed is high.

5.6 Material Removal Rate

Material removal rate is a crucial output parameter for ECMP. The material removal rate was calculated based on the initial and final weights of the copper wafer for various sets of experiments. The weights were measured in grams. The formula used to calculate the material removal rate (MRR) is:

$$MRR = \frac{Weight_{(initial)} - Weight_{(final)}}{Polishing\ Time}$$

Figure 5.2 shows the Sartorius digital weighing machine (Model 1712 MP8) used to measure the weights of the copper wafer. It has a resolution of 0.1 mg. It is a Dual Range SemiMicro Electronic Analytical Balance with weighing capacity of 160 grams. It was also used to weigh the chemicals used to prepare different slurry compositions for polish of copper wafers in this study.

Figure 5.2: Sartorius digital weighing machine

5.7 Surface Characterization

The surface characterization of the copper wafers was achieved by examining their surface profiles using an optical microscope and MicroXAM, an optical laser interference microscope.

5.7.1 Optical Microscope

A Nikon Epiphot 200 Inverted Optical Microscope was used to study the surface morphology of the copper wafers before and after ECMP. The copper wafers were examined at a 100 × magnification eye-piece to examine the micro structure properties. Different surface irregularities, such as scratches, pits, marks left by incomplete passivation removal, oxidation of the surface were observed under the optical microscope. The images obtained were crucial in identifying the surface characteristics of the polished copper wafer. Figure 5.3 shows the Nikon Epiphot 200 Inverted Optical Microscope used in this study.

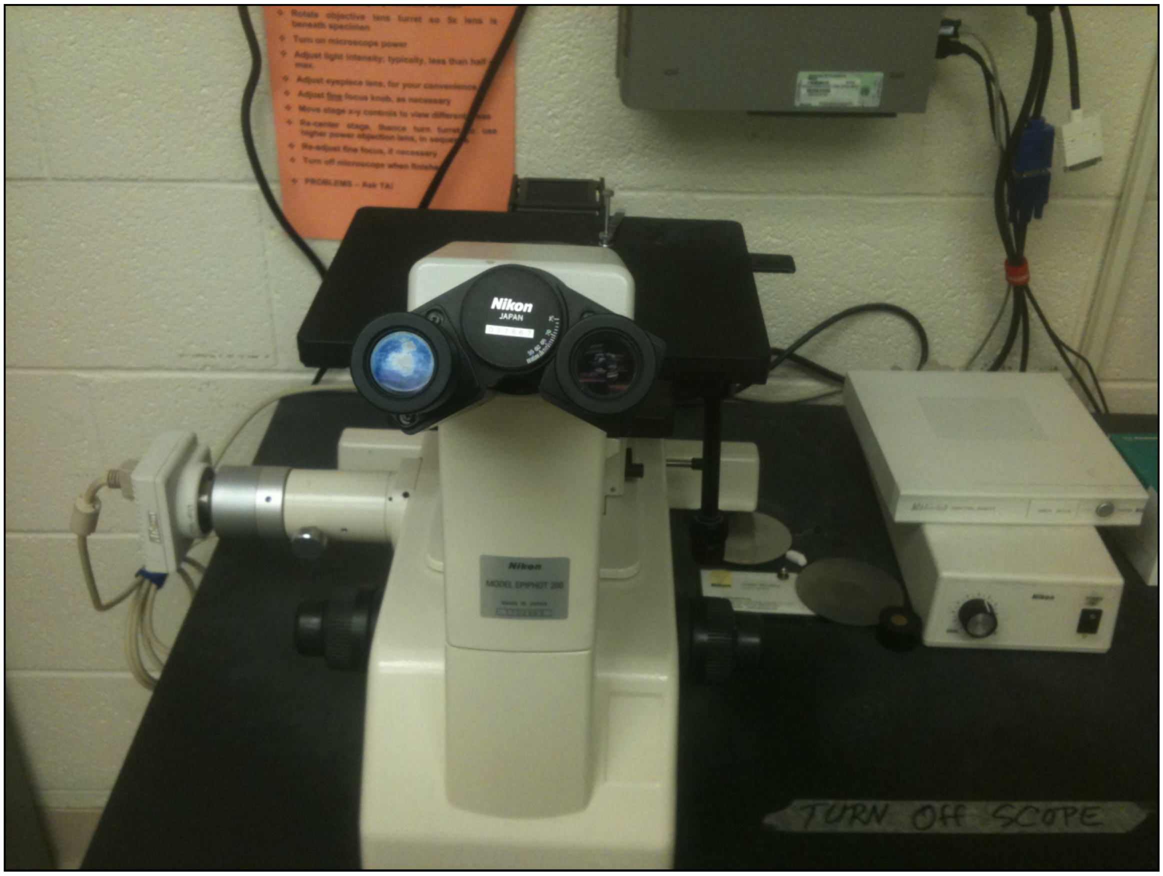


Figure 5.3: Nikon inverted optical microscope

5.7.2 MicroXAM

The surface roughness of the copper wafers was obtained using MicroXAM, an Optical Laser Interference Microscope from ADE Phase Shift Technologies. It is a non contact surface mapping microscope used to measure the finish, texture, and roughness of different surfaces. Resolution of the equipment is 0.1 nm. It is capable of measuring the surface in three different modes, namely, quantitative, visual, and confocal modes. MapVue mapping and analysis software is used to obtain the surface information. In this study it was used to plot 3-D images of the copper wafer to obtain the surface roughness value (Ra). Figure 5.4 shows the MicroXAM used in this study.

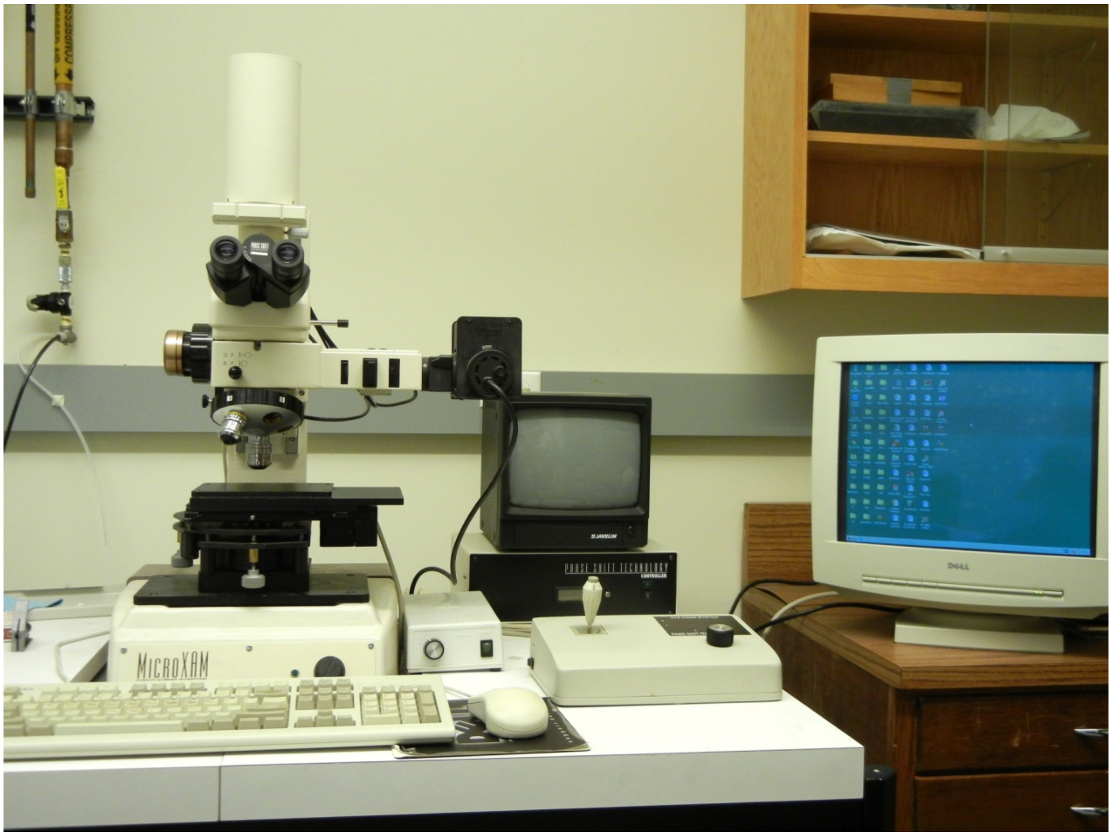


Figure 5.4: MicroXAM, optical laser interference Microscope (from ADE Phase Shift Technologies)

CHAPTER VI

RESULTS AND DISCUSSION

This chapter presents the results obtained in the experiments followed by discussions of the same. The effect of slurry composition on the material removal rate and the surface roughness is presented. The effect of slurry pH is also discussed. Other parameters which govern the ECMP process, namely, polishing time, voltage applied, pad speed and wafer carrier speed are studied as a function of material removal rate and surface roughness. Optical micrographs and 3-D surface plots are shown for each parametric study. Optimal values for each process parameter are given so as to improve the final surface condition of copper wafers.

6.1 Effect of Slurry Composition and pH

Table 6.1 summarizes the different slurry compositions investigated for Cu ECMP as presented in chapter 5. The first composition was made using sodium nitrate as the electrolyte. Sodium nitrate is an excellent electrolyte in an electrochemical cell. High values of current can be obtained using this slurry.

Table 6.1: Slurry compositions for Copper ECMP

S. No.	Composition of the Slurry	Remarks
1.	• 1 M Sodium nitrate • 2% (vol.) Sodium sulfate • 2% Ethylene glycol • 1% Glycerol • DIW	• pH value was increased (6 to 10) • Current was between 1.7 to 2.6 A • Abrasive less slurry • Corrosion occurred on the surface since there was no corrosion inhibitor such as BTA
2.	• 1 M Potassium phosphate • 0.01 M BTA • 0.01 M Potassium chloride • Ortho-phosphoric acid • 0.15% (wt) Alumina abrasives (0.05 micron) • DIW	• pH of the slurry 2 • High current up to 2.5 A • Passivation layer formed very fast • There was no leveling agent in the slurry • Some amount of polish was observed on the surface but there were still some areas which were not polished.
3.	• 1 M Acetic acid • 1% Hydrogen peroxide • 1mM BTA • 2% Ethylene glycol • 0.15% (wt) Alumina abrasive (0.05 micron) • Ammonium hydroxide • DIW	• pH of the slurry 4 • Current was low up to 0.4 A • Very pungent smell • Polish was achieved but mirror like finish was not observed on the surface

S. No.	Composition of the Slurry	Remarks
4.	• 6% (vol) Phosphoric acid • 2% (vol) Ethylene glycol • 0.3% (wt) BTA • 4% (vol) Potassium hydroxide • 0.45% (vol) Hydrogen peroxide • 0.15% (wt) Alumina abrasives (0.05 micron) • DIW	• pH of the slurry 6.5 • Current was up to 1.4 A which is good • Very good polish was obtained. (Glossy) • Mirror-like surface was achieved • Surface Planarization was uniform
5.	• Buehler MasterPrep alumina polishing suspension (0.05 μm)	• pH of the slurry 9 • Very good polish was obtained

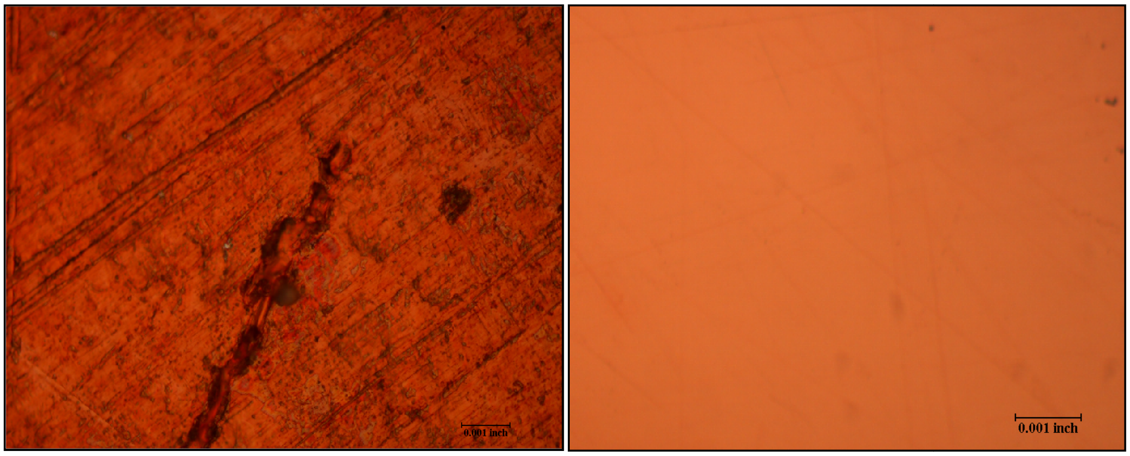
Glycerol was expected to stabilize the reaction but it was not able to inhibit the electrochemical reactions in the process. The copper surface began to peel away as there was no corrosion inhibitor in the slurry. The passivation layer formed was very weak so the surface beneath the layer was not protected. The copper wafer had a corroded surface and the polish was observed only in the center. Thus, corrosion inhibitors, such as BTA are very important in ECMP slurry.

There were no abrasives in the slurry which are important to produce a good finish. The slurry initially did not have any color but after polishing it turned into dark green color. This is due to the formation of copper oxide. The pH was 6.19 before polishing, but after the polishing it was 10.25. This indicates that the slurry changed from slightly acidic to highly basic. So, the change could be attributed to the basic salts/oxides that were formed in the slurry.

The next composition had a phosphate-based electrolyte which has been used for Cu ECMP by previous researchers [39]. BTA was used in this slurry to avoid the electrochemical corrosion which had occurred using the previous slurry. Potassium chloride was added to enhance the thickness of the passivation layer. Alumina abrasive in small quantities is added to produce good finish. The slurry was highly acidic with a pH of 2. The passivation layer formed very fast with this slurry. The current in the process was very high. The slurry pH did not change much and the slurry turned into light green color. The polish was observed on some parts of the wafer but the whole wafer was not polished, especially at the edges. Even though BTA was present, effective passivation of the wafer did not occur. This could also be due to absence of a leveling agent, like ethylene glycol. Also there was no oxidizer in the slurry which was necessary to enhance the passive layer by forming the required oxides. The pH of this slurry was very acidic which might be the reason why the surface was not so smooth. For the next slurry, the pH was reduced to 4 to see if the copper wafer was getting better polished.

Acetic acid is a very good complexing agent and has high planarization efficiency [37]. So, it was used as the electrolyte for the next composition. For this slurry, both BTA and ethylene glycol were added to enhance the passivation layer formation. Abrasives were also added to get the desired smooth finish. The pH of the slurry was maintained at 4 using ammonium hydroxide. The pH did not change after the polishing. Polishing was achieved on the surface, but mirror-like finish was not obtained. The surface was not uniformly polished. Thus slurry at pH 4 also did not give a good polish.

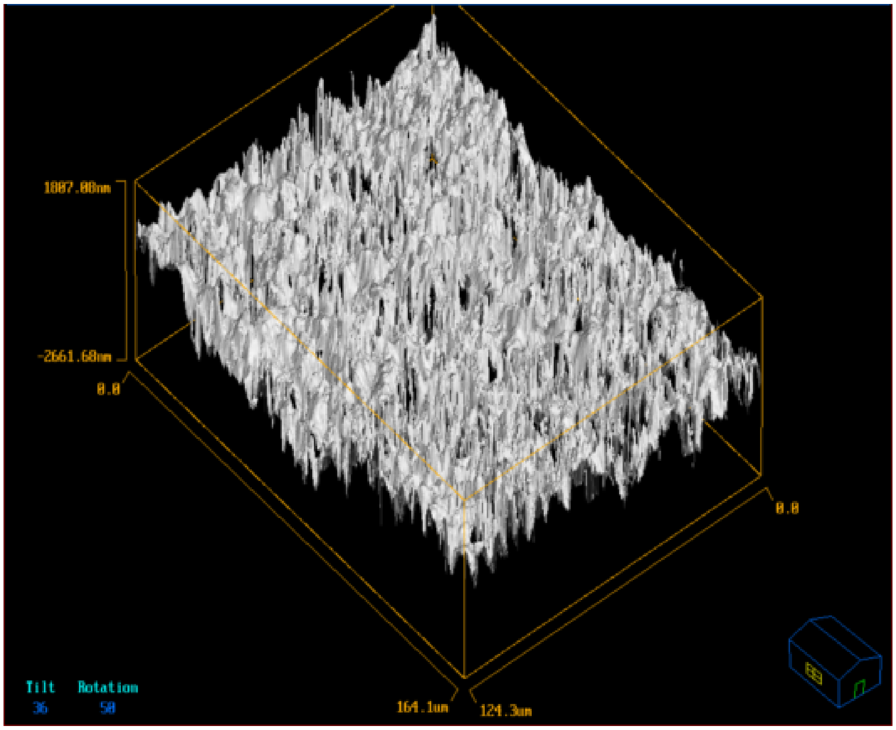
Phosphoric acid was used next as the electrolyte. BTA, ethylene glycol and abrasives were added to obtain a good surface finish. Potassium hydroxide was used to maintain the slurry at pH 6 and hydrogen peroxide was the oxidizer used. The pH did not change after polishing. Very good polish was obtained giving a glossy finish. The surface had a mirror like finish and was almost scratch-free. Experiments were repeated to confirm if the slurry was able to produce the same results. Thus, ECMP slurry should have a corrosion inhibitor, leveling agent, abrasives, oxidizer, and pH adjusting agent apart from the acid-based electrolyte.



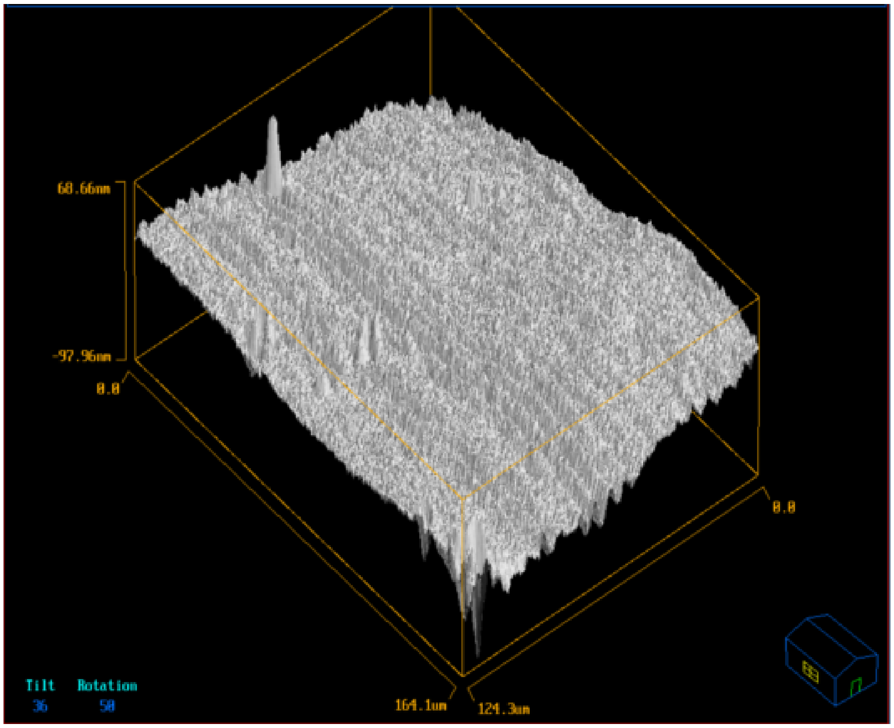
(a) (b)

Figure 6.1: Microstructure of the copper wafer (a) before polishing (b) after polishing with phosphoric acid-based slurry

Figure 6.1 (a) shows the initial condition of the copper wafer before polishing. Several scratch marks and deep pits are clearly visible. Figure 6.1 (b) shows the wafer after polishing using phosphoric acid-based slurry for 10 minutes. Most of the scratch marks were eliminated with hardly any pits on the surface. Uniform polishing of the surface was achieved. The surface was smooth with a glossy finish. The material removal rate was the lowest (namely, 0.0018 grams/min) when compared to all other compositions of slurries. The passivation layer formed was able to protect the surface of the wafer from electrochemical reactions. The anodic dissolution of the surface was low.



(a) Start of polishing, Ra = 364.53 nm

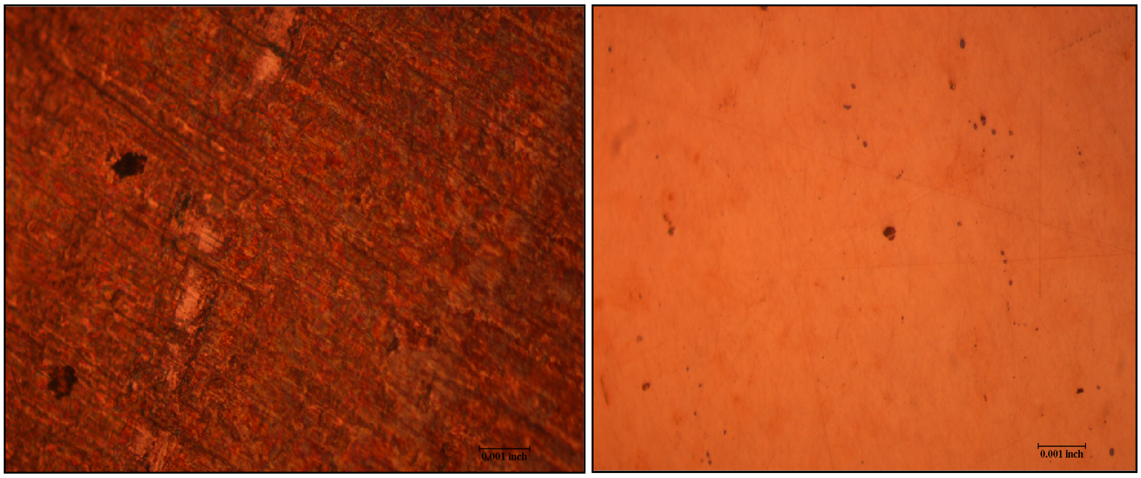


(b) After polishing with phosphoric acid-based slurry, Ra = 12.05 nm

Figure 6.2: MicroXAM images of the 3-D surface plot of the Copper wafer before polishing and after polishing with phosphoric acid-based slurry

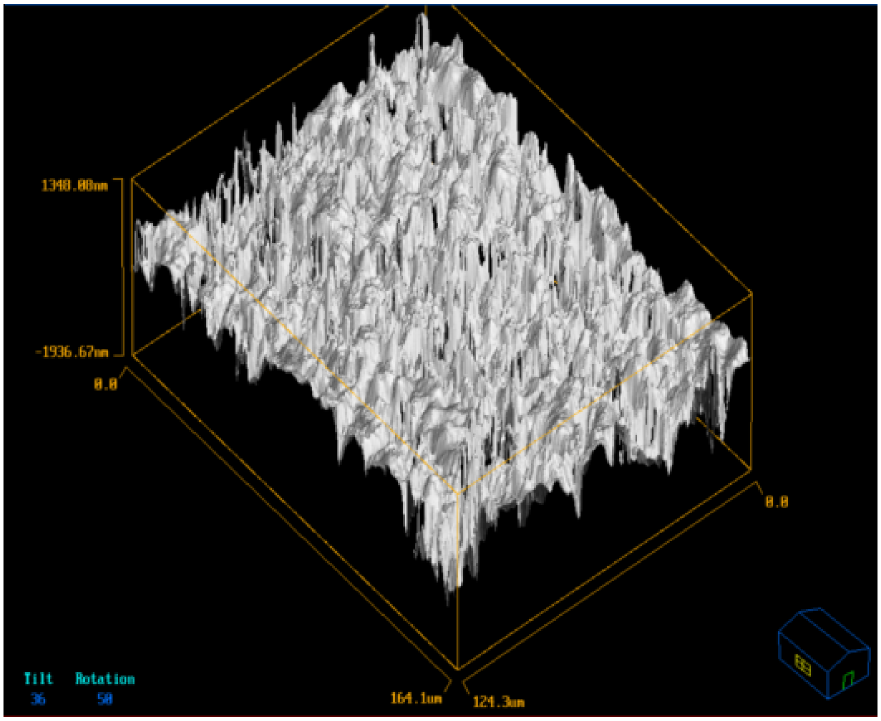
When the polishing pad came in contact with the surface, it removed the passive layer. There were many passivation-brush cycles with the pad which ultimately gave good finish. Figure 6.2 shows the 3-D surface plot of the copper obtained from MicroXAM before and after polishing. The surface roughness (Ra) at the start of polishing was 364.53 nm and after 10 minutes of polishing with phosphoric acid based slurry it was 12.05 nm.

MasterPrep alumina polishing suspension from Buehler was also used to polish copper wafers. The slurry was diluted in the ratio 1:5 with de-ionized water. Very good polish was obtained using this slurry. It is basic slurry with a pH of 9. The slurry did not change after polishing and the alumina abrasives in the slurry produced a smooth finish.

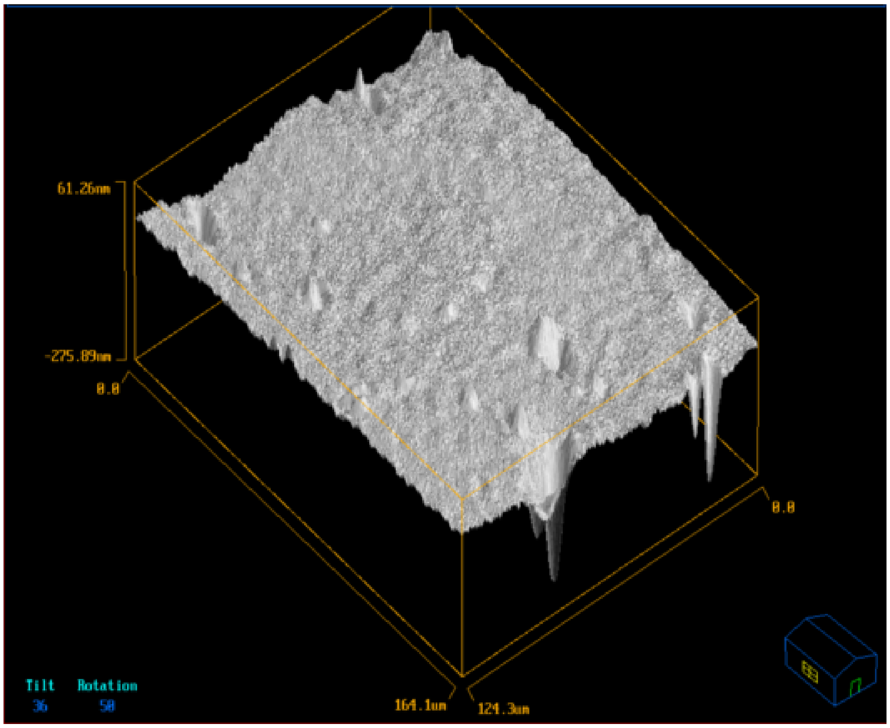


(a) (b)

Figure 6.3: Microstructure of a copper wafer (a) before polishing (b) after polishing with Buehler's alumina-based slurry



(a) Start of polishing, Ra = 328.34 nm



(b) After Polishing with Buehler alumina-based slurry, Ra = 16 nm

Figure 6.4: MicroXAM images of the 3-D surface plot of the copper wafer before polishing and after polishing with Buehler alumina-based slurry

Figure 6.3 (a) and (b) show the initial and final condition of the copper wafer after it was polished for 10 minutes. The surface looks clean except for very small pits. The overall wafer was uniformly polished. Here again the material removal rate was very low (0.0021 grams/min). This means that the anodic dissolution of the copper surface was very low and the material removed was mostly the passivation layer formed on the surface with the slurry components. Figure 6.4 (a) and (b) show the 3 D surface plots of the wafer obtained from MicroXAM before and after polishing. The surface roughness was 328.34 nm at the start of polishing and after 10 minutes of polishing with Buehler alumina-based slurry it was 16 nm.

The material removal rates for each slurry composition are summarized in the Table 6.2. Sodium nitrate-based slurry gave the highest material removal rate because of the absence of corrosion inhibitor. The slurry had vigorous electrochemical reactions which peeled away considerable material from the copper surface. The phosphate-based slurry also gave a high material removal rate because there was no leveling agent or oxidizer in the slurry. Thin passivation layer was formed which was easily removed by the pad. As more voltage was supplied, the electrochemical reactions removed more material from the surface of the copper. Hence, the passive layer should have enough thickness and stability to inhibit the electrochemical reactions.

The material removal rate in acetic acid-based slurry was lower than the previous two slurries as all the necessary components were there in the slurry. But good surface roughness was not achieved because the slurry was acidic in nature with a pH of 4. The phosphoric acid-based slurry and Buehler alumina-based slurry had low material removal rates when compared to the other slurries as the passivation layer protected the surface of the copper. Figure 6.5 shows the material removal rate as a function of different slurry compositions prepared for copper ECMP.

Table 6.2: Material Removal Rates for Different Slurry Compositions

S. No.	Composition of the Slurry	Initial wt. (grams)	Final wt. (grams)	Material Removed (grams)	Material Removal Rate (grams/min)
1.	Sodium nitrate, sodium sulfate, ethylene glycol, glycerol	90.1848	89.5762	0.6086	0.0608
2.	Potassium phosphate, BTA, potassium chloride, phosphoric acid, alumina abrasives	88.5164	88.0970	0.4194	0.0419
3.	Acetic acid, hydrogen peroxide , BTA, ethylene glycol, ammonium hydroxide, alumina abrasives	89.5920	89.4490	0.1430	0.0143
4.	Phosphoric acid, ethylene glycol, BTA,potassium hydroxide, hydrogen peroxide, alumina abrasives	89.0248	89.0061	0.0187	0.0018
5.	Buehler alumina-based slurry	92.7105	92.6887	0.0218	0.0021

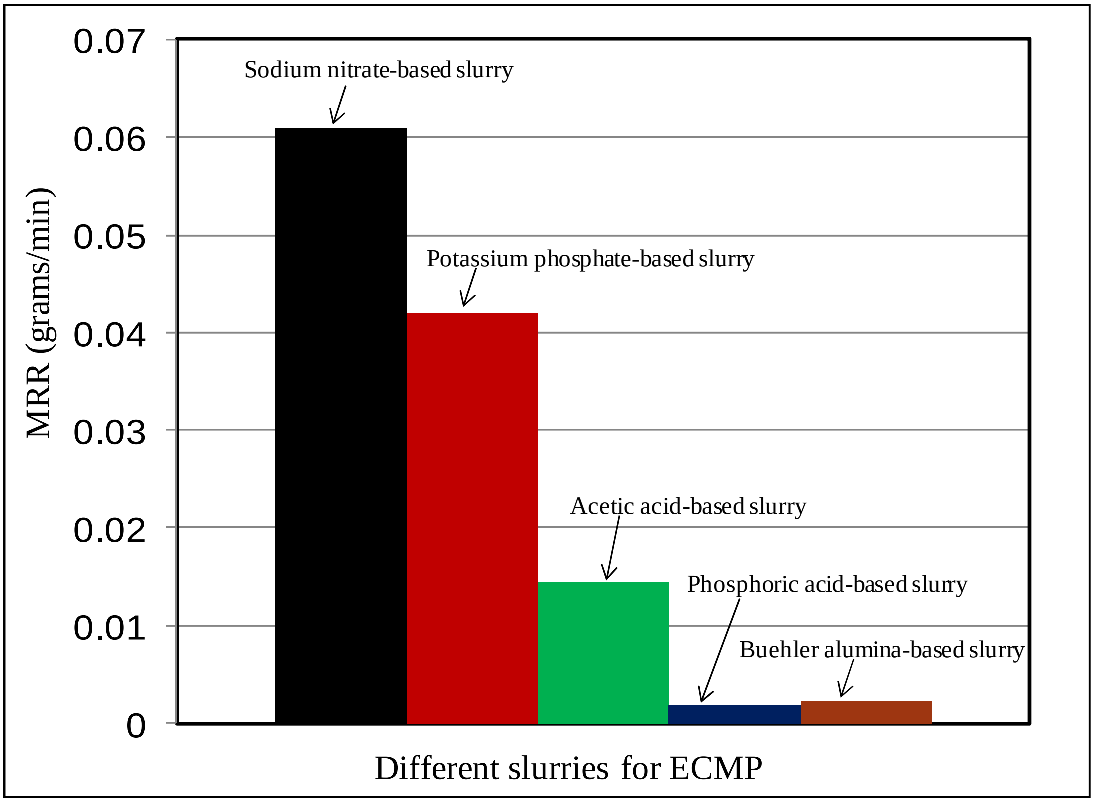


Figure 6.5: Material removal rates (MRR) for different slurry compositions in copper ECMP

Table 6.3 shows the surface roughness analysis of the copper wafers after they were polished. MicroXAM was used to measure the surface roughness at three different locations on the surface. The average value of the surface roughness (Ra) was calculated for each wafer. Phosphoric acid-based slurry and Buehler alumina-based slurry produced good surface roughness values.

Sodium nitrate based slurry produced a bad surface roughness as the wafer was had a corrosion layer on the surface. Potassium phosphate based slurry was acidic but due to the presence of BTA, the surface roughness was lower than the sodium nitrate based slurry. Acetic acid based slurry had a high surface roughness value because it was acidic and copper corrodes at a low pH value.

Table 6.3: Surface Roughness Analysis of Copper Wafers with Different Slurry Compositions

S. No.	Composition of the Slurry	Ra 1 (nm)	Ra 2 (nm)	Ra 3 (nm)	Average Ra (nm)
1	Sodium nitrate, sodium sulfate, ethylene glycol, glycerol	104.61	102.65	100.68	102.65
2	Potassium phosphate, BTA, potassium chloride, phosphoric acid, alumina abrasives	49.45	41.30	76.47	55.74
3	Acetic acid, hydrogen peroxide , BTA, ethylene glycol, ammonium hydroxide, alumina abrasives	93.85	78.25	91.11	87.74
4	Phosphoric acid, ethylene glycol, BTA,potassium hydroxide, hydrogen peroxide, alumina abrasives	20.53	14.83	12.05	15.80
5	Buehler alumina-based slurry	30.02	16.00	17.20	21.07

Figure 6.6 shows the surface roughness as a function of different slurry compositions obtained in Copper ECMP.

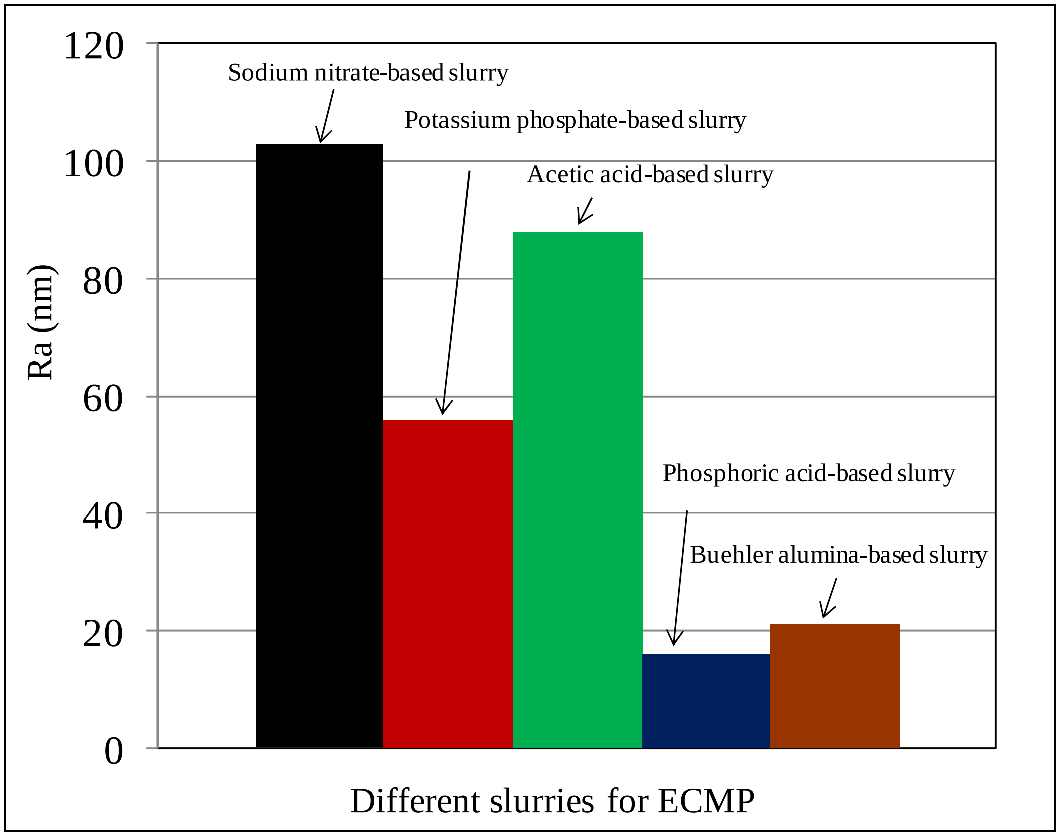


Figure 6.6: Surface roughness (Ra) with respect to different slurry compositions for copper ECMP

The pH of the slurry is a very important consideration while preparing the slurry for ECMP. Generally chemicals like potassium phosphate and ammonium hydroxide are used as pH adjusting agents. In this study, to understand the effect of pH, the slurries were prepared with different compositions. Some of them were acidic like potassium phosphate-based slurry and acidic acid-based slurry while others were slightly acidic like phosphoric acid-based slurry. Buehler alumina-based slurry was basic with a pH of 9.

The pourbaix diagram of copper as discussed in the literature review shows that corrosion occurs in the pH range of 1 to 4 [30]. The passivation layer is formed on the copper surface at a pH of 6 or above. The results obtained for the slurries investigated in this study were used to verify this behavior of copper in ECMP.

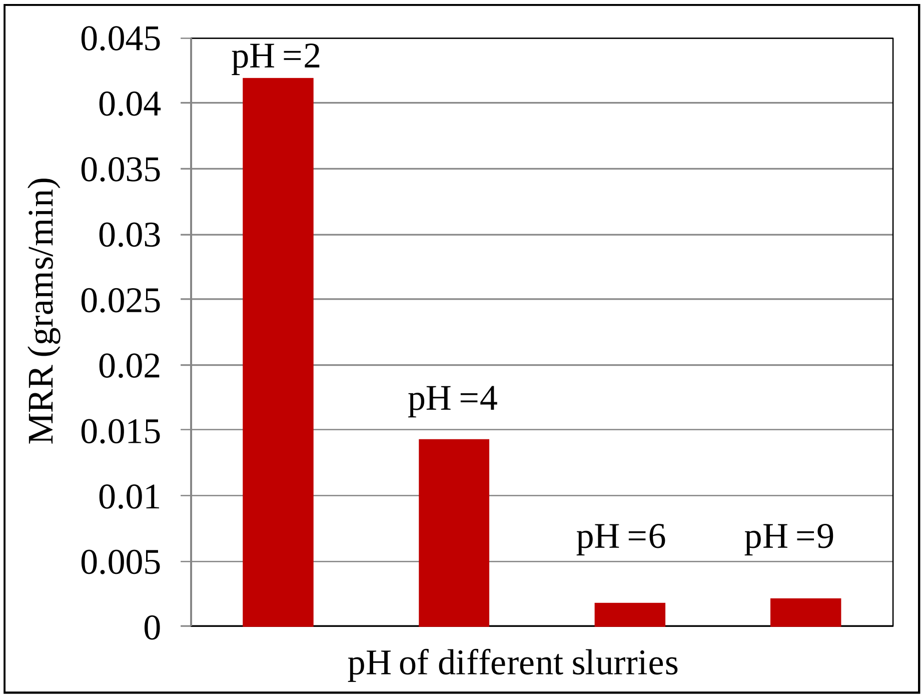


Figure 6.7: MRR as a function of slurry pH

Figure 6.7 shows the material removal rate as a function of pH of the slurry. The potassium phosphate based slurry with a pH of 2 gave the highest removal rate. From the experiments it was observed that the surface was not uniformly polished as the slurry was not able to effectively inhibit the electrochemical reactions. The acetic acid-based slurry was also acidic and it had a pH of 4. The material removal rate was also more in this case. At pH of 6, phosphoric acid-based slurry yielded lowest material removal rate. At pH of 9, Buehler alumina-based slurry also yielded the lowest material removal rate.

Figure 6.8 shows the surface roughness (Ra) as a function of pH of slurry. It can be seen that the slurries which had a pH of 6 or above gave good surface finish. The slurries which had pH 2 and pH 4 gave high roughness value which indicates that corrosion had occurred on the surface. Thus slurry of pH 6 or above gives good surface finish for copper in electrochemical mechanical polishing.

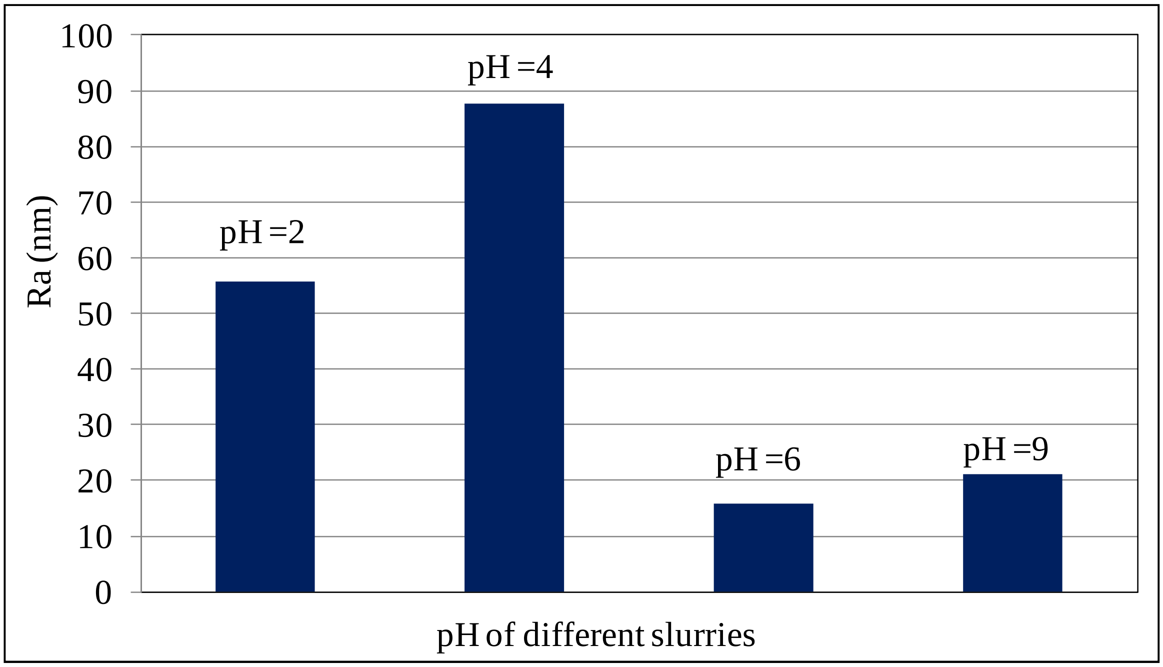


Figure 6.8: Surface roughness (Ra) as a function of slurry pH

6.2 Effect of Polishing Time

As mentioned in Chapter 5, four copper wafers were used to study the changes that can occur on the surface with polishing time. Figure 6.9 (a) shows the optical micrograph of the surface of the wafer after polishing for 2 minutes. The scratches on the surface are still prominent. Some pits are also observed which may be due to the active dissolution of the copper wafer in the electrochemical slurry.

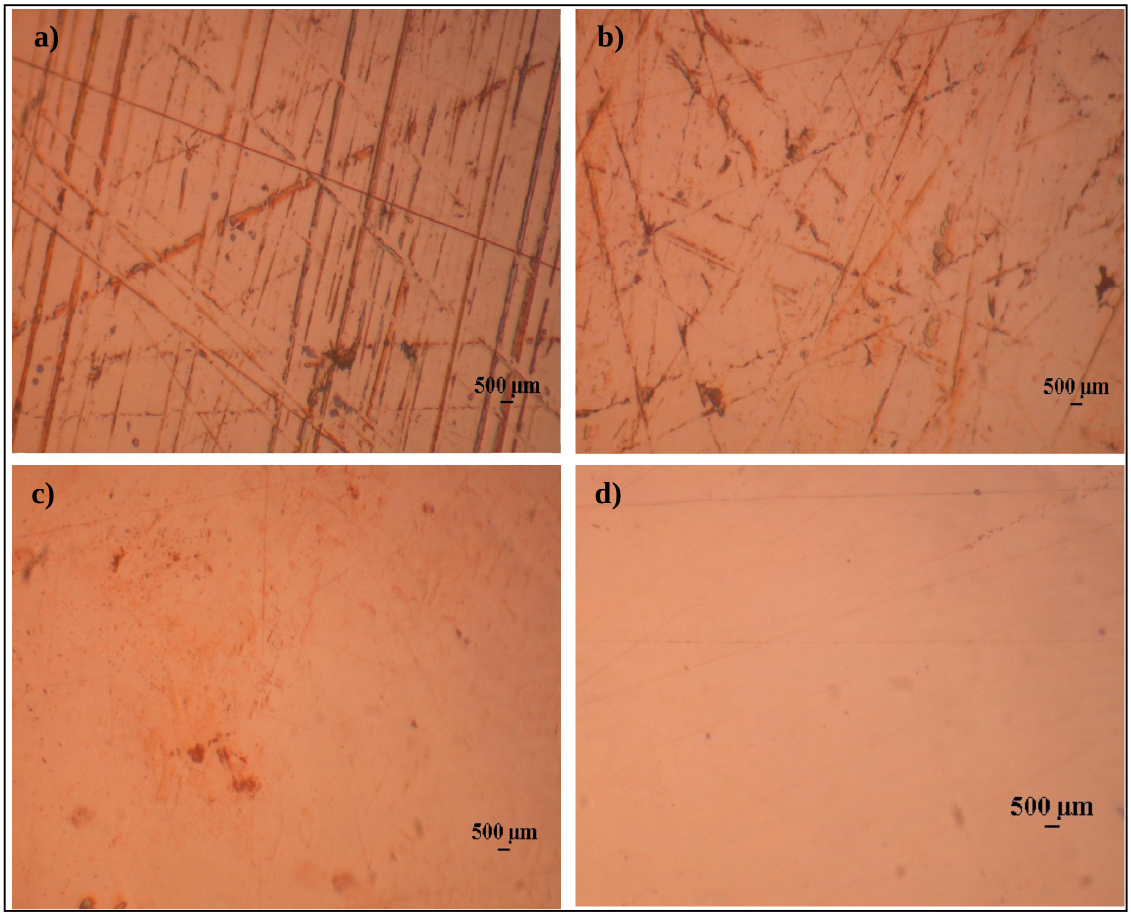


Figure 6.9: Microstructure of the copper wafers after (a) 2 minutes of polishing (b) 5 minutes of polishing (c) 7 minutes of polishing and (d) 10 minutes of polishing

Figure 6.9 (b) shows the wafer after polishing for 5 minutes. Some of the scratches were eliminated in this wafer. Layers of different colors appear on the surface. This can be attributed to the incomplete removal of the passivation layer formed on the surface. Figure 6.9 (c) shows the wafer after polishing for 7 minutes. A matte finish was observed in this wafer. There were some oxidation marks at some places which were very minute. Figure 6.9 (d) shows the copper wafer after polishing for 10 minutes. A mirror finish surface was obtained in this wafer. Pits, scratches and oxidation marks were almost eliminated in this wafer. So the optimal time for polishing the wafer by ECMP was found out to be 10 minutes.

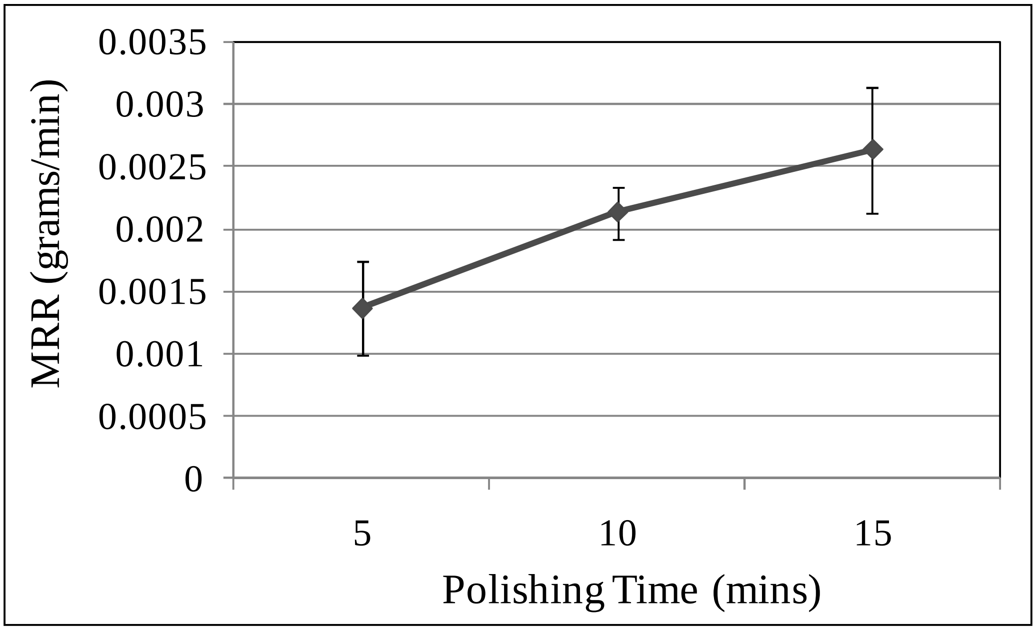


Figure 6.10: MRR as a function of polishing time

In order to study the effect of polishing time on MRR, three different wafers were polished at 5, 10, and 15 minutes. Figure 6.10 shows the material removal rate as a function of polishing time. They show that the MRR increases with polishing time. The surface finish of the wafer was not very uniform when it was polished for 5 minutes. The surface finish was good for a polishing time of 10 minutes. Figure 6.11 shows the 3 D surface profile of the wafer. The surface roughness was 13.74 nm. When the polishing time was increased to 15 minutes, scratches were observed on the wafer. This might be due to a weak passivation layer that is formed after 10 minutes. So the pad removes more material from the surface.

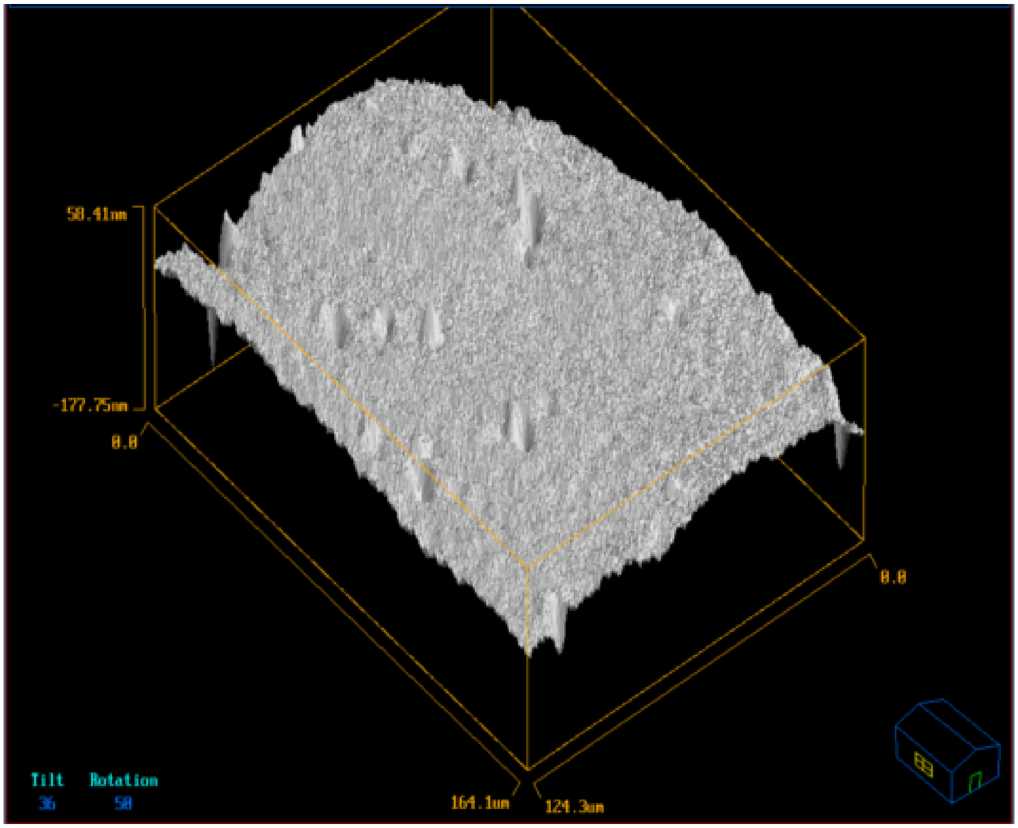


Figure 6.11: 3-D surface profile of the copper wafer after 10 min. of polishing

6.3 Effect of Voltage Applied

The operating voltage is a crucial parameter for ECMP. The extent of planarization can be controlled by changing the voltage. In order to study the effect of voltage applied on MRR and surface roughness, copper wafers were polished using three different voltage ranges. Figure 6.12 shows the variation of MRR with voltage. The high range voltage has the maximum material removal rate and the low range has the minimum material removal rate. This shows that the MRR increases with increase in the applied voltage.

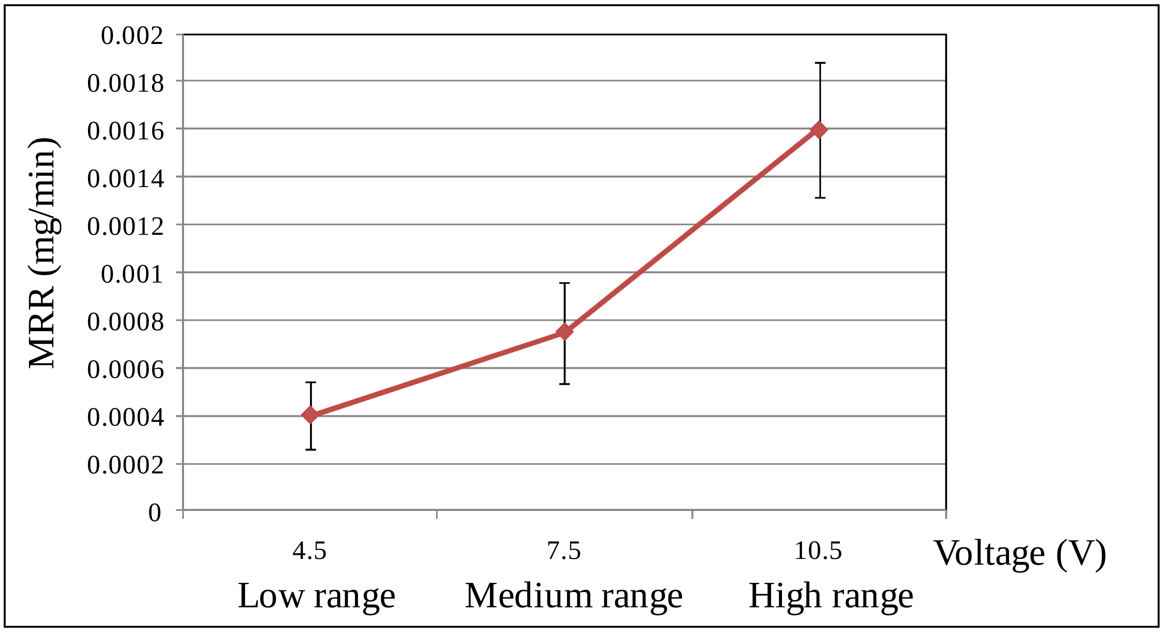


Figure 6.12: MRR as a function of applied voltage

Figure 6.13 shows the surface roughness (Ra) as a function of voltage applied. The surface roughness (Ra) was relatively high with an average surface roughness of 35.18 nm when low range voltage of 4.5 volts was applied. This could possibly be due to the fact that the current generated in the process is low. One more reason could be that at a low voltage, weak passivation layer might have been formed.

When medium range voltage of 7.5 volts was applied, the average surface roughness was 30.85 nm. So, there was a slight improvement in the surface finish. All these experiments were conducted for the same polishing time i.e. 10 minutes, so time was not a factor here. The surface finish was superior when the wafer was polished using a high range voltage of 10.5 volts. The average surface roughness was 27.8 nm. So the optimal voltage range for face-up electrochemical mechanical polishing was 9.5- 10.5 volts.

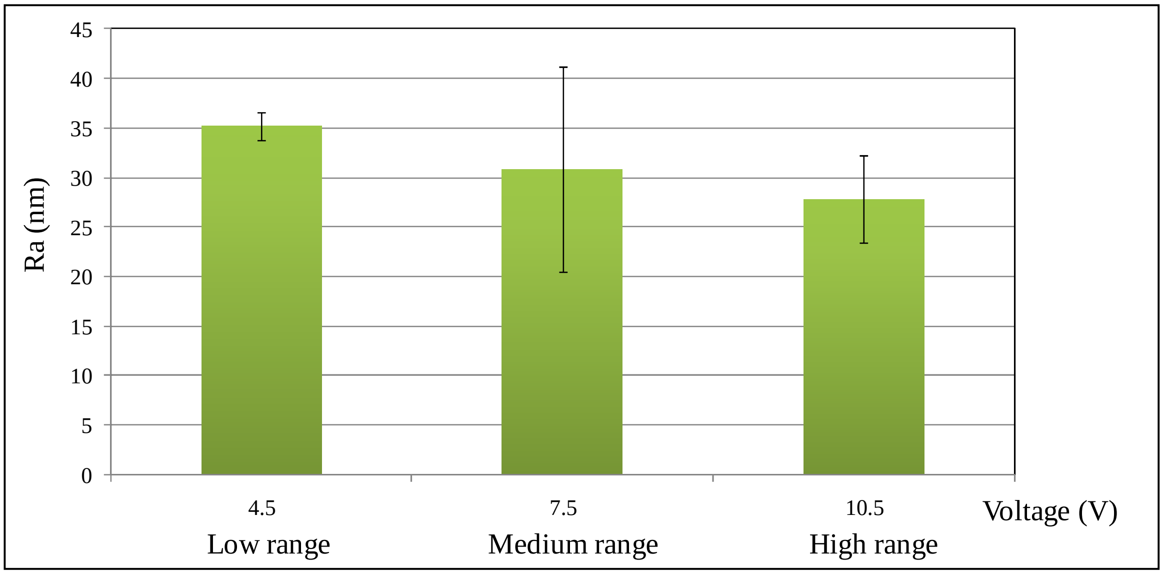


Figure 6.13: Surface Roughness (Ra) as a function of applied voltage

6.4 Effect of Pad Speed and Wafer Carrier Speed

Pad speed and wafer carrier speed are the kinematic variables in ECMP. Hocheng *et al.* [48] pointed out wafer speed and the pad speed determine the non-uniformity of the wafer for chemical mechanical polishing. This study was done to observe if these kinematic variables affect the electrochemical mechanical polishing process. Different speeds for the polishing pad and the wafer carrier were specified to see if it affects the uniformity of the surface.

In ECMP the pad has a very low mechanical down-force and it is not completely responsible for the material removal as in the case of conventional CMP. But the pad still has to remove the passivation layer formed on the surface in order to ensure that the wafer has good finish. Experiments were performed with pad speeds up to 500 rpm. But it was observed that when the pad speed was more than 325 rpm, superficial scratches were observed on the copper surface. Thus the pad rpm was not increased beyond 350 rpm for further experiments. Wafer carrier has slurry in it. So, a maximum speed of 25 rpm was used so that the slurry does not spill out.

In order to identify the effect of pad speed and wafer carrier speed on the material removal rate and surface finish of the copper wafer, experiments were performed with 9 different variations. First the wafer carrier speed was fixed at 15 rpm and experiments were performed with the pad speeds of 275, 300 and 325 rpm. Then the wafer carrier speed was changed to 20 rpm and experiments were repeated with the same pad speeds. Finally the wafer carrier speed was set to 25 rpm and again the experiments were repeated. Table 6.4 shows the material removal rate values with respect to variation in pad speed and wafer carrier speed.

Table 6.4: Material removal rate analysis as a function of pad speed and wafer carrier speed

Wafer No.	Wafer Carrier Speed (rpm)	Polishing Pad Speed (rpm)	Initial weight of the wafer (gms)	Final weight of the wafer (gms)	Material Removed (in gms)	MRR (gms/min)
1.	15	275	89.2663	89.2564	0.0099	0.00099
2.	15	300	90.4411	90.4321	0.009	0.00090
3.	15	325	89.0086	88.9972	0.0114	0.00114
4.	20	275	89.7596	89.7404	0.0192	0.00192
5.	20	300	92.1512	92.1387	0.0125	0.00125
6.	20	325	87.6997	87.6862	0.0135	0.00135
7.	25	275	88.0181	88.0013	0.0168	0.00168
8.	25	300	89.3106	89.2966	0.014	0.00140
9.	25	325	86.3368	86.3213	0.0155	0.00155

Figure 6.14 shows the material removal rate as a function of pad speed and wafer carrier speed. When the wafer carrier speed was 15 rpm, the amount of material removal was low and the finish obtained in the wafers was uniform. When the wafer carrier rpm was 20 and 25, the material removal rates increased. This is because the wafer had more contact with the polishing pad while rotating in the wafer carrier. Thus the material removal rates increased when the wafer carrier speed was increased.

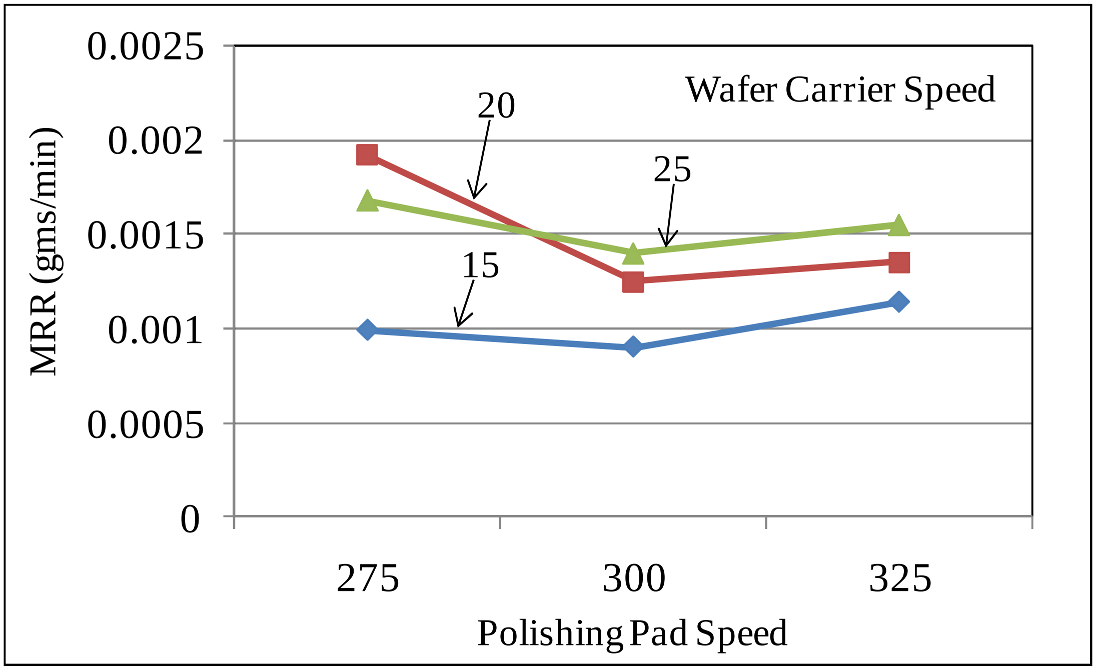


Figure 6.14: MRR as a function of polishing pad speed for various wafer carrier speeds

When the polishing pad speed was 275 rpm, the material removal rates were uneven. Spiral demarcations were observed on the surface. This could possibly be because the pad speed was not high enough to remove the passive layer form the surface. The material removal rates increased evenly with the increase in wafer carrier speed when the polishing pad speed was 325 rpm.

Table 6.5 shows the surface roughness values obtained with respect to variation in pad speed and wafer speed. When the wafer carrier speed was 15 rpm, the surface finish was higher compared to other wafer carrier speeds. The whole wafer was polished uniformly. At pad speed of 275 rpm the wafer had some scratches. At a pad speed of 300 rpm, a matte finish was obtained. The pad speed at 325 rpm gave better finish to the wafer surface. It had a more glossy finish than the other two wafers. It had the least surface roughness value Ra of 32.69.

Table 6.5: Surface roughness values with different pad speeds and wafer carrier speeds

Wafer No.	Wafer Carrier RPM	PolishingPad RPM	Surface Roughness (Ra)
1.	15	275	40.97
2.	15	300	37.08
3.	15	325	32.69
4.	20	275	42.17
5.	20	300	41.04
6.	20	325	37.54
7.	25	275	46.88
8.	25	300	51.93
9.	25	325	45.19

When the wafer carrier speed was 20 rpm, the entire surface of the copper wafer was not getting polished. The pad speed of 325 rpm again gave a good finish. At 25 rpm speed, the wafer carrier had a very slight wobble. This resulted in a non-uniform polish on the surface. Spiral demarcations were observed on the surface. The surface roughness values were increased in this case.

Figure 6.15 shows the surface roughness (Ra) as a function of pad speed and wafer speed. It can be clearly observed that the surface finish of the copper wafers was better when the wafer carrier speed was 15 rpm and the polishing pad speed was 325 rpm. The optimal conditions for the kinematic variables in this study were determined for electrochemical mechanical polishing.

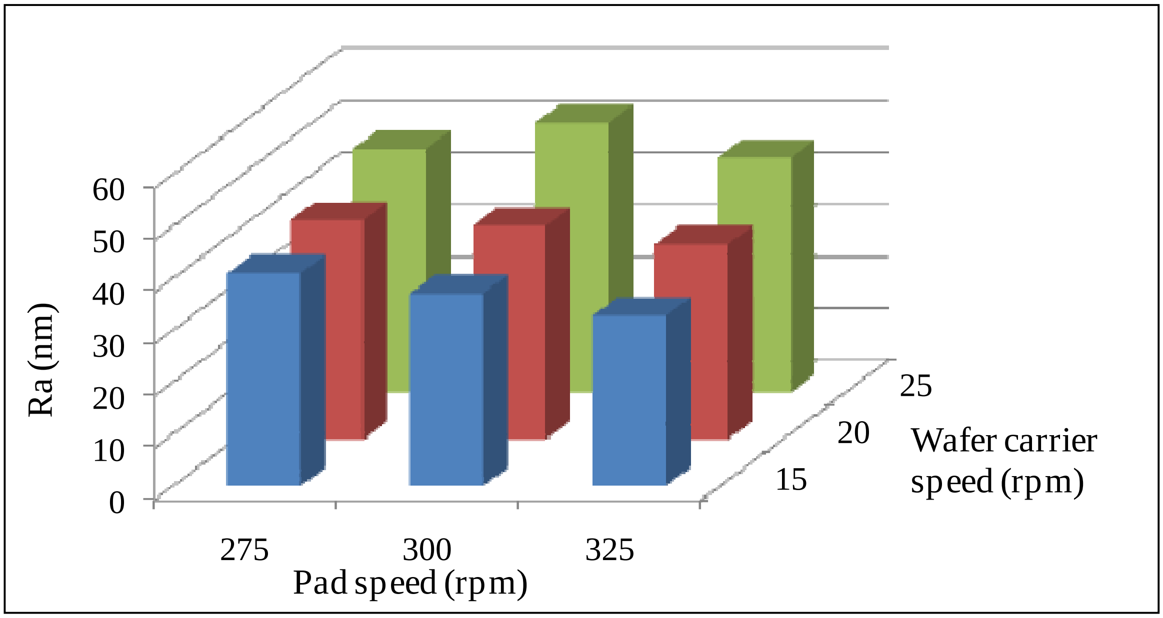


Figure 6.15: Surface roughness (Ra) as a function of pad speed and wafer speed

CHAPTER VII

CONCLUSIONS AND FUTURE WORK

In this thesis, the primary focus was to build an ECMP apparatus to polish 4 inch copper wafers and achieve a good surface finish. Initially, an apparatus was built by modifying an existing CMP apparatus. But since the wafer carrier was made of metal, it was not able to withstand the electrochemical reactions. A new set-up was made with polyethylene plastic, but planetary motion was not provided. Spiral demarcations and scratches were observed on the surface after polishing with this apparatus. So, an ECMP apparatus with planetary motion was developed using Pro/E software.

A ball bearing arrangement was used to provide the positive charge to the wafer in the wafer carrier. The wafer carrier assembly consisted of a base, bearing holder, ball bearing, anode shaft, V-belt pulley, and wafer carrier. Different materials such as high density polyethylene, polyvinyl chloride, ultra high molecular weight (UHMW) polyethylene and aluminum were used to fabricate the ECMP apparatus. Pad holders for various polishing pad sizes were machined. Two mini milling machines and a digital power supply unit were used to complete the experimental set up.

The other important aspect of this work was to study the slurry composition to achieve a nanometric surface finish on the copper wafer with fewer surface defects. Slurry for ECMP should be able to form a passivation layer on the surface of the wafer which will be subsequently removed by the polishing pad. Sodium nitrate-based slurry, potassium phosphate-based slurry, acetic acid-based slurry, phosphoric acid-based slurry and Buehler alumina-based slurry were the five different slurries used to polish the wafers. The effect of each slurry composition and its pH was studied as a function of material removal rate and surface roughness. The necessary components in the slurry to produce a good surface finish were an acid based electrolyte, a corrosion inhibitor, an oxidizer, a leveling agent, a pH adjusting agent and appropriate abrasive.

When the pH of the slurry was below 6, the surface of the copper wafer underwent corrosion while the wafer had a smooth uniform finish at a pH of 6 or above. This was validated using the Pourbaix diagram for copper. Good surface finish was obtained with phosphoric acid-based slurry and Buehler alumina-based slurry which had a pH of 6 and 9, respectively. The surface roughness obtained in the phosphoric acid-based slurry was 12.05 nm.

The effect of process parameters, such as polishing time, voltage applied and kinematic variables, including pad speed and wafer speed were studied with respect to material removal rate and surface finish. Good surface finish was obtained when the wafers were polished for 10 minutes with the applied voltage in the range of 9.5 V to 10.5 V. The wafer carrier had a speed of 15 rpm and the polishing pad had a speed of 325 rpm.

In the future, conductive pads can be used in the apparatus. Different slurry inlets can be provided to allow a uniform flow of the slurry on the surface of the wafer. Corrosion inhibitors such as ammonium dodecyl sulfate (ADS) and 5-phenyl-1-H-tetrazole (PTA) can be used in the slurry instead of BTA. Sensor based monitoring of the ECMP process can be performed by using multiple sensors which can provide a better understanding of the process variables.

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APPENDIX A

Table A: List of patents on methods and apparatus for electrochemical mechanical polishing

S. No.	**US Patent No.**	**Issue**	**Inventor Name**	**Assignee**	**Title**	**Summary**	**Remarks**
1.	5807165	Sept. 15, 1998	Uzoh *et al.* [49]	International Business Machines Corporation	Method of electrochemical mechanical planarization	The apparatus consists of workpiece carrier, platen with a polishing pad and electrodes which are attached to the carrier	The microelectronic components on the workpiece are not damaged
2.	5911619	June 15, 1999	Uzoh *et al.* [50]	International Business Machines Corporation	Apparatus for electrochemical mechanical planarization	The apparatus has a workpiece carrier, platen, pad disposed on the platen and electrodes disposed on the carrier	Electrodes can be made of copper, aluminum, silver gold, tin, nickel and rhodium

3.	6368190	April 9, 2002	Easter *et al.* [51]	Agere Systems Guardian Corp.	Electrochemical mechanical planarization apparatus and method	Apparatus has a rotatable platen and a polishing pad disposed on the platen	The platen electrode has a circular circumference for discharging electrons into the electrolyte solution
4.	6739951	May 25, 2004	Sun *et al.* [24]	Applied Materials Inc.	Method and apparatus for electrochemical-mechanical planarization	Multistage ECMP apparatus with an oxidizer-free slurry	The authors report that dishing characteristic of conventional CMP is reduced
5.	6776693	Aug. 17, 2004	Duboust *et al.* [25]	Applied Materials Inc.	Method and apparatus for face-up substrate polishing	The apparatus has a polishing head diameter smaller than the substrate supported by the carrier	Lower cost of consumables such as polishing pad
6.	6841057	Jan. 11, 2005	Wadensweiler *et al.* [52]	Applied Materials Inc.	Method and apparatus for substrate polishing	The apparatus removes entrained gas from the electrolyte flowing towards the pad	A membrane is disposed in the electrode which removes the entrained gas

7.	6858531	Feb. 22, 2005	Zhu *et al.* [53]	LSI Logic Corporation	Electrochemical mechanical polishing method	Slurry with a high viscosity is used	Slurry components are provided to achieve low defects on the wafer surface
8.	7285145	Oct. 23, 2007	Zhu *et al.* [54]	LSI Corporation	Electro chemical mechanical polishing method and device for planarizing semiconductor surfaces	Slurry having a high viscosity and a polishing agent is used in the apparatus	Components of the slurry such as BTA, abrasives, and surfactants are mentioned
9.	7438795	Oct. 21, 2008	Wylie *et al.* [4]	Cabot Microelectronics Corp.	Electrochemical-mechanical polishing system	An ECMP apparatus with improved flow and distribution of the slurry between the pad and the substrate	The polishing pad is made with plurality of pores

10.	7527722	May 5, 2009	S. Sharan [1]	Intel Corporation	Electrochemical mechanical planarization	An apparatus to remove a surface layer from the substrate using pad disposed over a platen, slurry, segmented cathode and an electrical current	ECMP apparatus with planetary motion
11.	20050016868	Jan. 27, 2005	Basol *et al.* [55]	ASM NuTool, Inc.	Electrochemical Mechanical Planarization Process and Apparatus	Apparatus has a wafer holder and a belt pad to polish the surface of the substrate	Electrical contacts are embedded in the belt pad
12.	20050173259	Aug. 11, 2005	Mavliev *et al.* [56]	Applied Materials, Inc.	Endpoint system for electro-chemical mechanical polishing	Multiple sensors such as optical or eddy current sensors are placed on the platen to provide an end point detection system	The planarization is performed until the dielectric layer is exposed

13.	20050173260	Aug. 11, 2005	Basol *et al.* [57]		System for electrochemical mechanical polishing	The polishing pad has openings to allow the solution to wet the wafer surface and the electrode surface	Linear motion of the conductive surface
14.	20060006073	Jan. 12, 2006	Basol *et al.* [58]		System and method for electrochemical mechanical polishing	The electrodes in the apparatus are separated from one another by an isolation region	The conductive surface has a linear motion with small electrodes
15.	20060154569	July 13, 2006	Doyle *et al.* [22]		Platen assembly utilizing magnetic slip ring	Method to transfer electrical power between the base and the rotating platen without any mechanical contact	Magnetic Slip rings were used
16.	20070151867	July 5, 2007	Hu *et al.* [59]	Applied Materials, Inc.	Apparatus and a method for electrochemical mechanical processing with fluid flow assist elements	The apparatus has a plurality of fluid flow assist elements disposed between the pad assembly and the platen	Polishing pad with elements to assist slurry flow

17.	20070161250	July 12, 2007	Wang *et al.* [60]	Applied Materials, Inc.	Method for electrochemically mechanically polishing a conductive material on a substrate	Multiple polishing steps are provided where different voltages are applied	The authors reported that arcing is minimized and copper residual cleaning is enhanced
18.	20070221495	Sept. 27, 2007	Manens, Antoine P. [61]	Applied Materials, Inc.	Electropolish assisted Electrochemical Mechanical Polishing Apparatus	The system has a ECP station and three ECMP stations	Combined effect of ECP and ECMP
19.	20070235344	Oct. 11, 2007	Jia *et al.* [62]	Applied Materials, Inc.	Process for high copper removal rate with good planarization and surface finish	In this apparatus the speed of the platen and head is provided in a controlled manner and the current applied to the pad is also controlled by changing the voltage	The smoothness of the wafer surface is same in the center, middle and edge of the wafer.

20.	20070251832	Nov. 1, 2007	Du *et al.* [23]	Applied Materials, Inc.	Method and apparatus for electrochemical mechanical polishing of cu with higher liner velocity for better surface finish and higher removal rate during clearance	Apparatus has a polishing belt instead of the usual polishing pad	Linear polishing station for ECMP
21.	20080188162	Aug. 7, 2008	Kobata *et al.* [63]		Electrochemical mechanical polishing apparatus conditioning method, and conditioning solution	Apparatus has a polishing table with divided electrodes, an electrolyte supply section, a detecting section, a variable resistance unit and a control section	The authors provided a conditioning solution for electrode and polishing pad

22.	20090078583	Mar. 26, 2009	Kobata *et al.* [2]		Electrochemical mechanical polishing method and electrochemical mechanical polishing apparatus	ECMP method of polishing in which the conductive film is polished so that its average thickness should not be more than 300 nm	The waveform of the voltage applied between the first and second electrode is either a rectangular, sine, or a ramp waveform
23.	20090239379	Sept. 24, 2009	Huang *et al.* [64]		Methods of Planarization and Electro-Chemical Mechanical Polishing Processes	In this apparatus, ECMP is performed with at least one voltage change during the overall process	Metal recess is decreased significantly and wafer planarity is improved
24.	20100116685	May 13, 2010	W. Lee [65]	Micron Technology, Inc.	Methods and Apparatuses for Electrochemical-Mechanical Polishing	The substrate is placed in electrical contact with two electrodes	The authors reported that ECMP has smoother surface finish than ECP

APPENDIX B

Table B: List of patents on slurry compositions for ECMP

S. No.	US Patent No.	Issue	Inventor Name	Assignee	Title	Composition of the Slurry
1.	20050263407	Dec. 01, 2005	Brusic *et al.* [66]	Cabot Microelectronics Corporation	Electrochemical-mechanical polishing composition and method for using the same	Potassium Sulfate, Benzotriazole (BTA), Poly-acrylic acid, lactic acid and propanol
2.	20100051474	Mar. 04, 2010	Andricacos *et al.* [67]		Method and composition for electro-chemical-mechanical polishing	1-hydroxyethane-1,1-diphosphonic acid (HEDP), Ammonium hydroxide (or Potassium hydroxide) and BTA
3.	20040248412	Dec. 12, 2009	Liu *et al.* [33]		Method and composition for fine copper slurry for low dishing in ECMP	Phosphoric acid, Ethylenediamine, Ammonium citrate, BTA, KOH, H_2O_2, Silica abrasives, Ethylene glycol, De-ionized water

4.	20070144915	June 28, 2007	Tian *et al*. [68]	Applied Materials, Inc.	Process and composition for passivating a substrate during electrochemical mechanical polishing	Acid based electrolyte, Corrosion inhibitor, Chelating agent, pH adjusting agent, Abrasives and Solvent
5.	7390429	June 24, 2008	Liu *et al*. [69]	Applied Materials, Inc.	Method and composition for electrochemical mechanical polishing processing	Phosphoric acid, Ethylenediamine, Ammonium citrate, BTA, Benzoylimidazol (BIA), KOH, H_2O_2, Silica abrasives, De-ionized water
6.	20070017818	Jan. 25, 2007	Emesh *et al*. [70]		Solution for electrochemical mechanical polishing	Citric acid, Ammonium oxalate, BTA, Trimethyl amine hydroxide, Urea, Colloidal silica
7.	7582564	Sept. 01, 2009	Wang *et al*. [36]	Applied Materials, Inc.	Process and composition for conductive material removal by electrochemical mechanical polishing	Phosphoric acid, Ethylenediamine, Ammonium citrate, BTA, KOH, H_2O_2, Silica abrasives, XP-1296, Polyethylenimine (PEI), De-ionized water

8.	20060249394	Nov. 09, 2006	Jia *et al*. [71]	Applied Materials, Inc.	Process and composition for electrochemical mechanical polishing	Phosphoric acid, Ammonium citrate, BTA, L-2001 (heterocyclic polymer/amine solution), Polyethylenimine (PEI), KOH and De-ionized water
9.	20070254485	Nov. 01, 2007	Mao *et al*. [72]		Abrasive composition for electrochemical mechanical polishing	Phosphoric acid, Ammonium hydrogen citrate, BTA, L-2001, Polyethyleneimine (PEI), XECP-7 polymeric abrasive, Ammonium hydroxide and De-ionized water
10.	20080142375	June 19, 2008	Doniat *et al*. [73]		Electrolyte formulation for electrochemical mechanical planarization	HEDP (1-hydroxyethane diphosphonic acid), Ammonium Citrate Tribasic, Oxalic acid, Ethylenediamine, 5 Phenyl 1H-tetrazole, Propanol, Triton X-100, Colloidal silica KOH and Water

APPENDIX C

Table C: List of Patents on Polishing Pad for ECMP

S. No.	**US Patent No.**	**Publication Date**	**Inventor Name**	**Assignee**	**Title**	**Summary**	**Remarks**
1.	20040259479	Dec. 23, 2004	Sevilla *et al*. [74]	Cabot Microelectronics Corporation	Polishing pad for electrochemical-mechanical polishing	Polishing pad has two set of grooves with different dimensions and are interconnected such that there is no alignment between them	Different channels are produced for the flow of slurry by the grooves in the pad
2.	7815778	Oct. 19, 2010	Bajaj [75]	Semiquest Inc.	Electro-chemical mechanical planarization pad with uniform polish performance	Polishing pad has a conductive polishing element, a guide plate, a cathodic element, and a slurry distribution layer	The conductive polishing element is made of polymer or graphite and the conductive pattern in the pad is made of copper

3.	7141155	Nov. 28, 2006	Bunyan *et al*. [76]	Parker-Hannifin Corporation	Polishing article for electro-chemical mechanical polishing	Polishing pad has an electrically conductive compound formed into a layer	The pad has stable physical and electrical properties with high durability and improved service life
4.	20060070872	Apr. 06, 2006	Mavliev *et al*. [77]	Applied materials, inc.	Pad design for electrochemical mechanical polishing	A rotating platen assembly has a controlled valve assembly	Platen is capable of supplying the electrolyte flow at a desired rpm
5.	20070111638	May 17, 2007	Chang *et al*. [78]	Applied materials, inc.	Pad assembly for electrochemical mechanical polishing	Polishing pad assembly includes a compressible layer disposed below a processing layer and an electrode	The processing rate and the surface uniformity of the substrate is improved
6.	20100000877	Jan. 07, 2010	Ameen *et al*. [79]		Method for electrochemical mechanical polishing	The polishing pad has a cellular polymeric layer of thickness less than 1.5 mm	The polymeric layer has a plurality of pores

7.	6893328	May 17, 2005	So *et al*. [80]	Rohm and Haas Electronic Materials CMP Holdings, Inc.	Conductive polishing pad with anode and cathode	Polishing pad consists of one or more anodes and cathodes	A wiring network is used to connect the anodes and cathodes
8.	6848977	Feb. 01, 2005	Cook *et al*. [81]	Rohm and Haas Electronic Materials CMP Holdings, Inc.	Polishing pad for electrochemical mechanical polishing	The polishing pad has grooves to facilitate flow of the slurry over the pad	Better flow of slurry in the apparatus
9.	7311592	Dec. 25, 2007	Chen *et al*. [82]	Applied Materials, Inc.	Conductive polishing article for electrochemical mechanical polishing	The apparatus has perforations and grooves in the pad which intersect with each other	The authors reported improved surface finish of the substrate
10.	20090088050	Apr. 02, 2009	Hsu *et al*. [83]		Conductive polishing article for electrochemical mechanical polishing	A conductive polishing article is provided with a polishing pad, a cathode, an anode, and an ion exchange membrane	The ion exchange membrane is used to prevent oxygen gas generated at the anodes

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Scope and Method of Study: Electrochemical mechanical polishing is a process wherein the surface layer of a substrate is smoothened using a combination of electrochemical reactions, chemical reactions and mechanical forces. It is an alternative technology to chemical mechanical polishing to prevent delamination in the porous low-k dielectric films in advanced IC devices. Copper is widely used in the metallization of these device structures. ECMP is excellent for bulk copper planarization because it has higher material removal rates and better planarization efficiency at low down force. Also, ECMP has proven to be better than electrochemical polishing (ECP) as it is not pattern sensitive. In the present study, a face-up electrochemical mechanical polishing apparatus with planetary motion was fabricated and tested to polish 4-inch copper wafers. A ball bearing arrangement was used to provide a positive charge to the rotating wafer in the wafer carrier. Five different slurry compositions were prepared to polish the copper wafers. Multi-Stage polishing was adopted to achieve a good surface finish on the wafer. Surface characterization was studied by optical microscope and MicroXAM, an optical laser interference microscope.

Findings and Conclusions: The slurry composition for ECMP should be such that it forms a passivation layer on the surface of the copper wafer which is subsequently removed by the polishing pad. The necessary components of the slurry, in order to produce a good surface finish are an acid-based electrolyte, a corrosion inhibitor, a leveling agent, an oxidizer, a pH adjusting agent and abrasive particles. The slurries with pH of 6 or above produced a smooth uniform surface. This was validated using Pourbaix diagram of copper. Phosphoric acid-based slurry with a pH of 6 and Buehler alumina-based slurry with a pH of 9 produced a good surface finish. The surface roughness obtained with the phosphoric acid-based slurry was 12.05 nm. Process parameters, such as polishing time, voltage applied, pad and wafer carrier speed were studied as a function of material removal rate and surface roughness. Material removal rates increased with increase in polishing time and the voltage applied. Good surface finish was obtained with a polishing time of 10 minutes at a voltage range of 9.5 to 10.5 V with a wafer carrier speed of 15 rpm and a polishing pad speed of 325 rpm.

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